Carolina Tavares Pinheiro

CHARACTERIZATION OF LUBRICANT OILS AND REGENERATION STUDIES BY GREEN SOLVENT EXTRACTION

Ph.D. thesis in Chemical Engineering, supervised by Doctor Licínio Manuel Gando de Azevedo Ferreira and co-supervised by Doctor Margarida Maria João de Quina and submitted to the Department of Chemical Engineering, Faculty of Sciences and Technology, University of Coimbra

May 2018

· U C ·

UNIVERSIDADE DE COIMBRA

Carolina Tavares Pinheiro

Characterization of Lubricant Oils and Regeneration Studies by Green Solvent Extraction

Ph.D. Thesis in the scientific area of Chemical Engineering, submitted to the Department of Chemical Engineering, Faculty of Science and Technology, University of Coimbra

Supervisors:
Doctor Licínio Manuel Gando de Azevedo Ferreira
Doctor Margarida Maria João de Quina

Host institutions:
Department of Chemical Engineering, University of Coimbra
CIEPQPF – Research Centre on Chemical Processes Engineering and Forest Products

Financing:
SOGILUB – Sociedade de Gestão Integrada de Óleos Lubrificantes Usados, Lda.

May 2018

· U C ·

UNIVERSIDADE DE COIMBRA

AGRADECIMENTOS

Em primeiro lugar, gostaria de agradecer aos meus orientadores, Professores Licínio Ferreira e Margarida Quina, pelo total apoio, conhecimentos transmitidos, permanente incentivo e inesgotável paciência com que orientaram este trabalho, e cuja amizade tanto contribuiu para o empenho e entusiasmo com que o desenvolvi. Em particular, ao Professor Licínio pela orientação prestada, pelo seu incentivo, disponibilidade e apoio que sempre demonstrou. À Professora Margarida, que com o sua boa disposição, entusiasmo e paixão pelo seu trabalho, será sempre uma inspiração e um exemplo a seguir.

À SOGILUB, sociedade de gestão integrada de óleos lubrificantes, Lda., pelo financiamento desta tese de doutoramento e pela concessão das amostras de óleos usados. Um agradecimento especial ao Engenheiro Carlos Cardoso e Dr. Aníbal Vicente por todo o apoio e valiosas contribuições para o desenvolvimento deste trabalho.

À Enviroil, em particular aos Engenheiros Roberto Barata e Catarina Neves pelos conhecimentos transmitidos e pela cedência dos equipamentos para efetuar parte das caraterizações físico-químicas. À Correia & Correia, Lda., na pessoa da Eng.ª Benvinda de Jesus, pela transmissão do seu vasto conhecimento das propriedades dos óleos e técnicas analíticas.

Ao Professor Marco Reis e Ricardo Rendall, pelo rigor e total disponibilidade na colaboração de vários trabalhos ao nível de tratamento estatístico e desenvolvimento de modelos de previsão de propriedades.

Ao Professor Abel Ferreira, pelo apoio, amizade, boa disposição, pelos conhecimentos transmitidos na área da termodinâmica e colaboração no trabalho de propriedades termofísicas.

Aos alunos de mestrado Giovanni Villanti, Joana Marques e Rodrigo Pais pela ajuda indispensável na elaboração de ensaios laboratoriais e pelo bom ambiente de trabalho.

Aos meus amigos, Aline, Vanessa, Deivídson e Luciano, por me acompanharem em todos os momentos desta caminhada. Em particular, à Aline, pela verdadeira amizade, por ter vivido e celebrado comigo os momentos de alegria, quer a nível profissional como pessoal e por me ter ajudado a ultrapassar os momentos de autêntica aflição que ambas partilhámos ao longo destes quatro anos. À Tânia Martins, por estar sempre à distância de um telefonema, pelo apoio constante, e por compreender a minha constante ausência.

Aos meus pais, Avelino e Graça, e ao meu irmão Nuno, o meu obrigada pelos valores que me transmitiram e que fazem de mim a pessoa que sou hoje, pelo apoio incondicional, por partilharem as minhas conquistas com orgulho, por me ajudarem a ultrapassar os momentos menos bons e por terem muita paciência comigo.

Por fim, ao José, por estar ao meu lado em todos os momentos, com amor, amizade, paciência e compressão, pelo apoio incondicional e conselhos que me ajudaram a ultrapassar todos os obstáculos e por me fazer acreditar que esta etapa chegaria ao fim.

ABSTRACT

Waste lubricant oil (WLO) is the most significant liquid hazardous waste stream in Europe that requires proper handling and treatment. Regeneration is an interesting treatment route to mitigate the significant environmental impacts of lubricants. Solvent extraction is one of the most effective deasphalting processes for the regeneration of WLO.

The current objectives towards a circular economy represent a challenge to continuously maximize the regeneration of this waste. The quality of WLO is a limiting factor regarding its potential for regeneration, in which producers have a great responsibility on the handling phase. In addition, with increasing awareness for environmental protection, it is becoming imperative to find not only sustainable but also economically attractive processes.

In this context, the main objectives of the thesis include the characterization of fresh and waste lubricant oils aiming to improve the management system of WLO in Portugal. In addition, the objectives of this work include studies of the regeneration process by solvent extraction, the development of a new methodology for the selection of sustainable solvents and the assessment of the best extraction conditions.

Regarding the characterization of fresh lubricant oil, the following properties were evaluated: viscosity; viscosity index; density; total acid number (TAN); saponification number; and percentage of aromatics, naphthenics and paraffinics. Regression models that can predict the desired properties based on FTIR spectra were developed. The density, percentage of aromatics, naphthenics and paraffinics were well predicted.

As regards the characterization of WLO, the temperature dependence of viscosity was investigated, and correlations for the estimation of viscosity and surface tension from density were assessed. The temperature dependence of viscosity at the Newtonian plateau of WLO deviated from the Arrhenius behavior, and was accurately described by four correlations: Williams–Landel–Ferry (WLF), MYEGA, power law and Ghatee. The glass transition temperature varied between 170.5 and 198.7 K. New correlations were found for the estimation of viscosity and surface tension from density at different temperatures.

The evaluation and improvement of a national management system was based on the physicochemical characteristics of WLO collected from different producers (garage, industry and others). The results revealed that chlorine nonconformities (Cl > 2000 ppm) were mostly registered in industrial producers. Therefore, the management system could be improved by segregating oils from industry. In addition, FTIR analysis showed that about 60% of the WLO collected in Portugal may be contaminated with glycol-containing compounds (e.g. brake fluid and antifreeze), regardless the producer.

The nature of the compounds responsible for the coagulation phenomena after alkaline treatments that may cause plant shutdown was studied. For that, an empirical test method was developed to assess the coagulation behavior of WLO. The coagulation phenomena were classified as A – negative, B – precipitate formation and C – positive. Spectral discriminating analysis revealed that class A oils did not have any compounds that negatively affect the alkaline treatment. Class B oils may be constituted by gear or hydraulic lubricants, which have low concentration of additives and oxidation products. Class C is mainly composed by synthetic esters, which form a gel-type oil after the addition of KOH and hamper regeneration processes in alkaline treatments. The classification based on statistical analysis applied to FTIR spectra properly categorize 83% of the WLO according to their coagulation class.

A new methodology for the selection of solvents for WLO regeneration, which takes into account technical, economical and greenness issues was proposed. In the first phase, five criteria were used: water and acidic properties; selectivity towards the base oil and flocculation capacity; number of carbon atoms between three and five; melting point lower than 10 ºC and a boiling point between 60 and 130 ºC; yield greater than 85%. In the second phase, three metrics of sustainability were employed: greenness, efficiency, and cost. Globally, a score was attributed to each solvent based on the assessment of individual metrics. From a list of 154 solvents, 1-butanol, isobutanol, and methylethyl ketone (MEK) are the most sustainable solvents.

Solvent extraction studies were performed using 1-butanol and MEK as “green” solvents. WLO with substantial different properties and segregated by coagulation classes (A, B and C) were tested. The extraction is not effective for class B oil, due to its low level of impurities. The addition of KOH in class C oils is less effective due to greater saponifiable matter in the oil. 1-Butanol is more efficient than MEK for both class A and C. The optimal solvent/oil ratio of 5 w/w and KOH dosage of 1.5 or 2 g/L was found for all systems.

RESUMO

Os óleos lubrificantes usados (OU) constituem o resíduo líquido perigoso mais significativo da Europa. A sua regeneração constitui uma interessante via de tratamento para mitigar o elevado impacto ambiental e está alinhada com os princípios da "economia circular", um desiderato nacional e europeu. De facto, sendo os OU um resíduo perigoso, a sua recuperação e reintrodução no ciclo de vida útil, é de relevância acrescida. Contudo, a qualidade dos OU é um fator limitante para o seu potencial de regeneração, no qual os produtores têm uma responsabilidade central. Além disso, para além da vertente ambiental, torna-se imperativo implementar abordagens holísticas que garantam o desenvolvimento de um ciclo de vida dos OU mais sustentável.

Neste contexto, os principais objetivos da tese envolvem a caraterização de óleos novos e usados com vista à melhoraria do sistema de gestão de OU em Portugal. Além disso, os objetivos deste trabalho incluem estudos do processo de regeneração por extração solvente, incluindo o desenvolvimento de uma nova metodologia para a seleção de solventes e a avaliação das condições ótimas de extração.

Relativamente à caraterização de óleos lubrificantes novos, foram avaliadas as seguintes propriedades: viscosidade; índice de viscosidade, densidade, índice de acidez; índice de saponificação e teor de parafínicos, nafténicos e aromáticos. Desenvolveram-se modelos de regressão para a previsão destas propriedades com base nos espetros FTIR. A densidade, percentagem de aromáticos, nafténicos e parafínicos foram corretamente previstas.

Em relação à caracterização de OU, investigou-se a dependência da temperatura com a viscosidade, e avaliaram-se correlações para estimar a viscosidade e tensão superficial a partir da densidade. A dependência da viscosidade com a temperatura dos OU desvia-se do comportamento de Arrhenius, sendo descrita com precisão por quatro correlações: Williams-Landel-Ferry (WLF), MYEGA, lei de potência e Ghatee. A temperatura de transição vítrea variou entre 170,5 e 198,7 K. Adicionalmente, foram desenvolvidas novas correlações para estimar a viscosidade e a tensão superficial a partir da densidade a diferentes temperaturas.

O potencial de melhoria do sistema nacional de gestão foi avaliado tendo em conta as características físico-químicas de OU recolhidos em diferentes produtores (oficinas, indústria e outros). Os resultados revelaram que as não conformidades de cloro (Cl> 2000 ppm) registam-se sobretudo em produtores industriais. Desta forma, o sistema de gestão poderia beneficiar da segregação dos óleos industriais. Além disso, a análise FTIR mostrou que 60% dos OU recolhidos em Portugal podem estar contaminados com glicol (e.g. fluido de travão e anticongelante), independentemente do tipo de produtor.

Foi estudada a natureza dos compostos responsáveis pelos fenómenos de coagulação após tratamento alcalino que podem causar problemas no processo industrial. Paral tal, de modo a avaliar o comportamento de coagulação dos OU foi desenvolvido em teste empírico. Os resultados foram classificados como A - negativos, B - formação de precipitados e C - positivos. A análise espectral discriminante revelou que os óleos classe A não possuem compostos que afetam negativamente o tratamento alcalino. Os óleos da classe B podem ser constituídos por óleos de engrenagem ou hidráulicos, que por terem baixa concentração de aditivos e produtos de oxidação, não reagem com o KOH, que acaba por precipitar. A classe C é composta por óleos sintéticos do tipo éster, que formam um gel após a adição de KOH e inibem a regeneração com tratamento alcalino. A classificação do teste de coagulação baseada na análise estatística aplicada ao FTIR categoriza corretamente 83% dos OU de acordo com sua classe de coagulação.

Propôs-se uma nova metodologia para a seleção de solventes para regeneração de OU, que contrabalança critérios técnicos, económicos e de "verdura". Na primeira fase, cinco critérios foram utilizados: água e propriedades ácidas; seletividade para com o óleo base e capacidade de floculação; número de átomos de carbono entre três e cinco; ponto de fusão < 10 ºC e ponto de ebulição entre 60 e 130 ºC; rendimento > 85%. Na segunda fase, três métricas de sustentabilidade foram aplicadas: "verdura", eficiência e custo. Globalmente, foi atribuída uma pontuação a cada solvente com base na avaliação das métricas individuais. De uma lista de 154 solventes, o 1-butanol, isobutanol e metiletilcetona (MEK) foram os mais sustentáveis.

Os estudos de extração realizados com 1-butanol e MEK (solventes "verdes") mostraram ser eficientes para recuperar os OU. Neste âmbito, foram testados OU com propriedades substancialmente diferentes e segregados por classe de coagulação (A, B e C). A extração não é efetiva para o óleo classe B, devido ao baixo nível de impurezas. A adição de KOH nos óleos da classe C é menos eficaz devido à maior quantidade de matéria saponificável no óleo. O 1-butanol é mais eficiente que o MEK para as classes A e C. A razão solvente/óleo ótima corresponde a 5 w/w e a dosagem de KOH a 1,5 ou 2 g/L.

TABLE OF CONTENTS

List of Figures xiii
List of Tables xvii
Abbreviations xix
Nomenclature xxi

PART A – THESIS SCOPE AND OUTLINE 1

1. Introduction 3
  1.1. From virgin to waste lubricant oils 3
  1.2. Impact of waste oils on health and environment 5
  1.3. Legislative framework 7
  1.4. Mitigating the environmental impacts by regeneration 9
  1.5. Objectives of the thesis 11
  1.6. Thesis outline 12
  1.7. References 13

2. Literature review 17
  2.1. Lubricants and lubrication 17
    2.1.1. Base oil 19
      2.1.1.1. Mineral oils 19
      2.1.1.2. Synthetic oils 22
    2.1.2. Mineral base oil production 27
    2.1.3. Additives 31
  2.2. Waste lubricant oil 40
    2.2.1. Main contaminants 40
    2.2.1. Treatment and disposal routes 42
    2.2.1. Handling, storage and collection 43
  2.3. Physicochemical properties of lubricant oils 45
    2.3.1. Prediction of properties using advanced statistical analysis 49
    2.3.2. Correlation of thermophysical properties 52
  2.4. Regeneration process 53
    2.4.1. Alkaline treatment 59
    2.4.2. Solvent extraction 59
  2.5. References 63

PART B – CHARACTERIZATION OF FRESH LUBRICANT OIL 71

3. Assessment and prediction of lubricant oil properties using infrared spectroscopy and advanced predictive analytics 73
  3.1. Introduction 74
  3.2. Materials and methods 75

3.2.1. Samples description 75
3.2.2. Physicochemical characterization 76
3.2.3. Predictive analytical methods and comparison framework 77

3.3. Results and discussion 79
3.3.1. Prediction of physicochemical properties 79
3.3.1.1. Density 82
3.3.1.2. Total acid number (TAN) 83
3.3.1.3. Aromatics 84
3.3.1.4. Naphthenics 85
3.3.1.5. Paraffinics 86

3.4. Conclusions 87

3.5. References 88

PART C – CHARACTERIZATION OF WASTE LUBRICANT OIL 91

4. Measurement and correlation of thermophysical properties of waste lubricant oil 93

4.1. Introduction 94

4.2. Materials and methods 95
4.2.1. Waste oil samples 95
4.2.2. Experimental methods 96
4.2.2.1. Temperature dependence of viscosity 96
4.2.2.2. Temperature dependence of density 96
4.2.2.3. Temperature dependence of surface tension 97
4.2.3. Theoretical background 98

4.3. Results and discussion 101
4.3.1. Temperature dependence of viscosity 101
4.3.2. Relation between density and viscosity 108
4.3.3. Relation between surface tension and density 109

4.4. Conclusions 112

4.5. References 113

5. An overview of waste lubricant oil management system: Physicochemical characterization contribution for its improvement 117

5.1. Introduction 118

5.2. Materials and methods 120
5.2.1. Samples description 120
5.2.2. Physicochemical characterization 120
5.2.3. Statistical analysis 121

5.3. Results and discussion 121

5.3.1. Portuguese waste lubricant oil management system 121
5.3.2. Physicochemical characterization 126
5.4. Conclusions 130
5.5. References 130
6. A data-driven approach for the study of coagulation phenomena in waste lubricant oils and its relevance in alkaline regeneration treatments 133
6.1. Introduction 134
6.2. Materials and methods 136
6.2.1. Sampling 136
6.2.2. Coagulation test 136
6.2.3. Physicochemical characterization 137
6.2.4. Classical statistical analysis 138
6.2.5. Chemometric methods 138
6.3. Results and discussion 139
6.3.1. Coagulation 139
6.3.2. Physicochemical characterization 140
6.3.3. FTIR analysis 145
6.3.4. Classification of the coagulation classes 146
6.3.5. Spectral discriminant analysis 148
6.4. Conclusions 152
6.5. References 152
PART D – TREATMENT BY SOLVENT EXTRACTION 157
7. A new methodology of solvent selection for the regeneration of waste lubricant oil using greenness criteria 159
7.1. Introduction 160
7.2. Methodology 161
7.2.1. Solvent dataset and metrics 161
7.2.2. Solvent selection methodology 161
7.2.3. Experimental extraction procedure 162
7.3. Solubility parameter 163
7.1. Sensitivity analysis 164
7.2. Results and discussion 164
7.2.1. Phase 1 164
7.2.1.1. Water & acids 164
7.2.1.2. Selectivity 165
7.2.1.3. Number of carbon atoms 168
7.2.1.4. Melting and boiling points 168

7.2.1.5. Yield 169
7.2.2. Phase 2 170
7.2.2.1. GSK greenness criteria 170
7.2.2.2. Performance of extraction 172
7.2.2.3. Cost 172
7.2.2.4. Sustainability score 173
7.3. Conclusions 174
7.4. References 175
8. Regeneration of waste lubricant oil with different properties using green solvents _ 179
8.1. Introduction 180
8.2. Materials and methods 181
8.2.1. Materials 181
8.2.2. Solvent extraction procedure 182
8.2.3. Physicochemical characterization 183
8.2.4. Design of experiments 183
8.2.5. Profiler and desirability function approach 184
8.3. Results and discussion 184
8.3.1. Selection of input variables 184
8.3.1.1. Effect of solvent/oil ratio 184
8.3.1.2. Effect of KOH dosage 186
8.3.2. Surface response modeling 187
8.3.2.1. Predicted models and statistical analysis 187
8.3.2.2. Desirability analysis 191
8.3.2.3. Validation of predictive models 192
8.3.2.4. Physicochemical characterization 193
8.4. Conclusions 195
8.5. References 195
PART E – CONCLUSIONS AND FORTHCOMING WORK 199
9. Conclusions and forthcoming work 201
ANNEX A. SUPPLEMENTARY MATERIAL 201
A.1. Chapter 3 A1
A.2. Chapter 4 A5
A.3. Chapter 5 A7
A.4. Chapter 6 A11
A.5. Chapter 7 A15
A.6. Chapter 8 A21

LIST OF FIGURES

Figure 1.1. Lubricant demand by region in 2016 (2007). 3

Figure 1.2. World lubricant consumption by product type in 2016. 4

Figure 1.3. Environmental burden of primary production of base oils from crude relatively to regeneration of WLO. 10

Figure 1.4. WLO collection, regeneration, reprocessing and energy recovery rates from 2006 to 2016 in Portugal. 10

Figure 1.5. Thesis structure and relation with the life cycle of lubricants. 12

Figure 2.1. Stribeck curve. 18

Figure 2.2. Typical classes of hydrocarbons present in base oils. 20

Figure 2.3. Typical polyalphaolefin oligomers. 23

Figure 2.4. Several families of synthetic ester base oils. 24

Figure 2.5. Polyalkylene Glycol general structure. 26

Figure 2.6. Classical crude oil refining process for lubricating oil production. 30

Figure 2.7. Coil expansion model to explain viscosity modifiers mechanism. 32

Figure 2.8. Most commonly used viscosity index improvers. 33

Figure 2.9. Effects of friction and wear on metallic surfaces: (a) damage of sealing surfaces; (b) damage to a gear rim; (c) melted material caused by solid particle contamination and temperature increase; and (d) embedded machining chip. 34

Figure 2.10. Structure of a zinc dialkyl dithiophosphate (ZDDP). 34

Figure 2.11. Mechanism of action of corrosion and rust inhibitors. 35

Figure 2.12. Mechanism of oxidative degradation in lubricant base oils. 36

Figure 2.13. Antifoaming agents mechanism. 37

Figure 2.14. Polar compounds suspension and acid-neutralization in lubricants by detergents. 38

Figure 2.15. Interaction of dispersants with residue particles . 39

Figure 2.16. The mechanism of action of pour point depressants. 39

Figure 2.17. Treatment and disposal routes currently adopted worldwide. 42

Figure 2.18. Life cycle of lubricants (QC – Quality Control). 44

Figure 2.19. Laminar flow of a fluid between two plates. 46

Figure 2.20. The viscosity index (VI) concept. 47

Figure 2.21. Surface tension and TAN of lubricants over the service time. 49

Figure 2.22. Methodology for the prediction of properties using chemometrics. 50

Figure 2.23. Typical regeneration process steps. 53

Figure 2.24. Regeneration industries in Europe, 2016. 56

Figure 2.25. The solvent extraction process. 60

Figure 3.1. PCA results obtained to the nine oil properties: (a) the scores of the 1st and 2nd principal components and (b) their respective loadings. 80

Figure 3.2. Results obtained with EN method to predict density: (a) predicted and measured density values, (b) representative spectrum of different sample classes and (c) EN regression coefficients in the comparison study. 83

Figure 3.3. Results obtained with PLS to predict TAN: (a) predicted and measured TAN values, (b) representative spectrum of different sample classes and (c) PLS regression coefficients in the comparison study. 84

Figure 3.4. Results obtained with iPLS to predict the percentage of aromatics: (a) predicted and measured percentages of aromatics, (b) representative spectra from different sample classes and (c) number of times each bin was included in the regression model. 85

Figure 3.5. Results obtained with LASSO to predict the percentage of naphthenics: (a) predicted and measured percentage of naphthenics, (b) representative spectra for different sample classes and (c) regression coefficients. 86

Figure 3.6. Results obtained with iPLS to predict the percentage of paraffinics: (a) predicted and observed response and (b) representative spectra for different sample classes and (c) number of times each bin was included in the iPLS model. 87

Figure 4.1. Viscosity behavior as a function of the shear rate at different temperatures for sample S8. 102

Figure 4.2. Dynamic viscosity as a function of the temperature for the analyzed waste oil samples. 102

Figure 4.3. Fitting of Eq. (4.2) to the WLO experimental viscosity data. The straight line corresponds to Eq. (4.15) (R^2=0.9999) and different symbols correspond to experimental data-points for different WLO. Parameters $C1$, $C2$ and T_g are given in Table 4.2. 104

Figure 4.4. Scaling of viscosity data ($\eta^{-\phi/-a}$) as a function of the scaled temperature (T/T_x) for waste lubricant oil. The straight line corresponds to a linear fit (with R^2=0.9999) and different symbols correspond to experimental data-points for different WLO. 107

Figure 4.5. Dependence on temperature of $\eta - 0.330$. 107

Figure 4.6. Dependence on ρ^2.ln(ρ) of ln (η) of waste lubricant oil. The symbols are data points off all the analyzed samples and the lines represent the fitting using Eq. (4.16). 108

Figure 4.7. (a) Parity plot and (b) relative percentage deviation for calculated viscosity, η_{calc}, compared with experimental values, η_{exp}, of WLO samples. 109

Figure 4.8. Correlation between density and surface tension of different waste lubricant oil. 110

Figure 4.9. (a) Parity plot comparing the experimental and calculated surface tension of waste lubricant oil using Eq. (4.14) and (b) relative percentage deviations between calculated and experimental values. 111

Figure 4.10. Surface tension of waste oil (samples S1 to S9) and of fresh lubricant oil from literature [15,16].112

Figure 5.1. Waste lubricant oil management in some Member States in 2011 [11]. a) Recycling versus collection rates (circles size represents the performance in terms of kg/cap./year); b) Regeneration rate. 119

Figure 5.2. WLO management system in Portugal (SIGOU). 123

Figure 5.3. Percentages of non-conforming samples collected from 2008 to 2015 with respect to sediments, water plus sediments and chlorine considering the legal thresholds. 125

Figure 5.4. Distribution of noncompliance with legal thresholds for collection from 2008 to 2015 by WLO producer: a) sediments (> 3 wt.%), b) water plus sediments (> 8 wt. %) and c) chlorine (> 2000 ppm). 126

Figure 5.5. Physicochemical characterization of WLO regarding a) Density at 15 °C, b) Viscosity at 40 °C, c) SN and d) TAN. 127

Figure 5.6. Content of P, Zn, Ca, S, Fe, and Si in waste oils according to the type of producer. 128

Figure 5.7. FTIR spectra of WLO collected from a) industry, b) garage and c) others. 129

Figure 6.1. Outcome of the coagulation test. The Figure shows the vessel in which the coagulation test was performed and the different behavior of WLO after the addition of KOH under specific conditions, which were classified as: (a) class A - negative; (b) class B1 - viscosity increase; (c) class B2 - precipitate formation and (d) class C - positive. 140

Figure 6.2. Physicochemical properties of waste oils by coagulation class: (a) TAN; (b) SN; (c) kinematic viscosity at 40°C; (d) water content; (e) surface tension. 141

Figure 6.3. Content of P, S, Ca, Zn, Fe, Al, Cl and Si in waste oils by coagulation class. 144

Figure 6.4. FTIR spectra of waste lubricant oils typically corresponding to classes A, B1, B2 and C. 145

Figure 6.5. Projection of FTIR spectra for all the WLO samples onto the two-dimensional output subspace of the composite PLS-DA/FDA mapping. 147

Figure 6.6. Wavenumbers selected for each coagulation class discrimination. 149

Figure 6.7. SEM-EDS results of the precipitate formed in two class B2 oil samples. 151

Figure 7.1. Solvent selection methodology. 162

Figure 7.2. Yield of extraction for different solvents (operating conditions: solvent/oil ratio = 5/1; contact time = 20 min; T = 25 °C and mixing speed = 500 rpm). 169

Figure 7.3. Green metric scores assigned by GSK for different (a) alcohols and (b) ketones. 170

Figure 7.4. (a) PSR for different solvents (at solvent/oil ratio = 5/1; contact time = 20 min; T = 25 °C and mixing speed = 500 rpm), (b) PSR score assignment. 172

Figure 7.5. (a) Sustainability score for different solvents weighting evenly the greenness, performance and cost scores. (b) Sensitivity of the sustainability score to the variation of the weights assigned. 174

Figure 8.1. Effect of solvent/oil ratio on the sludge removal for different types of waste oil using (a) 1-butanol and (b) MEK. 185

Figure 8.2. Effect of KOH dosage on the sludge removal for different types of waste oil using (a) 1-butanol and (b) MEK. 187

Figure 8.3. Response surface plots for WLO class A using (a) and (b) 1-butanol, and (c) and (d) MEK. 190

Figure 8.4. Response surface plots for WLO class C using (a) and (b) 1-butanol, and (c) and (d) u MEK. 191

Figure 8.5. Prediction profiler and desirability function for (a) class A oil using 1-butanol and (b) class C using MEK. 192

Figure 8.6. FTIR spectra of different classes of waste oil and after extraction with 1-Butanol and MEK. 194

Figure A.1. Predicted and measured density values for all samples (samples 7, 57 and 59 are identified since they were removed from the results presented in the paper). Note that there are multiple instances of samples 57 and 7, representing different double-cross validation iterations where they were in the left-out fold. A3

Figure A.2. FTIR spectra of WLO samples from a) Industry, b) Garage and c) Others. A9

Figure A.3. FTIR spectrum of coagulation class B2 precipitate. A11

Figure A.4. FTIR spectra of waste oil class C treated with 1-butanol and a KOH dosage of 0, 1.5 and 3 g/L. A21

LIST OF TABLES

Table 1.1. General hazardous properties of WLO. 5

Table 1.2. Technical specifications of WLO defined by the Portuguese Environmental Agency (APA). 9

Table 2.1. API base oil categories. 18

Table 2.2. Composition of crude oils. 19

Table 2.3. Performance characteristics of mineral base oil components. 22

Table 2.4. Properties of commercial low- and high-viscosity PAO. 24

Table 2.5. Typical properties of a series of ester types. 25

Table 2.6. General properties of several PAG. 26

Table 2.7. Comparison between mineral and synthetic base oils. 27

Table 2.8. Crude oil molecules and their contribution to base oil properties. 28

Table 2.9. Typical composition of fresh lubricant oils. 40

Table 2.10. Main contaminants and their sources. 41

Table 2.11. Physicochemical properties of fresh and waste lubricant oils assessed in this work. 45

Table 2.12. Prediction of properties using chemometrics and infrared spectroscopy. 51

Table 2.13. Correlations for the temperature dependence of viscosity, between the density and viscosity, and between density and surface tension. 52

Table 2.14. Waste oil re-refining technologies. 57

Table 2.15. Overview of solvent extraction studies for the regeneration of WLO. 61

Table 3.1. Classification categories of lubricant oil samples 76

Table 3.2. Prediction results for oil properties. 81

Table 4.1. Aromatic, naphthenic, paraffinic and water contents, and viscosity, density and surface tension range of the analyzed waste oil samples for the liquid at temperature T and pressure P = 101.86 kPa. 96

Table 4.2. Fitting parameters of WLF equation (Eq. 4.2) for waste oil samples. 103

Table 4.3. Fitting parameters of experimental data using the MYEGA equation (Eq. 4.6). 105

Table 4.4. Results of the fitting using the power law equation (Eq. 4.7). 105

Table 4.5. Fitting parameters (ϕ, a and b) of Eq. (4.8) and the values of γ, $\eta 0$ and Tx calculated using Eq. (4.9). 106

Table 5.1. Technical performance achieved in 2015 and targets for 2015 to 2019 (*Despacho n. º 4383/2015*). 123

Table 5.2. Technical specifications of WLO defined by Portuguese legislation into force from 2015. 124

Table 6.1. Possible outcomes of the coagulation test. 137

Table 6.2. Physicochemical characterization of 56 samples of fresh lubricant oils. 142

Table 6.3. Coagulation accuracy rate for different clusters of coagulation classes. 147

Table 7.1. Categories of solvents rejected due to lack of selectivity. 166

Table 7.2. Difference between the solubility parameter of solvents (δ_1) and base oil (δ_2=18 MPa$^{1/2}$). 167

Table 7.3. GSK greenness, efficiency and cost scores. 171

Table 8.1. Properties of the analyzed waste oil classes A, B and C. 182

Table 8.2. Full factorial design of experiments. 183

Table 8.3. Critical clarifying ratio for different types of waste oils. 186

Table 8.4. Experimental sludge removal and yield obtained for class A and C, using 1-butanol and MEK. 187

Table 8.5. Regression coefficients of the predicted models. 188

Table 8.6. Analysis of variance and goodness of fit of the models for the responses PSR and Yield. 189

Table 8.7. Experimental validation of predictive models. 193

Table 8.8. Properties of different classes of waste oil and after extraction with 1-Butanol and MEK. 194

Table A.1. Physicochemical characteristics of lubricant oil samples used for model development. A1

Table A.2. Prediction results for nine oil properties, including all samples and regression methods initially considered. A3

Table A.3. Viscosity, density and surface tension determined experimentally for waste lubricant oil samples at temperature T and pressure *P* = 101.86 kPa. A5

Table A.4. Physicochemical characteristics of WLO sub-dataset analyzed. A7

Table A.5. Discriminant bands of coagulation classes B1, B2 and C A12

Table A.6. List of solvents from the 2016 GSK solvent selection guide. A15

Table A.7. GSK solvent selection guide metrics, categories and areas of assessment. A18

Table A.8. Percent sludge removal (PSR), solvent acquisition cost, enthalpy of vaporization. A19

Table A.9. List of data values from which the scores are calculated. A19

ABBREVIATIONS

APA	Portuguese Environmental Agency
API	American Petroleum Institute (USA)
ASTM	American Society of Testing Materials (USA)
BRT	Bagging of Regression Trees
BT	Boosted Trees
CCR	Critical clarifying ratio
CLS	Classical Least Squares
DGAE	General Directorate of Economic Activities (PT)
DIN	Deutsches Institut für Normung
DoE	Design of experiments
EDS	Energy-dispersive X-ray spectroscopy
EDXRF	Energy-dispersive X-ray fluorescence
EHS	Environment, Health, and Safety
EN	Elastic Nets
EO	Ethylene Oxide
FDA	Food and Drug Administration (USA)
FDA	Fisher Discriminant Analysis
FSR	Forward Stepwise Regression
FTIR	Fourier Transform Infrared Spectroscopy
GHG	Greenhouse Gas
GFL	Gas Forming Fluids
GNP	Gross National Product
GSK	GlaxoSmithKline
HP	Hazardous Property
IARC	International Agency for Research on Cancer
iPLS	interval Partial Least Squares
IQR	Interquartile Range
IR	Infrared spectroscopy
IS	Indian Standard
ISO	International Organization for Standardization
LASSO	Least Absolute Shrinkage and Selection Operator
LECA	Light Expanded Clay Aggregated
LoW	European List of Waste
MEA	Etanolamine
MEK	Methyl Ethyl Ketone
MIBK	Methyl Isobutyl Ketone
MLR	Multiple Linear Regression
NIST	National Institute of Standards and Technology (US)
NMP	N-methyl-2-pyrrolidone
OCP	Olefin Copolymer
PAG	Polyalkylene Glycol
PAH	Polycyclic Aromatic Hydrocarbon
PAO	Polyalphaolefin

PC	Principal Component
PCB	Polychlorinated Biphenyl
PCR	Principal Component Regression
PCR_FS	PCR with Forward Stepwise
PCT	Polychlorinated Terphenyl
PFPE	Perfluoropolyether
PIB	Polyisobutilene
PLS	Partial Least Squares
PLS-DA	Partial Least Squares for Discriminant Analysis
PMA	Polymethacrylate
PPD	Pour Point Depressants
PO	Propylene Oxide
PSR	Percentage of Sludge Removal
QC	Quality Control
QL	Quantitation Limit
RF	Random Forests
RR	Ridge Regression
RSM	Response Surface Methodology
SAE	Society of Automotive Engineers
SEM	Scanning Electronic Microscopy
SIGOU	Integrated system for the management of waste oils (PT)
SPE	Styrene Polyester
STOT	Specific Target Organ Toxicity
SVR	Support Vector Regression
TDA	Thermal Deasphalting
TFE	Thin Film Evaporation
TPH	Total Petroleum Hydrocarbons
VI	Viscosity Index
WFD	Waste Framework Directive
WLF	Williams–Landel–Ferry model
WLO	Waste Lubricating Oil
ZDDP	Zinc Dialkyl Dithiophosphate

NOMENCLATURE

AARD	Absolute average relative deviation	[%]
d_i	Desirability function	[-]
E	Energy of vaporization	[J.mol^{-1}]
E_a	Activation energy	[J.mol^{-1}]
m	Fragility parameter	[-]
P	Pressure	kPa
R	Gas constant	[cm^3.MPa.K^{-1}.mol]$^{-1}$
R^2	Coefficient of determination	[-]
$\mathrm{R}^2_{\mathrm{Adj}}$	Adjusted R^2	[-]
RE	Relative Error	[%]
RMSE	Root mean square error	[%]
$\mathrm{RMSE}_{\mathrm{CV}}$	Root mean square error of cross validation	[%]
$\mathrm{RMSE}_{\mathrm{DCV}}$	Root mean square error of double cross validation	[%]
SN	Saponification number	[mg KOH/g]
t	Time	[min]
T	Temperature	[K]
TAN	Total acid number	[mg KOH/g]
TBN	Total base number	[mg KOH/g]
T_g	Glass transition temperature	[K]
T_m	Melting temperature	[K]
T_r	Reference temperature	[K]
T_x	Dynamic crossover temperature	[K]
V_m	Molar volume	[cm^3.mol^{-1}]
V_{mix}	Molar volume of mixture	[cm^3.mol^{-1}]
$W_{waste\ oil}$	Weight of waste oil	[g]
$W_{base\ oil}$	Weight of base oil	[g]
$W_{dry\ sludge}$	Weight of dry sludge	[g]
α_T	Shift factor	[-]
$\dot{\gamma}$	Shear rate	[s^{-1}]
δ	Solubility parameter	[MPa]
ΔH	Enthalpy of vaporization	[J.mol^{-1}]
ΔG^M	Free energy of mixing	[J.mol^{-1}]
$\Delta G^M_{noncomb}$	Noncombinatorial free energy of solution	[J.mol^{-1}]
ΔH^M	Heat of mixing	[J.mol^{-1}]
ΔS^M	Entropy change in the mixing process	[J.mol^{-1}.K^{-1}]
η	Dynamic viscosity	[mPa.s]
η_g	Dynamic viscosity at T_g	[mPa.s]
η_∞	Dynamic viscosity at infinite temperature	[mPa.s]
κ_T	Isothermal compressibility	[Pa^{-1}]
ρ	Density	[kg.m^{-3}]
σ	Surface tension	[mN.m^{-1}]
τ	Structural relaxation time	[s]
υ	Kinematic viscosity	[cSt]
ϕ	Fluidity exponent	[-]
ϕ_i	Volume fraction of the component i	[-]

PART A – THESIS SCOPE AND OUTLINE

The first part of the thesis presents an overview of the different phases of the life cycle of lubricant oils, the management practices adopted for the treatment of the generated waste in Europe and in Portugal as well.

Chapter 1 presents the framework of regeneration as an environmentally sound treatment route for mitigating the negative impacts of waste lubricant oil.

Chapter 2 points out the composition of fresh and waste lubricant oils, the available treatment routes, the properties monitored, and an overview of the regeneration technologies is given. Special focus is on the alkaline and extraction phases of the process. Since this thesis deals with very different topics within the scope of the waste lubricant oil management system and regeneration by solvent extraction, in Chapter 2 the opportunities for improvement are discussed, which served as motivation for the development of the subsequent chapters.

1. INTRODUCTION

Nowadays some products are essential for humans to sustain living standards and comfort. Lubricants are one of those essential products. Its main function is to reduce friction and wear of metal surfaces, extending the service life of equipment and saving resources and energy. Scientific research has shown that the direct costs of friction and wear phenomena may be responsible for nearly 10% of gross national product (GNP) in many industrialized countries. In addition, it is estimated that 1% of GNP could be saved in terms of energy if current tribological knowledge (the science of friction) wear and lubrication was applied to lubricated systems [1,2].

Currently, the sustainability principles are considered a driving force for the industry, and thus saving energy, resources and cutting emissions have become central issues. The scarcity of resources and the responsibility towards the future generations are also fundamental topics. Lubricants and its recovery are increasingly attracting public awareness, since they contribute to the sparing use of resources and support sustainable development [3].

1.1. FROM VIRGIN TO WASTE LUBRICANT OILS

In 2016, the world lubricant market was estimated at around 35.7 Mt. Accounting for 42% of the global market, Asia-Pacific has the highest share and is the region with the fastest growth in the consumption of lubricants. Europe is responsible for 19% of lubricants demand, consuming 6.8 Mt of lubricating oils every year [4]. The 2016 and 2007 (shown between brackets) world demand by geographic area is presented in Figure 1.1.

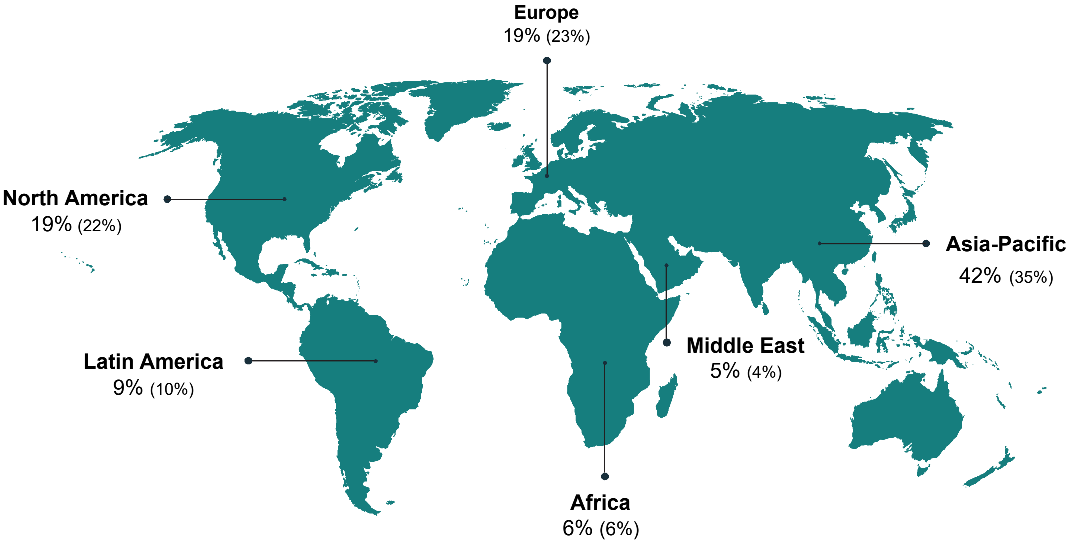


Figure 1.1. Lubricant demand by region in 2016 (2007). Adapted from [5].

Lubricants may be classified into several categories, but the three major groups are automotive, industrial and process lubricants, as illustrated in Figure 1.2. In 2016, the automotive segment accounted for 57% of the total global share. Industrial lubricants are sub-divided into industrial oils and industrial specialties (metalworking fluids and greases). The term lubricant is also loosely applied to many other fluids that do not specifically perform the main function to reduce friction and wear. Some examples include power and heat transmission fluids, hydraulic fluids, dielectric fluids, process oils, and others. Process oils are also included in the lubricant statistics shown in Figure 1.2. These oils are faced as raw materials in industrial processes, for instance, when are used as plasticizer agents in plastic and rubber industries. Process oils are only linked with lubricants because they are mineral oil products resulting from the refining of crude [6].

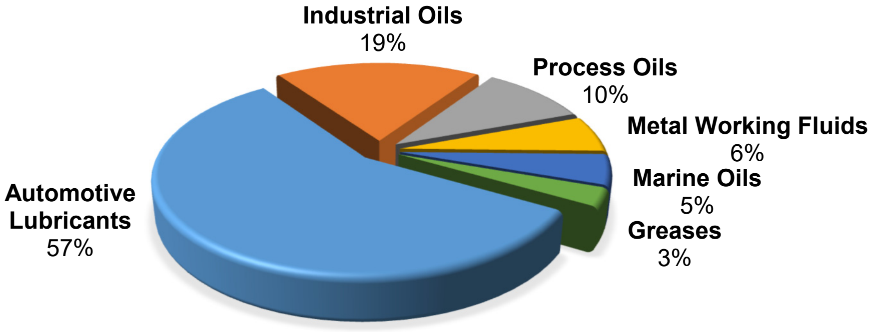


Figure 1.2. World lubricant consumption by product type in 2016. Adapted from [4].

Lubricants are generally subject to degradation and contamination from several sources during its long-term operation. Water, unburned fuel, solid impurities such as dirt, dust, soot, metal shards, metal oxide particles, heavy metals and other miscellaneous debris can irreversibly damage machinery. Moreover, oxidation, nitration, sulfation and other undesirable reactions can occur, leading to the accumulation of a variety of contaminants [7].

Contamination can have serious adverse effects on the physical and chemical properties of the lubricant. The loss of crucial properties, which are central to the useful service life can result in inefficient system performance, accelerated mechanical and chemical wear processes, shorten service life of equipment, and cause premature failures [5, 6]. Thus, just like everything else, lubricants have a lifespan and after a certain time they must be changed. The level of chemical changes and accumulation of contaminants increases with the oil use and depends on the original base oil, refining process used, additives package, application type, time of service, etc. [8].

As aforementioned, some oils are consumed in the process, and some are partly lost by combustion processes, evaporation, residues remaining in the containers, etc. [9]. Therefore, just about 50% of the lubricants consumed will generate waste. Consequently, huge amount of waste lubricant oil (WLO) is generated every year that require proper handling and treatment.

1.2. IMPACT OF WASTE OILS ON HEALTH AND ENVIRONMENT

According to the European List of waste (LoW), which intends to provide a harmonization of waste classification in the EU, all waste oils are absolute hazardous entries in the list. Therefore, WLO is considered hazardous waste, regardless of its composition and source, since exhibit at least o least one of the hazardous properties (as listed in the Commission Regulation (EU) No 1357/2014 of 18 December 2014) shown in Table 1.1. Certain oils may also possess other hazardous properties, due to the presence of substances such as metals, chlorine, polychlorinated biphenyls (PCB), polychlorinated terphenyls (PCTs) or polybrominated byphenyls (PBB). In addition, unburned fuel and products arising from fuel combustion may cause the accumulation of compounds such as polycyclic aromatic hydrocarbons (PAH). These compounds consisting of multiple rings such as benzo[a]pyrene are classified as carcinogenic to humans by the International Agency for Research on Cancer (IARC) [10]. Although unmetabolized PAHs can have toxic effects, a major concern is the ability of the reactive metabolites, such as epoxides and dihydrodiols, to bind to cellular proteins and DNA [11].

Table 1.1. General hazardous properties of WLO. Adapted from [12].

Hazardous Property	Risk Phrase	Limit concentration
HP5 – Specific Target Organ Toxicity (STOT)/Aspiration Toxicity	R65 – may cause lung damage if swallowed	TPH < 25 wt.%
HP7 – Carcinogenic	R45 – may cause cancer	TPH < 0.1 wt.%, unless total concentration of PAH is < 10 mg/kg
HP14 – Ecotoxic	R53 – May cause long-term adverse effects in the aquatic environment	TPH < 25 wt.%

TPH – Total Petroleum Hydrocarbons (C_6 to C_{40}) concentration

Therefore, the indiscriminate disposal of WLO into the environment may be a serious problem to ecosystems, posing a high risk of damage to soil, water, and air [8].

SOIL

Soil contamination with WLO is derived from leaks and losses of engines, indiscriminate dumping into sewers, or into the ground that can have devastating consequences in the soil in terms of physical, chemical and microbiological properties.

The fate of the oil released into the soil is controlled by the nature, porosity and organic matter of the soil. Soil with higher organic content tend to absorb the oil and prevent its flow downward, whereas permeable soil with little organic matter allows migration of the oil and contamination of groundwater [13]. The portion that remains in the soil undergoes slow volatilization due to low vapor pressures (<0.001 mm Hg at 25 °C), slow hydrolysis and/or microbial degradation [8].

The presence of WLO in the soil induces significant changes in the community of organisms involved in the nitrogen cycle. It fills the pores between the particles hindering the access of oxygen, inducing a significant number of anaerobic zones, and leading to the appearance and increase of metabolic activity by aerobic microorganisms that oxidize hydrocarbons [14].

The presence of heavy metals can strongly inhibit primary production, carbon mineralization, nitrogen transformations and mineralization of sulfur and phosphorus [15]. The pollution with WLO leads to the accumulation of essential and non-essential elements in the soil, such as Mg, Pb, Zn, Fe, Co, Cu, etc., and its possible translocation into plant tissues [16]. High concentrations of toxic metals can cause metabolic and growth inhibition for most plant species [17]. It has been shown that plant growth is inhibited in soils contaminated with engine oil. The concentration of lead in the surviving plants was found to be 450 (for turnips) and 150% (for beans) higher than in uncontaminated soils [13]. These metal levels can have a harmful effect on the food chain [18].

Plants absorb PAH present in the soil, especially the low molecular weight molecules and rapidly translocate them to the above ground tissues. Bioaccumulation phenomena may occur and it has been demonstrated in rats and invertebrates that PAH levels were 30-60 times higher than the concentrations in the soil. The oral toxicity of these compounds varies from very toxic to moderately toxic (50 to 1000 mg/kg body weight) in rats. Other effects on terrestrial organisms may include adverse effects on reproduction and immunity systems [19].

WATER

Lubricants in contact with water form an impermeable film, preventing the oxygenation of living beings. The different constituents undergo different processes of volatilization, emulsification, agglomeration, photodegradation and biodegradation [20].

Bioavailability of hydrocarbons is dependent on the solubility of saturated and aromatic hydrocarbons in water [21]. Studies on alkanes indicate that the solubility of carbon chains ≥C10 in water is limited (<1 mg/L) to cause toxicity [22]. Several studies have reported the results of mutagenicity tests of different bases oils, concluding that base oils with low concentrations of polycyclic aromatic compounds with 3-7 aromatic rings have low levels of mutagenicity [23].

As in the soil, the main effect of the presence of hydrocarbons in aquatic environments is the change in the community of microorganisms. Typically, common organisms are inhibited by the presence of many contaminants, such as metals, although an increase of microorganisms capable of biodegrading low molecular weight hydrocarbons may occur [17].

One year after a spillage in the soil, the biodegradation of the oil is only 24%, and in lakes is just 20% after 100 days. It was found that the WLO is one of the most important mutagenic agents in the aquatic environment [24]. Indeed, hydrocarbons have greater resistance to biodegradation, compared with other organic substances existing in typical wastewater treatment plants. Contaminated water, can ultimately reach water receptors, causing adverse effects on the human health and the environment [25].

AIR

WLO has a heat of combustion similar to petroleum fuels (~12,240 kcal/kg), but is much less expensive [17]. For this reason, it can be used as a primary or supplemental fuel for industrial boilers, domestic oil burners, rotary cement kilns, waste disposal incinerators, among others. However, as aforementioned, the WLO accumulates large amounts of metals and other contaminants, that if not properly controlled, will be released into the combustion gases.

The indiscriminate burning of WLO, without a demetallization pretreatment, generates significant emissions of metal oxides including Pb, Zn, Cr, Al, Ni, Cu, etc. In addition, the combustion produces other harmful compounds such as dioxins, sulfur oxides, nitro compounds, hydrochloric acid, nitrogen oxides, phosphates, among others. High concentrations of hydrochloric acid are formed during the combustion of certain oils, such as cutting oils, and metal processing oils which may contain up to 5% chloride [17,20].

Some studies showed that during the burning of WLO, about 50% of lead contained therein is expelled in the form of particles of size less than 1 μm and, therefore, easy to capture by living organisms. Besides these particulate emissions, it has been reported the presence of hydrocarbons having carcinogenicity, of polycyclic type, which are not burned at temperatures below 1400 °C [18].

1.3. LEGISLATIVE FRAMEWORK

With ever-growing global environmental awareness, many countries have developed regulations guiding the management of hazardous waste. In European Member States, the Waste Framework Directive (WFD) 2008/98/EC is the principal legislation that establishes the framework for handling WLO. This Directive introduces measures to protect the environment and human health by preventing or reducing the negative impacts of waste generation and management, as well as reducing general consequences of resources use and improving the efficiency of such use. The Directive sets an ambitious goal – approximation of the European Union to "society of recycling". It states that the management of WLO should be conducted in accordance with the waste hierarchy (1 – prevention, 2 – reuse, 3 – recycling, 4 – energy recovery and 5 – disposal), and preference should be given to options that deliver the best overall environmental outcome. The Article 21 states that Member States shall take the necessary measures to ensure that:

- waste oils are collected separately, where this is technically feasible;
- waste oils are treated in accordance with the waste hierarchy and without endangering human health or harming the environment;

- where this is technically feasible and economically viable, waste oils of different characteristics are not mixed and waste oils are not mixed with other kinds of waste or substances, if such mixing impedes their treatment.

Based on the general principles stated on the Directive, Member States are encouraged to develop national legislation and policies that ensure a fully transparent management process, accounting rules about the involvement of citizens and stakeholders. Additional measures can be applied, including waste management planning, quantitative and qualitative technical requirements, extended producer responsibility, economic instruments, voluntary agreements, or treatment annual targets.

The Directive 2008/98/EC has been transposed into Portuguese legislation by *Decreto Lei nº* 153/2003 amended by *Decreto Lei nº* 152-D/2017, that establishes the legal framework for management of WLO in Portugal. Therefore, the operations should be conducted according to the following hierarchy:

- Regeneration - any recycling operation whereby base oils can be produced by refining WLO, by removing the contaminants, oxidation products and additives contained in such oils;
- Other forms of recycling, excluding regeneration - recycling is the commonly generic term used for the reprocessing and regeneration of WLO by an appropriate selection of physical and chemical treatments. The reprocessing solutions in Portugal include i) the conversion of WLO into fuel oil by thermal cracking, which is then used to produce energy in co-generation engines, and ii) the production of light expanded clay aggregated (LECA), where WLO is used as expanding agent.
- Other forms of recovery such as incineration.

In Portugal, fresh lubricant oil producers transfer the responsibility for the management of the generated WLO to an entity duly licensed according to *Despacho n.º* 4383/2015. SOGILUB – Sociedade de Gestão Integrada de Óleos Lubrificantes Usados, Lda was granted the license to manage the integrated system for the management of waste oils, known as SIGOU, and is responsible to meet the annual management targets. These targets include: i) the collection of at least 85% of the WLO generated every year; ii) regeneration of all the collected WLO as long as they comply with the technical specifications, and in any case, ensure regeneration of at least 50% of the collected WLO; iii) recycling of at least 75% of the collect WLO and iv) recovery of all collected WLO which was not recycled by regeneration or other route.

The WLO shall meet physicochemical specifications, which are monitored at the several stages of the management system, including during collection, pre-treatment, as well as after regeneration, as described in Table 1.2. Waste oil regeneration operators shall ensure that the base oils resulting from such operation do not have on their composition dangerous substances in accordance with the applicable legislation. The waste oils containing PCB/PCT with concentrations greater than 50 ppm are excluded from the regular management of WLO and are regulated by *Decreto Lei nº* 277/99 of 23 July. In this case, the wastes contaminated with PCB must be destroyed by incineration.

Table 1.2. Technical specifications of WLO defined by the Portuguese Environmental Agency (APA) [26].

Parameter	**Test Method**	**Waste Lubricant Oil**			
		Collection	**Pre-treatment**	**Regeneration**	**Other forms of Recycling**
Density at 15 °C (kg/m^3)	ASTM D1298	-	800-980	800-1000	800-1000
Viscosity at 40 °C (cSt)	ASTM D445	-	-	10-100	10-100
Water (wt %)	ASTM D6304	≤ 8 (a)	< 1	< 1	< 1
Sediments (wt %)	ASTM D893	≤ 3	< 1	< 1	< 1
Chlorine (ppm)	ISO 15597	≤ 2000	-	≤ 2000	≤ 2000
PCB (ppm)	EN 12766	< 50	< 50	< 50	< 50
Flash point (°C)	ASTM D92	> 65	> 120	> 120	> 120
Glycol content (wt %)	ASTM D4291	-	-	< 1	-
Saponification	Coagulation test	-	-	Negative	-

(a) water plus sediments.

1.4. MITIGATING THE ENVIRONMENTAL IMPACTS BY REGENERATION

The most economic and environmental sound way to manage WLO is the recycling to its original use. High quality base oils and other useful by-products such as fuels, asphalt, gas oil, etc., can be recovered a limitless number of times by regeneration. In the EU, about 13% of the base oil consumed is obtained from regenerated WLO, which contributes to the circular economy and helps to reduce the dependence on natural resources, limit waste and harmful emissions, and promote economic growth [27].

Research has shown that regeneration alleviates the environmental burden of primary production of lubricants by bringing net relief with respect to six environmental performance indicators: resource depletion; global warming; acidification; eutrophication, carcinogenic risk potential and fine particle emissions (Figure 1.3). The regeneration process saves up to 8% of energy throughout the operation compared to the primary production of base oil from crude [28].

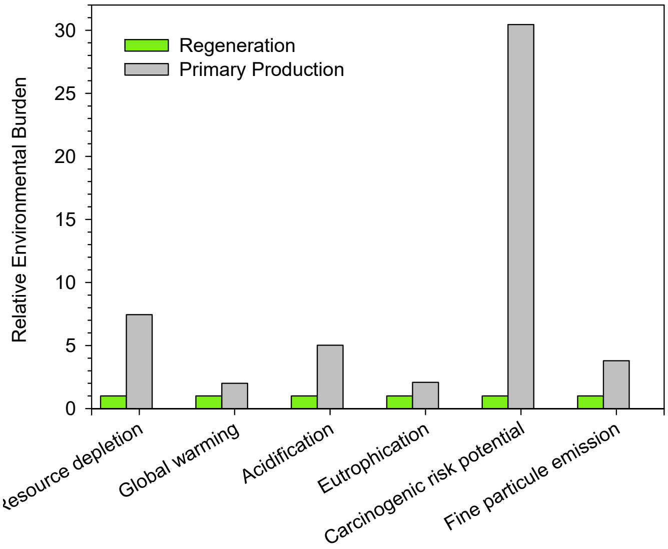
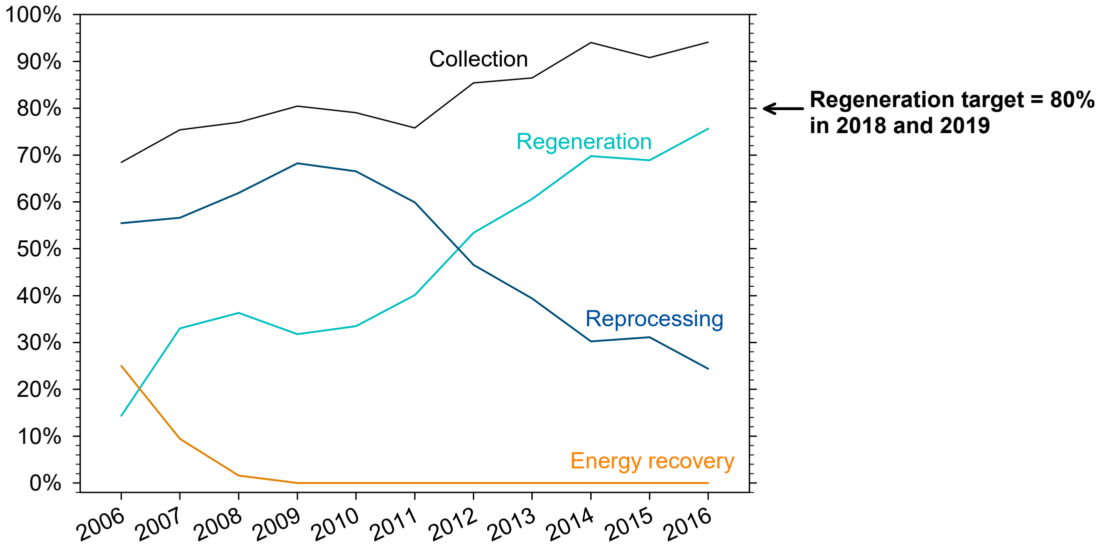


Figure 1.3. Environmental burden of primary production of base oils from crude relatively to regeneration of WLO. Adapted from [28].

The European Commission outlined in its Environmental Action Programme for 2020 that the energy recovery should be limited to non-recyclable products, which can be supported with recycling targets.

In Portugal, demanding targets established by local regulations lead to the employment of best-practices and the achievement of increasingly rates of collection and regeneration over the years (Figure 1.4). The recycling of WLO for energy recovery has not been done since 2007 in Portugal and, priority was given to the treatment by regeneration, fulfilling the waste hierarchy. High collection rates reduce the potentially severe risks for human health and the environment arising from illegal dumping in water or soil or uncontrolled incineration.



Regeneration target = 80% in 2018 and 2019

Figure 1.4. WLO collection, regeneration, reprocessing and energy recovery rates from 2006 to 2016 in Portugal.

In 2016, 76% of the pre-treated WLO was undergone to the regeneration process. The composition of the generated WLO is limiting the increase of regeneration rate, which by 2018 and 2019 are expected to reach 80%. Improper handling and storage of WLO by producers has caused contamination with chlorine and glycol that hampers the potential for regeneration. In addition, the increasing use of synthetic lubricants based on esters are increasing the amount of sapofiable matter present in the WLO, which will give rise to the coagulation phenomena responsible for blocking regeneration plants using alkaline treatments.

Among the available technologies, solvent extraction is one of the most efficient and cost effective processes for the regeneration of WLO due to its low energy consumption (e.g., external heat and pressure), lower equipment cost, and simplicity of operation.

The application of solvents to selectively extract contaminants from WLO enables to obtain good-quality base oils. However, solvents may pose environment, health and safety (EHS) concerns, including ecotoxicity issues, process safety hazards and waste management problems. Thus, to reduce the negative impacts of WLO management by regeneration, it should be also included the incorporation of green chemistry and green engineering principles into the sustainable design of the process.

1.5. OBJECTIVES OF THE THESIS

Ongoing developments in European and local waste management policies, such as the circular economy initiative, have the potential to significantly influence waste management practices and costs. The requirement of compliance with demanding targets in terms of collection and regeneration rates, has led to a commitment in order to identify opportunities for the improvement of the WLO management system.

The development of a strategy for the segregation of WLO at its source aiming at maximizing the regeneration potential is one of the approaches that could allow its continuous improvement. It is well known that segregate storing and collecting waste, reduces the potential for contamination and contributes to a high quality processing and rational waste disposal. This knowledge would require an in-depth understanding of the physicochemical characteristics of the fresh lubricant oils placed on the market and of the WLO generated, whose determination is typically costly and time-consuming.

In addition, due to the increasing awareness of the need for environmental protection, it is becoming more and more important to find processes that are sustainable.

In this context, the specific objectives of this work are:

- Characterization and prediction of fresh and waste lubricating oils properties through simple, quick and inexpensive techniques;
- Analysis of the WLO management system in Portugal;

- Improvement of the Portuguese management system based on the physicochemical characteristics of WLO collected by different producers (garage, industry and others);
- Study the nature of the compounds responsible for the coagulation phenomena in WLO to maximize the regeneration potential through the segregation at source;
- Selection of sustainable solvents for the regeneration process by solvent extraction;
- Evaluation of the treatment of segregated WLO on the efficiency of the extraction using green solvents;
- Assessment of the best extraction operating conditions.

1.6. THESIS OUTLINE

The thesis is structured in five parts, which will focus on the different phases of the life cycle of WLO, as illustrated in Figure 1.5.

.

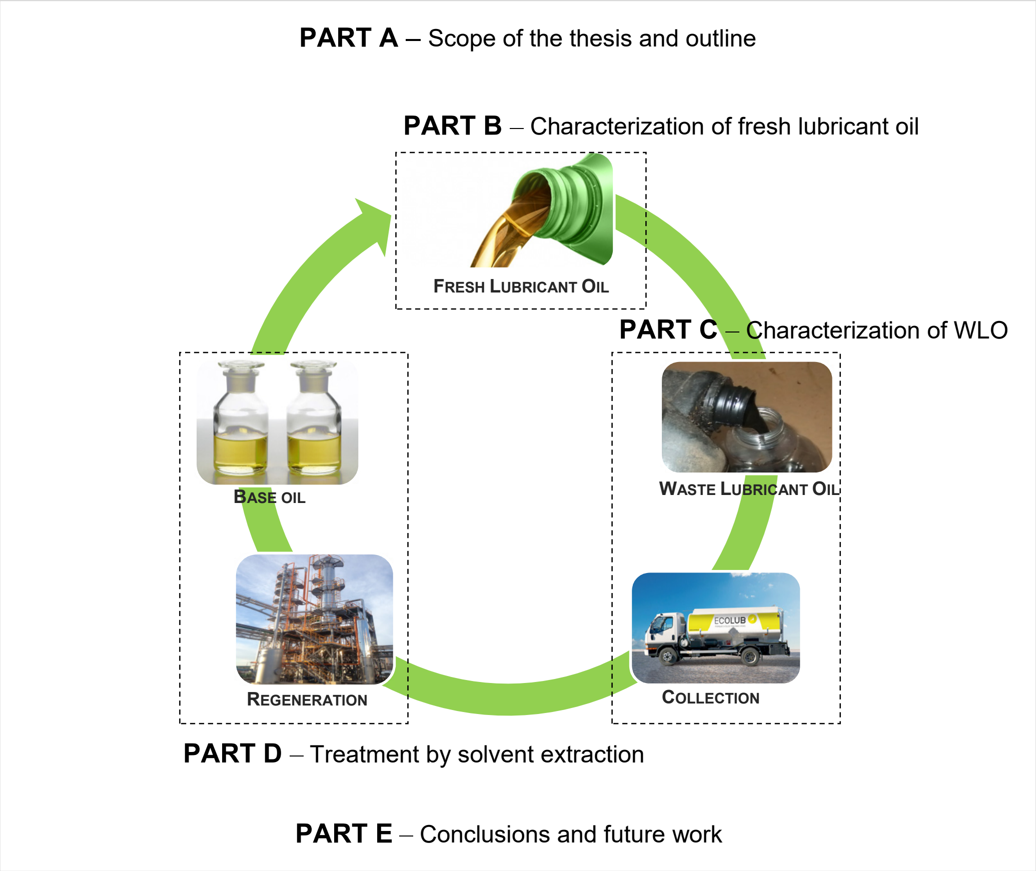


Figure 1.5. Thesis structure and relation with the life cycle of lubricants.

The Part A comprises the first two chapters of the thesis. Chapter 1 comprehends the introduction, which contextualizes the generation of waste oils, the environmental and human health impacts associated with its indiscriminate disposal, and the regulations that govern the appropriate collection and treatment. The advantages of the valorization of WLO by regeneration and the opportunities for improvement of the management system and for boosting the sustainability of the process that constitute the scope of this work are also addressed. In Chapter 2 the composition of fresh lubricant oils and the main contaminants that build up to generate the waste oil are described. The main treatment and disposal routes available and the practices adopted regarding the handling, storage and collection of the residue are reviewed. The physicochemical properties assessed in this work are enumerated and a review of several methods for predicting those properties is presented. Additionally, the regeneration process is described and an overview of the main technologies applied in industry is presented. The fundamentals of the alkaline treatment and solvent extraction are presented to better understand the related mechanisms and operating conditions.

Parts B, C and D focus on the methodologies adopted and the main findings of this thesis and are based upon the publication of peer-reviewed articles.

Part B comprises Chapter 3, dedicated to the characterization and prediction of fresh lubricant oil properties using FTIR and advanced statistical methods.

Parte C is constituted by three chapters that address different topics but are based on the characterization of WLO. Chapter 4 assesses the characteristics of WLO and finds correlations between properties. Chapter 5 explores the WLO management system of Portugal and compares it with the European systems. The characteristics of WLO and the possibility of segregation of WLO by type of producer (garage, industry and others) are addressed. In Chapter 6, an in-depth study of the coagulation phenomena that occurs after alkaline pretreatment is performed. The characteristics of WLO are evaluated by coagulation class and advanced statistical methods used for the classification and discrimination of compounds among the different types of oils.

Part D is devoted to solvent extraction studies and is divided in two chapters. Chapter 7 encompasses the development of a methodology for the selection of sustainable solvents including process constraints, greenness, performance and cost metrics. Chapter 8 addresses the performance of the solvents selected in Chapter 7 and evaluates the possibility of segregate treatment according to the classes of WLO defined in Chapter 6.

Finally, Part E summarizes the main conclusions of the thesis and the perspectives of future work.

1.7. REFERENCES

[1] G.W. Stachowiak, A.W. Batchelor, Engineering tribology, fourth ed., Elsevier, Amsterdam, 2014.

[2] L.A. Bronshteyna, J.H. Kreiner, Energy efficiency of industrial oils, Tribol. Trans. 42 (1999) 4677-4694.

[3] R.E. Cantley, The effect of water in lubricating oil on bearing fatigue life, A S L E Trans. 20 (1977) 244–248.

[4] Fuchs, Fuchs Group – Setting Standards Worldwide. https://www.fuchs.com/fileadmin/Home/Praesentation/2017/FUCHS_Investor_May.pdf, 2017 (accessed April 4, 2018).

[5] Fuchs, Tomorrowing today ─ ….Futuring Fuchs. https://www.fuchs.com/fileadmin/Home/Nachhaltigkeit/Praesentation_Konferenzen/BASF_Global_Sustainability_Meeting_May_2017.pdf, 2017 (accessed April 4, 2018).

[6] G. Totten, S. Westbrook, R. Shah, Fuels and Lubricants Handbook: Technology, Properties, Performance, and Testing, West Conshohocken, PA, 2003.

[7] F. Audibert, Waste Engine Oils. Rerefining and Energy Recovery, Elsevier Science & Technology Books, Amsterdam, 2006.

[8] J.G. Speight, D.I. Exall, Rerefining of Used Lubricating Oils, CRC Press, Boca Raton, 2014.

[9] V. Monier, E. Labouze, Critical review of existing studies and life cycle analysis on the regeneration and incineration of waste oils, 2001.

[10] IARC, List of classifications, Volumes 1–120. http://monographs.iarc.fr/ENG/Classification/latest_classif.php, 2018 (accessed March 29, 2018).

[11] Environment–Agency, Technical Guidance WM3: Waste Classification – Guidance on the classification and assessment of waste. https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/427077/LIT_10121.pdf, 2015 (accessed February 15, 2018).

[12] Environment Agency, How to find out if waste oil and wastes that contain oil are hazardous. https://www.hazwasteonline.com/marketing/media/Regulations/How_to_find_out_if_waste_oil_.pdf, 2007 (accessed January 23, 2018).

[13] R.L. Raymond, J.O. Hudson, V.W. Jamison, Oil degradation in soil, Appl. Environ. Microbiol. 31 (1976) 522–535.

[14] R.C. John, A.Y. Itah, J.P. Essien, D.I. Ikpe, Fate of nitrogen–fixing bacteria in crude oil contaminated wetland ultisol, Bull. Environ. Contam. Toxicol. 87 (2011) 343–53.

[15] H. Babich, G. Stotzky, Heavy metal toxicity to microbe–mediated ecologic processes: A review and potential application to regulatory policies, Environ. Res. 36 (1985) 111–137.

[16] D.E. Vwioko, G.O. Anoliefo, S.D. Fashemi, Metal concentration in plant tissues of Ricinus communis L. (Castor oil) grown in soil contaminated with spent lubricating oil, J. Appl. Sci. Environ. Manag. 10 (2006) 127–134.

[17] R. Vazquez–Duhalt, Environmental impact of used motor oil, Sci. Total Environ. 79 (1989) 1-23.

[18] ATSDR, Toxicological profile for lead, Atlanta, Georgia. https://www.atsdr.cdc.gov/toxprofiles/tp13.pdf, 2007 (accessed January 29, 2018).

[19] F.A. Jahromi, N. Kannan, M.P. Zakaria, A.Z. Aris, Persistent Contaminants in waste oils: A short review on pcbs and pahs as main contaminants, in: From Sources to Solution, Springer, Singapore, 2014, pp. 107–110.

[20] CEPA, Priority substances list assessment report: Waste crankcase oils, Beauregard Printers LTD, Ottawa, Canada, 1994.

[21] J.P. Swigert, C. Lee, D.C.L. Wong, P. Podhasky, Aquatic hazard and biodegradability of light and middle atmospheric distillate petroleum streams, Chemosphere 108 (2014) 1–9.

[22] ECHA, Support document for identification of alkanes, C10–13, chloro as a substance of very high concern. https://echa.europa.eu/documents/10162/2edcfedb-ec53-4754-8598-e787a8ff7a58, 2008 (accessed February 3, 2018).

[23] T.A. Roy, S.W. Johnson, G.R. Blackburn, C.R. Mackerer, Correlation of mutagenic and dermal carcinogenic activities of mineral oils with polycyclic aromatic compound content, Fundam. Appl. Toxicol. 10 (1988) 466–476.

[24] ATSDR, Toxicological profile for used mineral-based crankcase oil, Atlanta, GA. https://www.atsdr.cdc.gov/toxprofiles/tp102.pdf, 1998 (accessed February 1, 2018).

[25] J.G. Speight, Environmental organic chemistry for engineers, Butterworth-Heinemann, Amsterdam, 2017.

[26] APA, Especificações Técnicas dos Óleos Usados. https://www.apambiente.pt/_zdata/Politicas/Residuos/FluxosEspecificosResiduos/OU/Especificacoes_Tecnicas_Oleos_usados-Aprovado.pdf, 2015 (accessed February 15, 2018).

[27] GEIR, Waste Framework Directive revision: European waste oil re-refining industry position, (2016).

[28] N. Abdalla, H. Fehrenbach, Updating the study Ecological and energetic assessment of re-refining waste oils to base oils Substitution of primarily produced base oils including semi-synthetic and synthetic compounds, Heidelberg. https://bva-altoelrecycling.de/files/uploads/2017/10/oekobilanz_ifeu_2017.pdf, 2017 (accessed February 25, 2018).

2. LITERATURE REVIEW

2.1. LUBRICANTS AND LUBRICATION

The primary purpose of lubrication is to minimize friction and wear by introducing a lubricant film between mechanical moving parts [1]. The term “lubricant” is also used to describe materials that are able to perform several functions in addition to reducing friction and wear to prolong its useful life, including [2]:

- **Cooling –** metal surfaces moving in relative opposite directions produce heat. Lubricants must act as a heat sink medium providing enough heat transfer to prevent thermal runaway and to dissipate the heat generated during operation.
- **Inhibit corrosion or rust –** water and oxygen are the main corrosive elements found in tribological systems. They are responsible for the oxidation of lubricant oils, leading to the formation of acids, such as sulfuric and nitric acids, that react with iron forming rust (FeO, Fe_2O_3, and Fe_3O_4). Lubricants should neutralize the acid contaminants and prevent rust and corrosion on metal surfaces.
- **Cleaning and suspending –** prevent potentially harmful products such as wear metals, or sludge and varnish, from depositing on the surfaces and forming adherent films by suspending those impurities and keep the metal surfaces free of deposits.
- **Sealing –** depending upon the application, lubricants can provide an intermediate physical barrier to absorb and/or reject contaminants. Internal combustion engines are a practical example as the lubricant film between the cylinder walls, the segments and the grooves of the piston must prevent the gases passage into the crankcase during combustion/expansion, as well as prevent the crankcase oil entering the cylinders, during the aspiration period.
- **Power transmission and motion agent –** lubricants can be used to transfer energy within a closed system, such as hydraulic or circulating systems.

In lubricated systems, depending on the load, sliding speed and viscosity of the lubricant, different lubrication regimes are formed. These regimes are often displayed on a Stribeck curve, which illustrates the variation of the friction coefficient as a function of the Hersey number (viscosity.speed/load), as shown in Figure 2.1. The knowledge of the lubrication regime in which the metal surfaces will operate is crucial to the formulation and selection of a suitable lubricant [3].

Lubricants form a very thin viscous layer adjacent to metal surfaces. Operating at low sliding speed or low viscosity and high loads, the surfaces are separated only by a molecular lubricant film and most of the load is carried by the surface asperities. This regime is called *boundary lubrication*. Additives have an important role in this regime, forming a protective film on the surfaces to protect from wear. As the speed of revolution increases, at sufficient viscosity and load, a thicker lubricant film is created that separates the surfaces, causing a significant reduction in the coefficient of friction. This regime, where the surfaces are partly separated, is called *mixed lubrication*. If speed or viscosity continues to increase, a thicker and uninterrupted film is formed, completely separating the surfaces and causing a sharp reduction in the coefficient of friction. As speed increases further, the Stribeck curve reaches a minimum coefficient of friction, from which a slight increase is observed caused by viscous shear stress proportional to the viscosity of the lubricant. This regime is called *hydrodynamic lubrication*. Usually this last regime is preferred due to its capacity to sustain dramatic changes in the system viscosity [3–5].

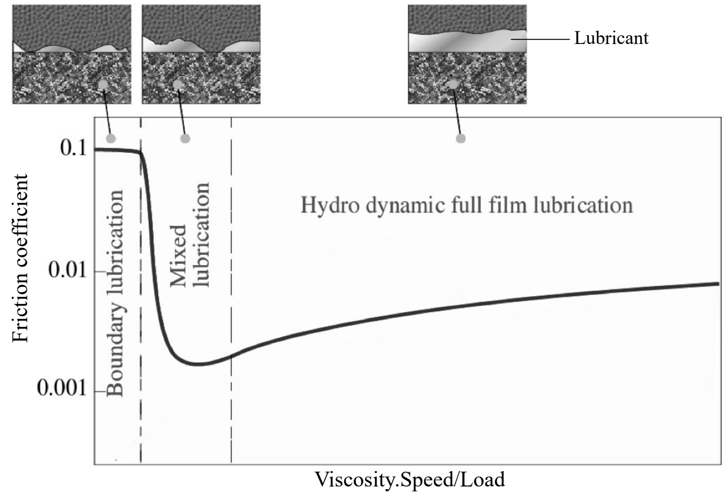


Figure 2.1. Stribeck curve [18].

Manufacturers may blend a variety of base oils and additives in different ratios, each engineered to perform specific functions under particular operating conditions [2]. Not all base oils have similar physical or chemical properties, or provide equivalent performance. To ensure that the performance of engine oil products is not adversely affected when different base oils are used interchangeably by engine oil blenders, the American Petroleum Institute (API) developed a classification system were the base stocks where categorized into five categories as shown in Table 2.1. This classification is based on three parameters: sulfur content, saturates composition and viscosity index (see Section 2.3).

Table 2.1. API base oil categories.

Base Oil Category		Sulfur (%)		Saturates	Viscosity Index
Mineral	**Group I (solvent refined)**	> 0,03	and/or	<90	80 to 120
	Group II (hydrotreated)	≤ 0,03	and	≥90	80 to 120
	Group III (hydrocracked)	≤ 0,03	and	≥90	> 120
Synthetic	**Group IV**	PAO Synthetic Lubricants*			
	Group V	All other base oils not included in Groups I to IV (naphthenics, polyalkylene glycols, esters, etc.)			

*PAO – polyalphaolefin

API group I and II are mineral base oils derived from solvent refining and hydrotreatement of crude oil, respectively. Group III is highly refined mineral oil obtained through hydrocraking which is considered synthetic base oil in the lubricants industry, for marketing purposes. Group IV is reserved for poly-alpha-olefins and Group V includes all other base oils not included in Groups I to IV.

An overview of the chemical composition of fresh lubricant oils, its influence on physicochemical properties and the main production process of base oils from crude oil will be presented in the next sections.

2.1.1. BASE OIL

The primary element of lubricants is the base oil, which is originated from three main sources:

- **Mineral oil –** from the distillation of crude oil;
- **Synthetic oil –** obtained by chemical synthesis from hydrocarbons or other molecules;
- **Bio-based oil –** obtained from natural resources other than crude (fats, waxes, vegetables, etc.).

Bio-based oils are outside the scope of this work. Thus, the composition of base oils from mineral and synthetic sources will be discussed.

2.1.1.1. MINERAL OILS

Most of lubricants are based on mineral oils due to their low cost, availability, and overall acceptable performance. The properties of a mineral base oil are related to the crude oil source, viscosity, and degree of refining.

Crude oil generally consists of a complex mixture of components, including hydrocarbons with carbon number ranging from C1 to > C40, and non-hydrocarbon compounds such as organosulfur compounds, nitrogen- and oxygen-containing compounds, traces of organometallics, resins and asphaltenes of high molecular weight, etc. [2,6,7]. The chemical composition of crude oil varies with geological conditions in the drilling location. Despite the diversity of hydrocarbons and other organic molecules found in crude oils, they are classified on the basis of the predominant hydrocarbon type present [7]. Table 2.2 summarizes the typical composition of some crude oils around the world.

Table 2.2. Composition of crude oils [8].

Crude	Sulfur (%)	Composition Par/Naph/Arom (%)	Crude Type
Tapis	0.02	70 / 20 / 10	Highly Paraffinic
West Texas Intermediate	0.3	52 / 32 / 16	Paraffinic
Brent	0.4	50 / 34 / 16	Paraffinic
Arabia Light	2.0	63 / 18 / 19	Highly Paraffinic
Arabia Heavy	2.8	58 / 22 / 20	Highly Paraffinic
Venezuela Heavy	2.3	35 / 53 / 12	Naphthenic
Alaska North Slope	1.1	29 / 37 / 34	Mix

Based on the predominant type of structure in the crude, mineral oils can be classified as paraffinic, naphthenic or aromatic (Figure 2.2). This is a simplified classification since hydrocarbons may be a combination of them, e.g. alkyl-substituted cyclic or mixed polycyclics containing both aromatic and fully saturated rings [8].

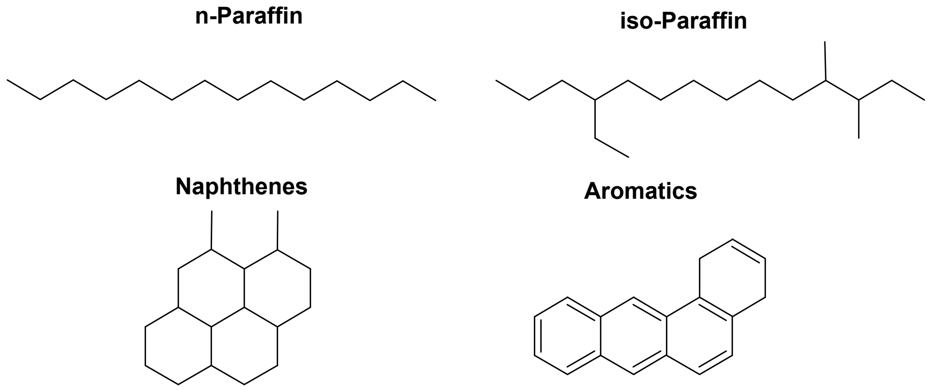


Figure 2.2. Typical classes of hydrocarbons present in base oils.

Different types of hydrocarbons with the same molecular weight have remarkably different physical properties, which affect the viscometric characteristics of the lubricants, and the chemical stability of each class to oxidation and degradation during use [8].

PARAFFINICS

Paraffinic hydrocarbon fractions are saturated linear (n-paraffin) or branched (iso-paraffin) alkanes with general formula C_nH_{2n+2} [9]. The name paraffin is derived from Latin *paraffinum* (*parum*, “barely” + *affinis*), so called from its slight affinity for other substances indicating their relatively stable and resistant chemical bonds.

Paraffins have good viscosity-temperature characteristics, i.e. they show relatively little change in viscosity with temperature (see ‘Viscosity and Viscosity Index (VI)’ in Section 2.3) [10]. This behavior is suitable in specific applications, such as for engine oil applications. The lubricating may have to function at low temperatures when the engine is cold or during the winter, and at high temperatures when it is operating or hot ambient conditions. Since lubricants are designed to meet certain viscosity performance parameters, it is important that the change in viscosity with changes in temperature is within acceptable limits and that it does not become too “thin” at higher temperatures, or too “thick” at low temperatures. In general, lower dependence of viscosity changes from the temperature leads to better performance for lubricating purposes[6].

On the other hand, isomeric paraffins present significant physicochemical differences as the degree of branching increases (Figure 2.2). Linear alkanes (n-paraffins) exhibit good viscosity-temperature properties but their high melting points causes their crystallization as wax. Waxy paraffins have exceptionally high pour points (the minimum temperature at which a lubricant is still able to flow) for use at low temperature, and therefore n-paraffins must be removed by dewaxing. In contrast, highly branched alkanes (iso-paraffins) are not waxy but have poor viscosity/temperature properties [2,11,12].

Paraffinic base stocks are the most widely used base oils for lubricants applications comprising about 85% of world supply [11].

NAPHTHENICS

Alicyclic hydrocarbons, known as naphthenes are saturated cyclic structures based on more than one and up to six-membered rings. Single-ring alicyclics with long alkyl side chains share many properties with branched alkanes and can be highly desirable components for lubricant base oils [8].

Naphthenes tend to have low pour points, providing outstanding low-temperature properties, and making them ideal in the formulation of several industrial lubricants. Furthermore, its high solvency power contributes not only to the dilution of additives, but also to dissolve deposits and debris during use. This characteristics also allows to improve the seal compatibility, which is of great importance in many applications, such as in hydraulic fluids and gear oils [2,6].

On the other hand, the main disadvantages of naphthenic oils are the low stability to oxidative processes and viscosity-temperature characteristics, which is one of the most important properties in tribological systems [3,13].

AROMATICS

Aromatic oils are cyclic unsaturated hydrocarbons comprising one or more benzene rings with general formula C_nH_{2n-6} [9]. This type of oils has even higher densities and viscosities than both paraffinics and naphthenics. Aromatic oils have poor oxidative stability and pour viscosity-temperature properties that limit its use for lubricants formulations. However, they have the best solvency power for additives, making their combination with paraffins advantageous to provide desirable viscosity-temperature behavior. Alicyclic compounds, such as single-ring aromatics with long side chains (alkylbenzenes) are base oils with very desirable properties in some applications [8,9].

Depending on the application, the composition of different components in a lubricant formulation must be optimized. Table 2.3 summarizes the key performance properties of mineral base oils.

Table 2.3. Performance characteristics of mineral base oil components [8].

Base Oil	Viscosity Index	Oxidative Stability	Volatility	Pour Point	Solvency
Paraffinic					
n-Paraffin	+++ (100 - 140)	+++	–	+	–
iso-Paraffin	+ (90 - 100)	+++	0	–	–
Naphthenic	0 (50 - 75)	0	0	0	0
Aromatic	– (0 - 50)	–	++	+++	+++

Note: – Poor; 0 Moderate; + Good; ++ Very Good; +++ Excellent.

2.1.1.2. SYNTHETIC OILS

Synthetic lubricants were originally developed simultaneously in Germany and in the United States, in the early 1930s. In Germany, the need for lubricants with advanced oxidative stability and good low-temperature behavior boosted the development of synthetic lubricants based on olefins and esters [14]. In the United States, synthetic lubricating oils were developed for use in internal combustion engines based on the catalytic polymerization of olefins [10]. The high production cost of these new synthetic base oils allied to the improvement of mineral base oils properties by finishing processes led to its poor commercialization at that time [2].

Nowadays, the variety of lubricants has grown to meet the increasingly technological requirements of modern machines, which operate under severe conditions and challenging environments. Global synthetic lubricant demand represented 8-10 % of total lubricants demand in 2013 and is expected to grow at an annual growth rate of 2.9 % from 2014 to 2020 [15].

Synthetic base oils are lubricants produced by chemical synthesis from one or more raw material components, rather than occurring naturally as petroleum elements [16]. They can be originated from natural sources using chemically modified petroleum constituents, coal, seed oils or animal fat renewable sources, but can also be synthesized from other raw materials [17].

Unlike mineral base stocks derived from crude oil, synthetics have well-defined molecular structures with well-defined molecular weight distributions. In general, it provides superior mechanical and chemical properties than traditional mineral oil required for many applications [6,17].

The worldwide demand for synthetic base oils are dominated by three main components – polyalphaolefins (PAO), synthetic esters and polyalkylene glycols (PAG). Their market share in 2014 was nearly 90% of total synthetic base stocks demand, where PAO accounted for 44%, followed by 30% for esters and 13% for PAG [15].

In this section, a review of the three main synthetic base oils used – PAO, esters and PAG will be presented.

POLYALPHAOLEFINS (PAO)

Polyalphaolefins (PAO) are saturated olefin polymers belonging to a class of high performance synthetic base stocks. PAO are produced from linear α-olefins usually having 10 carbons – α-decene, which is itself produced from ethylene. The most investigated oligomerization processes of α-olefins for base oil production are free radical processes, Ziegler catalysis and cationic Friedel–Crafts catalysis [7]. Several PAO oligomers with different viscosity grades are obtained, commonly 2, 4, 6, 8, 10, 40 and 100 cSt at 100 °C, that originate the properties shown in Table 2.4 [18].

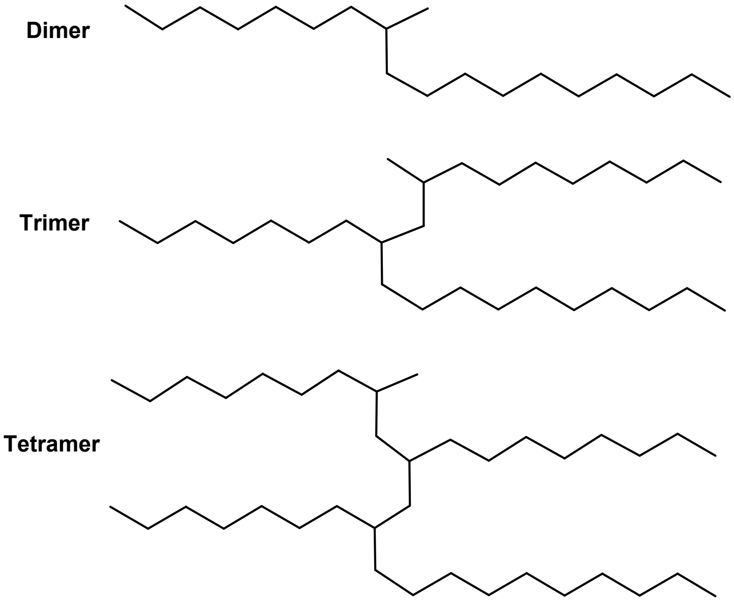


Figure 2.3. Typical polyalphaolefin oligomers. Adapted from [2].

The alkyl groups present in the polymer backbone chain can have several molecular conformations (Figure 2.3), which prevents the orderly alignment of the molecules. This characteristic provides excellent low-temperature properties to the base oil. Thus, the molecules do not crystallize at low temperatures, maintaining the ability to flow. Because of this characteristic, PAO have been widely used in automobile applications such as engine oil that are supposed to operate over a wide range of temperatures [19]. PAO are also characterized by a high thermal and oxidation stability, high viscosity index and low volatility for higher molecular weight polymers. Table 2.4 present the main properties of several PAO viscosity grades.

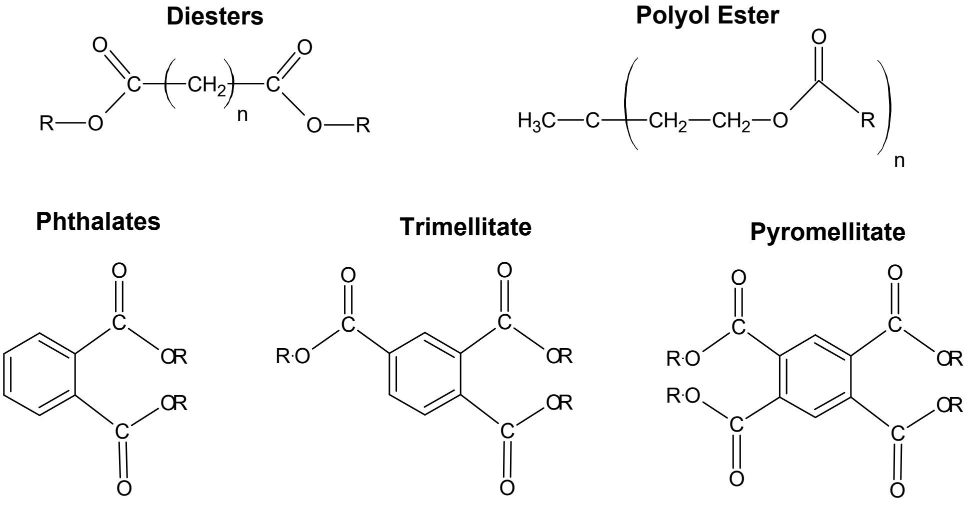
The excellent characteristics of PAO at high and low temperatures, makes them one of the most used synthetic base oils in several applications [6]. On the other hand, the low polarity of these compounds leads to lower solvency power, which affects the miscibility with polar additives and can cause sealing problems [2,10]. Their total miscibility with mineral and ester based oils, makes them an attractive alternative to enhance base oil quality specifications [20].

Table 2.4. Properties of commercial low- and high-viscosity PAO [10].

	Viscosity at 40°C (cSt)	Viscosity at 100°C (cSt)	Viscosity Index	Pour Point (°C)	Flash Point (°C)
PAO 2	5.54	1.80	---	-63	165
PAO 4	16.68	3.84	124	-72	213
PAO 6	30.89	5.98	143	-64	235
PAO 8	46.30	7.74	136	-57	258
PAO 10	64.50	9.87	137	-53	270
PAO 40	399 to 423	40 to 42	147	-36 to -45	275 to 280
PAO 100	1260 to 1390	103 to 110	170	-21 to -27	280 to 290

ESTERS

Ester-based lubricant oils are a broad and diverse family of high performance synthetic base oils, used in severe environment applications due to their custom-tailored properties (Figure 2.4). Their composition is primarily based on branched hydrocarbons in the presence of oxygen in the form of ester groups (COOR) that impart polarity to the base oil [16].



R = C_5 to C_{18} linear or branched alkyl groups

Figure 2.4. Several families of synthetic ester base oils [10].

The polarity has a direct impact on the performance characteristics of ester based oils, namely [10]:

- Low volatility and high flash point – the strong dipole moment cause the molecules to be attracted to each other, requiring greater energy to transfer the lubricant molecules to the gaseous state, which translate to higher flash points;
- Lubricity – because of their high polarity, esters attracts themselves to positively charged metal surfaces creating a protective film and making them good boundary lubricants;

- Thermal stability – the ester connection is known to have excellent thermal stability;
- High solvency – the polarity caused by the ester linkage enhances the solvency power;
- High detergency/dispersion – polarity allows to solubilize or disperse contaminants arising from oxidation or combustion by-products preventing deposits;
- Biodegradability – the ester connection is a vulnerable site to microorganisms. Therefore, esters are biodegradable base oils that allow more environmentally friendly products to be formulated.

A summary of the typical properties of several ester types are presented in Table **2.5** 2.5.

Table 2.5. Typical properties of a series of ester types [11].

	Viscosity at 40°C (cSt)	Viscosity at 100°C (cSt)	Viscosity Index	Pour Point (°C)	Flash Point (°C)	Oxidative Stability
Diesters	6 to 46	2 to 8	0 to 90	-70 to -40	200 to 260	Good
Phthalates	19 to 100	3 to 9	75 to 130	-50 to -30	200 to 270	Very good
Trimellitates	46 to 320	7 to 20	120 to 150	-55 to -25	270 to 300	Very good
Dimerates	90 to 184	12 to 20	50 to 140	-50 to -5	240 to 310	Good
Polyols	7 to 320	2 to 30	40 to 170	-60 to 7	250 to 320	Excellent

One of the main concerns of using ester base oils is the seal compatibility. Many elastomers used as seals are incompatible with esters. Another disadvantage is that esters are hygroscopic, and water molecules tend to be attracted by the polar bond. Under certain conditions, water can catalyze the reverse reaction of esterification (acid hydrolysis of the ester to give carboxylic acids), affecting hydrolytic stability [16].

Ester base oils can be used alone in high temperature applications or in combination with PAO or other synthetic base stocks to improve the finished product. In full synthetic engine oils, esters are often combined with PAOs to balance the negative effect on seals, decrease volatility, solubilize additives, and reduce energy consumption by increasing lubricity. Depending on the desired properties, 5 to 25 % of different types of esters can be combined with PAOs [21].

POLYALKYLENE GLYCOLS (PAG)

Polyalkylene glycols (PAGs) are one of the most versatile types of synthetic base oils. They are produced by polymerization of ethylene oxide (EO) and/or propylene oxide (PO) in different ratios (Figure 2.5). The production process can control the structural conformation, and the most representative conformations are homo-polymers and random co-polymers [10].

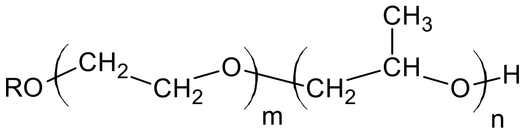


Figure 2.5. Polyalkylene Glycol general structure [10].

High polarity and low coefficient of friction are the most important characteristics of PAG. Table 2.6 presents the general properties of several random co-polymers with a ratio of 50:50 wt% and 75:25 wt% of EO and PO, respectively. PAG can have a wide range of viscosity grades and can reach very high viscosities and VI compared to mineral oils or some synthetic oils, which is related with the molecular weight of the polymers [22]. Depending on the amount of EO used in the reaction, PAG can be either more soluble or insoluble in water. In addition, PAG base oils offer low volatility and have desired properties high and low temperatures [23]. They also are fire-resistant and have high loading capacity to withstand high pressures [10].

However, one of most relevant limiting characteristic is its incompatibility with mineral oils or other synthetic base oils and additives due to their limited miscibility [2].

Table 2.6. General properties of several PAG [8].

EO:PO wt% Random Co-Polymer	Viscosity at 40°C (cSt)	Viscosity at 100°C (cSt)	Viscosity Index	Pour Point (°C)	Flash Point (°C)
50:50	19	4.6	165	-58	183
	66	13.5	210	-50	232
	217	41	239	-42	240
	477	83	262	-40	241
	1000	163	281	-39	230
75:25	2 025	300	335	6	252
	30 000	4 200	430	6	240
	55 000	7 900	430	6	240

Table 2.7 presents a summary of the synthetic base oil properties compared with mineral oils.

Table 2.7. Comparison between mineral and synthetic base oils [1].

Property	Mineral oil	PAO	Aliphatic Di-ester	Polyol Ester	Phosphate Ester	PAGs
Fluidity range	0	+	++	++	0	+
Viscosity Index	0	+	+++	++	–	+
Low T fluidity	–	+	+	+	0	+
Oxidation stability	0	++	++	0	+	–
Hydrolytic stability	+++	+++	0	0	0	+
Thermal stability	0	0	+	+	0	+
Mineral oil compatibility	–	+++	+	0	0	–
Additive solvency	+++	+	++	++	+	0
Volatility	0	+	+++	+++	+	+
Rust control	+++	+++	0	0	0	+
Boundary lubrication	+	+	++	++	+++	+
Fire resistance	–	–	0	0	+++	0

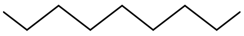
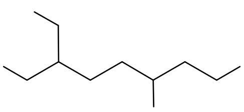
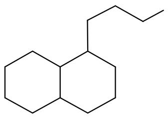
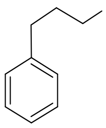
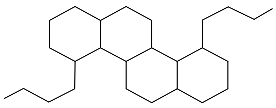
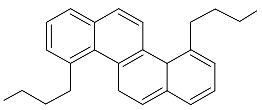
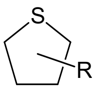
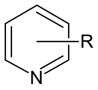
Note: – Poor; 0 Moderate; + Good; ++ Very Good; +++ Excellent.

2.1.2. MINERAL BASE OIL PRODUCTION

Most lubricants are mineral based produced by crude oil refining. This predominance can be justified by simple and obvious reasons - price, availability and performance. The conventional refining process produces base oils with satisfactory performance specifications at economically attractive prices. In this regard, non-petroleum or synthetic base oils are used when enhanced properties are needed, representing about 8-10% of the lubricants market nowadays [7,24].

As previously mentioned, a diversity of hydrocarbons and other organic molecules rich in sulfur, oxygen and nitrogen are found in crude oils. Most of these molecules are undesirable since they tend to cause instability, color, deposits, or contributing to low viscosity index reducing the base oil properties [6,7]. Therefore, they need to be removed during the refining process through several technologies, as reported in Table 2.8. Typically, it is desirable a product composed mostly of iso-paraffins [25].

Table 2.8. Crude oil molecules and their contribution to base oil properties [9].

Molecule	Structure	Property Affected	Removal Process
n-paraffin		High Pour Point, High VI	Dewaxing
iso-paraffin		High VI, Medium Pour Point	---
2-Ring Naphthene		Medium VI, Low Pour Point	Extraction, Hydrofinishing
1-Ring Aromatic		Medium VI	Extraction
Multi-Ring Naphthene		Low VI, Low Pour Point	Extraction, Hydrofinishing
Multi-Ring Aromatic		Low VI, Low Pour Point	Extraction
Organic Sulfur	 	Good Stability, Antioxidant	Hydrofinishing
Organic Nitrogen	 	Poor Stability	Hydrofinishing
Aliphatic Sulfur or Nitrogen	R-S R-N	Poor Stability	Hydrofinishing
Asphaltenes	Condensed Multi-Rings	Poor Color	Distillation, Deasphalfing

The conventional crude oil refining process to obtain base oils comprises atmospheric and vacuum distillation, deasphalting process, solvent extraction, dewaxing and finishing process.

ATMOSPHERIC DISTILLATION

In a typical refining process, the crude oil is initially fractioned by atmospheric distillation. Components with boiling point below 350 °C (gases, gasoline, naphtha, kerosene jet, diesel fuel, and gas oil) are sent to the fuel refinery plant for further processing. Higher temperatures are likely to cause thermal decomposition of the remaining residue that contains the components of interest for lube oil production. Therefore, further separation of higher molecular weight components (C>26) is carried out at reduced pressure (from 10 to 50 mm Hg) in a vacuum distillation column [9,26].

VACUUM DISTILLATION

The vacuum distillation unit must promote a narrow separation of fractions such as vacuum light/heavy gas oil, lube distillates and the vacuum residue. These may have well established viscosity grade and boiling range for further processing. The performance of the vacuum distillation unit is critical to control viscosity and volatility of lube fractions and operation of the downstream units [27].

DEASPHALTING

The vacuum residuum obtained contains heavy lube components of high viscosity, asphalt and resins. The separation of these components is performed by an operation called ‘deasphalting’, which is an extractive precipitation process. The process is based on the preferential solubilization of lower molecular weight paraffinic components in a solvent, typically propane, and precipitation of the heavy asphaltic compounds. The so called deasphalted oil has low metal content, high content of saturates, improved viscosity index and color. The oil is further processed by refining using the same method as the lube distillates [11].

SOLVENT EXTRACTION

The deasphalted oil and the lube distillates contain undesirable components (aromatics, in particular polynuclear aromatic compounds, naphthenes, sulfur-, nitrogen-, and oxygen- containing components, etc.) that also should be removed to improve its viscosity index and oxidation stability. Liquid-liquid extraction using a selective solvent such as furfural, phenol or more recently N-methyl-2-pyrrolidone (NMP) have been used to remove these constituents from the base oil [12].

DEWAXING

The refined product from the extraction contains wax (linear *n*-paraffinic compounds), which have high pour points. The wax may crystalize causing poor flow properties at low temperatures. Wax removal is achieved by solvent dewaxing followed by a crystallization/filtration process using as solvent mixtures of MEK (methyl ethyl ketone)/toluene, MEK/MIBK (methyl isobutyl ketone), etc. at low temperatures. The *n*-paraffin compounds crystallize and are filtered to be separated from the filtrate [12,27].

FINISHING PROCESS

The filtrated oil is normally hydrofinished or treated with adsorbent clay to improve base oil color and oxidation stability. Hydrofinishing is carried out by reacting oil with hydrogen in a fixed bed reactor in the presence of a selective catalyst (cobalt/molybdenum). In this process, compounds of sulfur, nitrogen and trace impurities are removed so increasing the purity of the oil [46]. This technique is necessary in the manufacture of food or pharmaceutical grade oils to meet the quality requirements set out by the Food and Drugs Administration (FDA) [23]. The adsorption process has been replaced by hydrofinishing but is still in limited use for the manufacture of refrigeration, transformer or turbine oils. Adsorbents based on bentonite-type aluminosilicates are used [2]. In the typical batch process, the clay is mixed with the oil at elevated temperatures (150 °C – 370 °C) for a short period followed by separation of the oil. The significant amount of spent clay that must be disposed of, which constitutes an environmental problem [6].

The conventional crude oil refining process arrangement is presented in Figure 2.6.

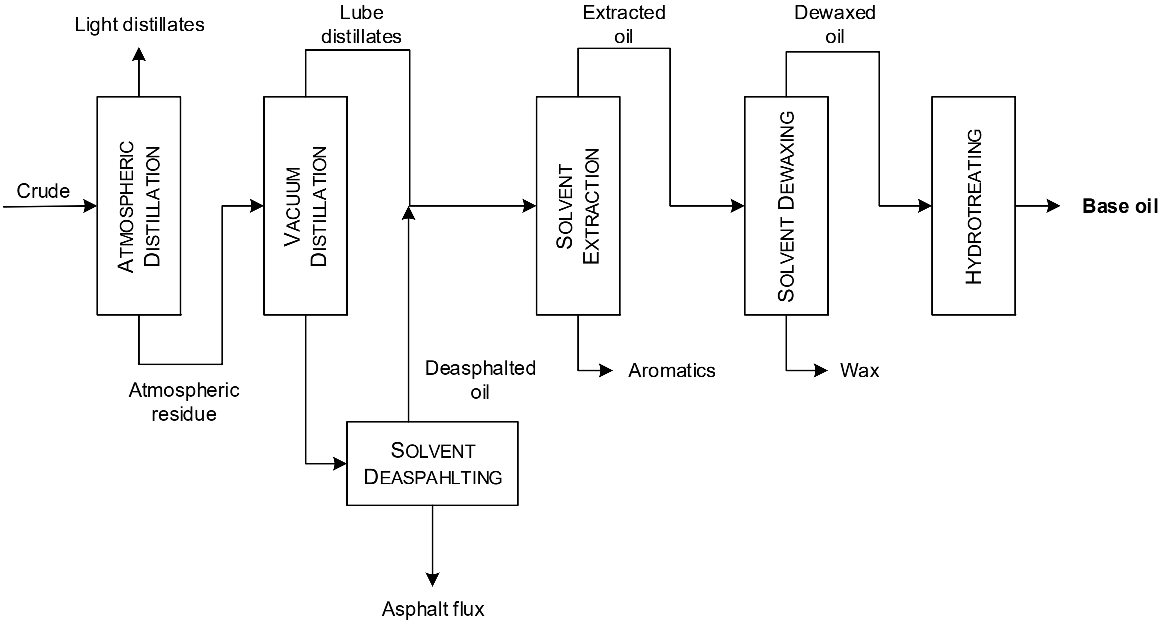


Figure 2.6. Classical crude oil refining process for lubricating oil production [27].

The conventional crude oil refining processes produces API Group I base oils. Higher quality Group II and III base oil, which have higher viscosity index, lower volatility, and higher saturate content, are becoming more prevalent on the modern market due to their improved properties.

Base oil production technologies are shifting to meet increasing demand for high quality lube oils, improved fuel economy and lower emissions. The conventional solvent-based processes are increasingly being replaced either by hybrid processes such as the combination of solvent extraction with catalyst dewaxing, or by advanced processes such as complete hydroprocessing-based plants that include hydrocracking, catalyst dewaxing or wax isomerization [8,25].

HYDROCRACKING

Hydrocracking is a more severe treatment than hydrofinishing. It involves on the chemical reaction of the distillates with hydrogen in the presence of a catalyst at high temperature and pressure (about 420°C and 200 bar). During the hydrocracking process the molecules are converted and some are broken into smaller ones. Sulfur and nitrogen compounds are removed, and the aromatic and naphthenic hydrocarbons are saturated or cracked and opened to form an iso-paraffin structure. Smaller hydrocarbons such as diesel, jet fuel and naphtha are by-products of this method. Nevertheless, wax components are not altered by hydrocracking and a subsequent process of dewaxing must be performed to reduce the pour point [24,26].

CATALYTIC DEWAXING AND WAX ISOMERIZATION

Catalytic dewaxing is a high temperature and pressure process in which waxy compounds are cracked into lighter products (p.e. gas and naphtha) in the presence of hydrogen and a selective catalyst. High pour point base oils are obtained. The wax isomerization process is similar to catalytic dewaxing, but in the last one the wax is selectively converted into more desirable iso-paraffin structures. Although catalytic dewaxing is an efficient process to decrease the pour point, wax which is a valuable by-product in the market is converted in lower valuable gas and naphtha. The wax isomerization process is a more profitable process that results in higher viscosity index base oils and higher yields [24,26].

2.1.3. ADDITIVES

Additives are chemical compounds added to base oil to enhance its natural properties, provide specific properties, increase chemical stability and prevent undesirable changes during service life [1,28]. Additives have been used since the 1920s, and their use has increased massively. Nowadays, basically all types of lubricants contain at least one specific additive. There are lubricant grades (e.g. some compressor or hydraulic lubricants) in which chemical additives only account for 1% of total base oil mass, while others (e.g. some metalworking fluids or gear lubricants) can contain up to 30% of additives [29]. The choice of additives and the balance between them is very important and can differentiate, for instance, an hydraulic oil from a turbine oil [6].

Additives may act based on two main operation mechanisms [30,31]:

- Change the physicochemical properties of base oils;
- Change the metal surface properties to inhibit corrosion or reduce friction.

Additives increase complexity of the lubricants matrix, which can influence the effectiveness of the regeneration process. Thus, an overview of the most used additives and their primary industry are discussed in this Section.

VISCOSITY INDEX IMPROVERS

Viscosity is probably the most important property of a lubricant, which can undergo changes with temperature during use, decreasing the lubricating ability of the oil. Viscosity index improvers, also referred as viscosity modifiers, comprise five main class of polymers (PMAs, OCPs, SPEs and combination of PMA/OCPs) and are used to reduce the magnitude of viscosity change as a function of temperature [1,32].

Viscosity index improvers are long chain, high molecular weight polymers, that change their physical configuration depending on the temperature [31]. At lower temperatures, the polymer molecules contract adopting a coiled form so that their impact on the fluid viscosity is minimized. At higher temperatures, the polymer chains relaxes tending to straighten out, and their interaction with the oil produces a proportionally "thickening" effect, increasing viscosity [2,7,28]. The process of coil expansion and contraction is reversible and is illustrated in Figure 2.7.

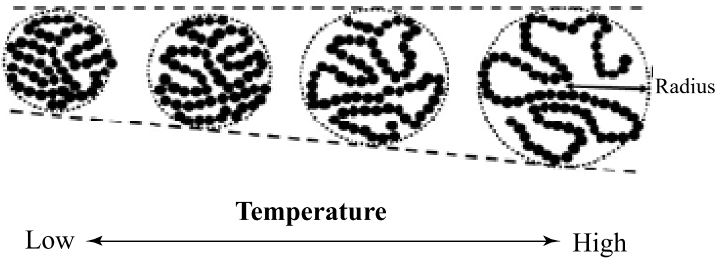
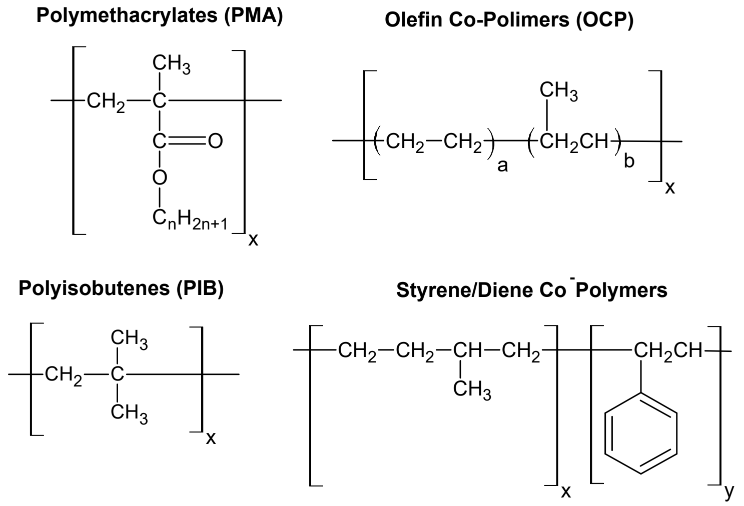


Figure 2.7. Coil expansion model to explain viscosity modifiers mechanism [33].

Thus, compared to non-polymer-containing oils, as temperature increases, there is less "thinning" of the lubricant, i.e. a lower decrease on viscosity occurs. Therefore, their use allows the formulation of products that are able to maintain acceptable performance over a much wider temperature range [8].

Among the most significant commercial VI improvers are polymethacrylates (PMA), olefin copolymers (OCP), polyisobutilene (PIB), and styrene-butadiene copolymers, which are represented in Figure 2.8 [6,7,31,34]. The degree of VI improvement from these materials depends on the molecular weight distribution of the polymer [8].

Viscosity improvers are widely used in multigrade oils, which can maintain good performances at high and low temperatures. Usually, viscosity index improvers are used in engine oils, automatic transmission fluids, multipurpose tractor fluids, and hydraulic fluids (industrial, automotive, aircrafts), gear lubricants (industrial, automotive), etc. [7,31].



Polymethacrylates (PMA)

Olefin Co-Polimers (OCP)

Polyisobutenes (PIB)

Styrene/Diene Co Polymers

Figure 2.8. Most commonly used viscosity index improvers [31].

ANTIWEAR AND EXTREME PRESSURE

During equipment operation, friction will cause wear of unprotected metal surfaces. As the power of engines has risen, the use of additives to prevent wear has become increasingly indispensable [35].

Antiwear additives are mainly designed to reduce frictional wear and consequently damage under conditions of low load and moderate mechanical stress, whereas extreme pressure additives are used when the system is exposed to very high loads [3,8]. Their mechanisms of action are similar and sometimes it is not possible to differentiate between them accurately [2].

Antiwear and extreme pressure additives act by thermo decomposing to yield compounds that react with metal surfaces. They are normally activated by temperature, generated by the metal-metal contact. These surface-active compounds have a polar structure that forms a protective solid film, called tribofilm, that preferentially shears in metal parts experiencing boundary lubrication, where the majority of the load is carried by the surface asperities (see Stribeck curve, Figure 2.1) [5,10,31]. The formed tribofilm has sufficient cohesion to resist to extreme surface pressures, allowing new load distribution and minimizing direct contact between surfaces [31,36].

Figure 2.9 shows effects of friction and wear on mettalic surfaces caused by lubricant contaminantion and additive depletion.

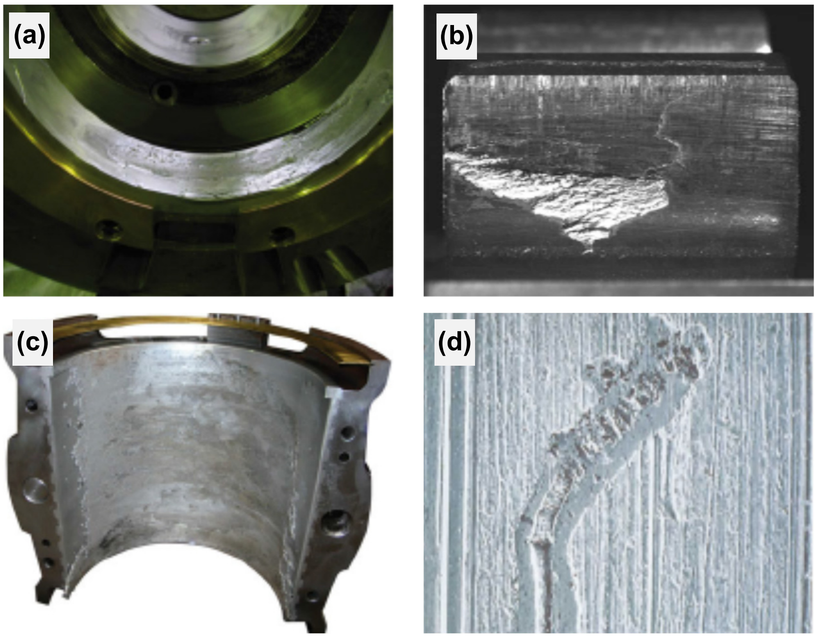


Figure 2.9. Effects of friction and wear on metallic surfaces: (a) damage of sealing surfaces; (b) damage to a gear rim; (c) melted material caused by solid particle contamination and temperature increase; and (d) embedded machining chip. Adapted from [37].

Antiwear and extreme pressure additives are generally used in engine oil, hydraulic or metalworking fluid. Some of the most commonly used antiwear additives include organosulfides, phosphate esters, metal dithiophosphates (e.g. zinc or molybdenum dithiophosphates), dithiocarbamates, etc. [10,31,36]. Organic compounds containing phosphates or sulfur are normally used as extreme pressure additives [38]. Zinc dialkyl dithiophosphate (ZDDP) has been the most used of all antiwear additive (Figure 2.10).

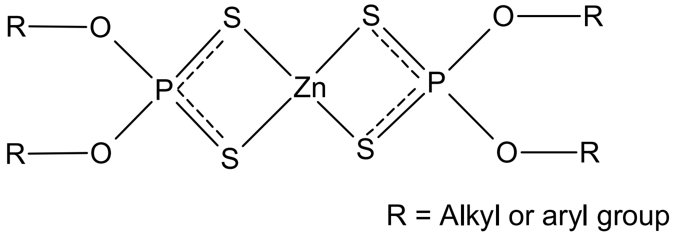


Figure 2.10. Structure of a zinc dialkyl dithiophosphate (ZDDP) [39].

CORROSION AND RUST INHIBITORS

Acidic products may be formed by the thermal and oxidative decomposition of the lubricant (base oil and additives), brought in directly from the environment (acid atmosphere) or caused by the specific application (aggressive blow-by gases in internal combustion engines). Lubricants must provide protection against these aggressive contaminants that can cause corrosion [2,30]. Corrosion inhibitors are substances with polar functional groups that form a protective barrier to prevent corrosive species from reaching the metal surface [6,34]. Corrosion inhibitors have two variants: antirust additives when the purpose is the protection of ferrous metal surfaces and metal passivators for non-ferrous metal surfaces [29,34].

The mechanism of anticorrosion and antirust additives is rather simple. Long alkyl chains and polar groups can be either adsorbed on the metal surface or chemically bonded to it, forming packed hydrophobic layers (Figure 2.11) [13].

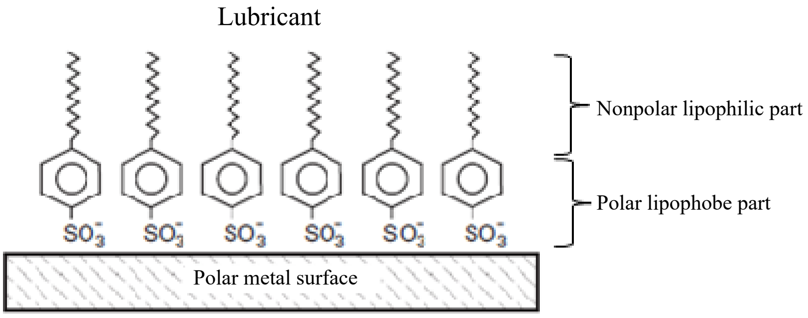


Figure 2.11. Mechanism of action of corrosion and rust inhibitors [2].

It is important to note that their mechanism is similar to other additives such as antiwear and extreme pressure, competing with each other for the same sites, therefore reducing their efficiency [7]. Most commonly used anticorrosion and antirust additives are zinc dithiophosphates, dithiocarbamates, benzotriazoles and derived from sulfonates, amines and succinates [10,17].

ANTIOXIDANTS

Oxidation is a complex chemical degradation process which involves a series of chain reactions producing acid compounds. Further polymerization reactions yield products that cause an increase of the oil viscosity, corrosion of metallic parts and formation of sludge and varnish. Temperature, wear metals, the presence of water and other contaminants act as a reaction catalyst [40].

The mechanism of oxidation is described by free radical reactions via alkyl and peroxide radicals, as outlined in Figure 2.12 [41]. The oxidation process starts with the uptake of hydrogen from hydrocarbons by oxygen attack, forming an alkyl radical which in turn reacts with oxygen and forms a peroxide radical. Chain propagation occurs because of the hydrogen abstraction by a peroxide radical from another hydrocarbon yielding a hydroperoxide and an alkyl radical which may react again with oxygen continuing the oxidation process. The next step is the chain branching by homolytic cleavage of hydroperoxide, which increases the number of reactive free radicals. Several oxidation products are formed, such as hydroperoxides (ROOH), alcohols ($R'CH_2OH$), aldehydes (R'CHO), ketones ($R'COCH_3$), carboxylic acids (RCOOH), esters (RCOOR'), among others [2,31].

High molecular weight oxidation products are formed by polycondensation, which are responsible by the typical increase in viscosity of lubricants. The occurrence of additional polymerization reactions leads to the formation of oil insoluble polymers that separate from the lubricant and form deposits on the surface such as sludge and varnish. Finally, termination reactions occur by recombination of two free radicals, forming inactive species [2,6,28,31].

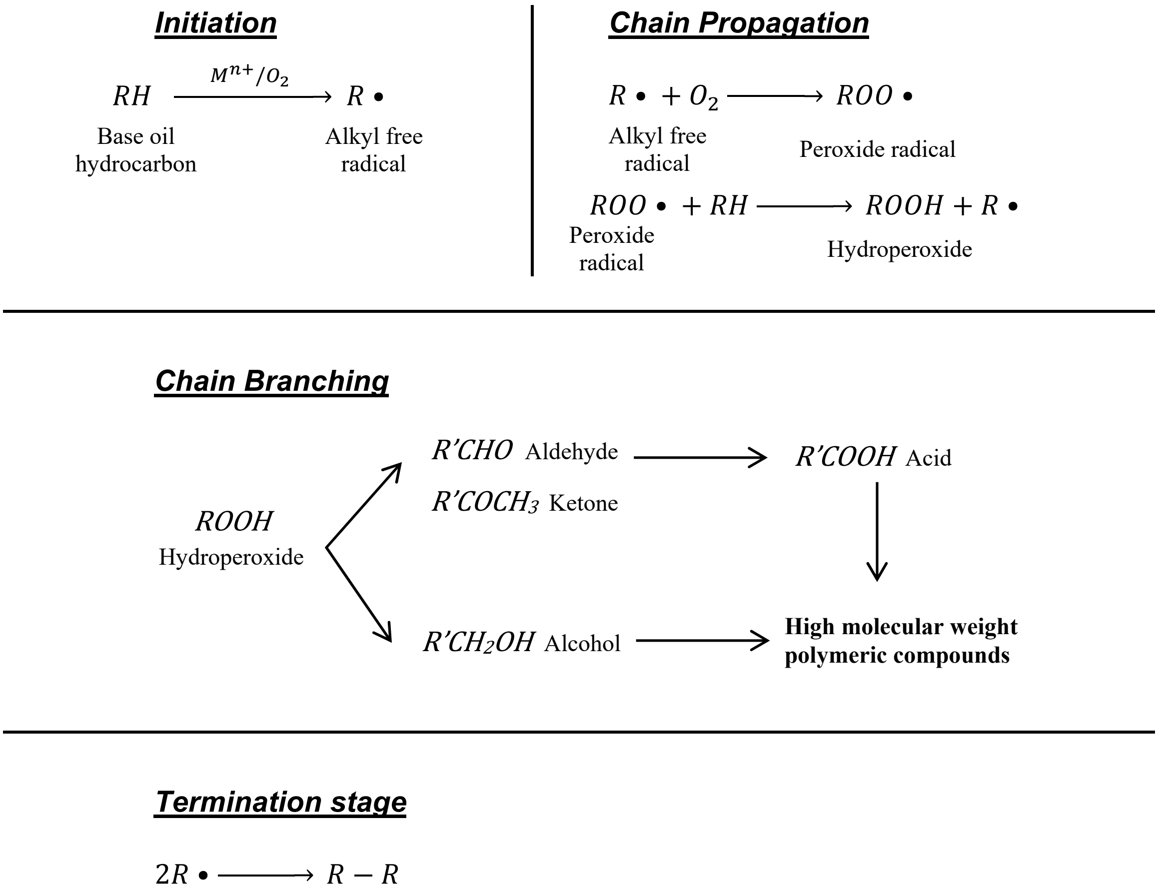


Figure 2.12. Mechanism of oxidative degradation in lubricant base oils [40].

Antioxidants are additives used to improve oxidation stability and extend the useful life of lubricants [30]. They can be differentiated as:

- Primary antioxidants or radical scavengers – act as radical inhibitors of one of the oxidation steps by donating hydrogen atoms that neutralize the free radicals, interrupting the chain propagation reaction. Sterically hindered phenols and aromatic amines are typical primary antioxidants. [6,7].
- Secondary antioxidants or peroxide decomposers – promote the reduction of hydroperoxide radicals into non-radical, less-reactive alcohols, therefore preventing the propagation of oxidation. Well known secondary antioxidants are sulfur and/or phosphorus compounds, zinc dialkyl dithiophosphate, etc. [28,31].
- Antioxidants can be combined with metal deactivators or passivators to suppress the catalytic activities of the metals [30]. Metal deactivators can be classified into two major types: chelating and film forming agents. Chelating agents trap metal ions to form a stable, inactive or less-reactive complex, which decreases their catalytic activity. Film-forming agents act by forming a protective

layer on the metal surface, preventing the interaction between the metal ions and the oil. They can also restrict the contact of corrosive species with the surface [28].

The use of antioxidant additives is of great importance in several applications of the lubricant oils such as engine oils, gear oils, automatic transmission fluids, metal-working fluids, compressor oils, hydraulic fluids, etc. [31]. One of the most affected applications by oxidation is in engine oils. The internal combustion engines are excellent chemical reactors where the oxidation process is catalyzed by metallic parts mainly made of iron and copper [28].

ANTIFOAM AGENTS

Under certain conditions, agitation of the lubricating oil creates air bubbles that result in the formation of foam. Foaming is an undesirable effect that not only enhances oil oxidation through intensive mixture with air, but also causes cavitation, as well as insufficient oil transport that can lead to insufficient supply of lubricant to the surface (lubrication starvation) [1,35]. Foaming predisposition is influenced by the surface tension of the base oil and is boosted in the presence of surface-active substances such as detergents and dispensing agents, corrosion inhibitors, antioxidants, etc. [31].

To reduce the foaming effect, small amounts (ppm) of antifoam agents should be added to the lubricants. The defoamants (antifoams agents) are oil-insoluble low molecular weight compounds that remain at the liquid-air interface. The antifoam attacks the oil film surrounding the air bubbles, reducing the interfacial tension. The bubbles quickly coalesce into larger ones and float more readily to the surface, releasing the air (Figure 2.13) [28,42]. The most common antifoaming agents are based on silicones and low molecular weight polymethacrylates [6].

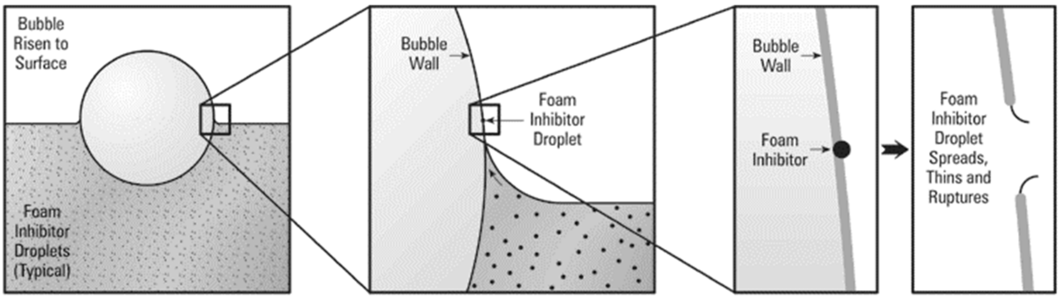


Figure 2.13. Antifoaming agents mechanism [42].

DETERGENTS AND DISPERSANTS

Antioxidants, detergents and dispersants form a general class of additives known as ‘stabilizers and deposit control agents’. This package of additives is used to prevent the deposit formation, by inhibiting the oxidative breakdown of the lubricant and by suspending the harmful products as they arise [28].

Detergents are metal salts of organic acids used to prevent deposition of residues on metal surfaces [7]. They contain two components: a surfactant and a colloidal inorganic phase. Their performance is affected by the surfactant type (usually a sulfonate, phenate or salicylate), by the metal type (mostly Ca, Mg or Na), and the degree of overbasing, which is the level of basicity of the inorganic phase present relative to the amount of surfactant [2]. This combination results in a micellar structure that provides cleaning action by suspending polar materials (oxidation products, sludge, dirt particles, etc.) in the bulk. In addition, they have the ability to neutralize acidic products formed in combustion and oxidation by the dispersed colloidal phase, providing an alkaline reserve to the oil, shown in Figure 2.14 as basic carbonate ($CaCO_3$) [43].

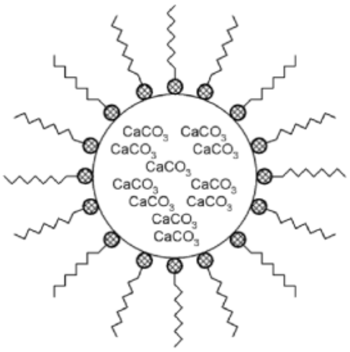


Figure 2.14. Polar compounds suspension and acid-neutralization in lubricants by detergents [67].

Dispersants are non-metallic agents of higher molecular weights than detergents that inhibit flocculation or coagulation of colloidal matter, thereby mitigating the deleterious effects of large agglomerates on surfaces [28]. Dispersants comprise a hydrocarbon backbone, usually of polyisobutylene (PIB), connected to a polar group, normally an amino group, by a phenol or succinic anhydride group, the so-called Mannich or succinimide dispersants, respectively [43]. The polar head group is tailored specifically for strongly adsorb combustion by-products, such as soot, resin, varnish, lacquer, and carbon deposits. The dispersants polar group associates with the individual polar particles (Figure 2.15), and the non-polar hydrocarbon group keeps such particles suspended in the bulk, which are unable to agglomerate [29,43].

Detergents and dispersants are often mistaken as having the same function. In practice, dispersants also solubilize polar contaminants, as well as detergents, but dispersants have a longer tail to provide greater steric stabilization in the micellar structure and prevent coalescence of contaminants. Moreover, dispersants have little or any neutralization capacity for the acidic contaminants [28,31].

Detergents and dispersants are extensively used in engine oils, transmission and hydraulic fluids. They constitute about 45-50% of the total volume market of additives [1].

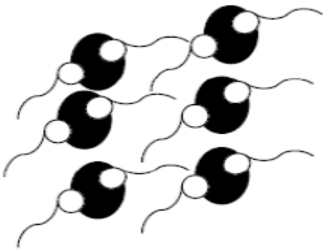


Figure 2.15. Interaction of dispersants with residue particles [31].

POUR POINT DEPRESSANTS

The pour point is the lowest temperature at which the lubricating oil may still be able to flow when cooled under defined conditions. Although most of the wax is removed during crude refining, mineral oils generally contain some dissolved wax. When the oil is cooled, this wax forms crystals that connect to form a rigid structure, trapping the hydrocarbons to a point where the oil will no longer be able to flow, as illustrated in Figure 2.16. To increase mineral oils performance at lower temperatures, pour point depressants (PPD) are used [28,29].

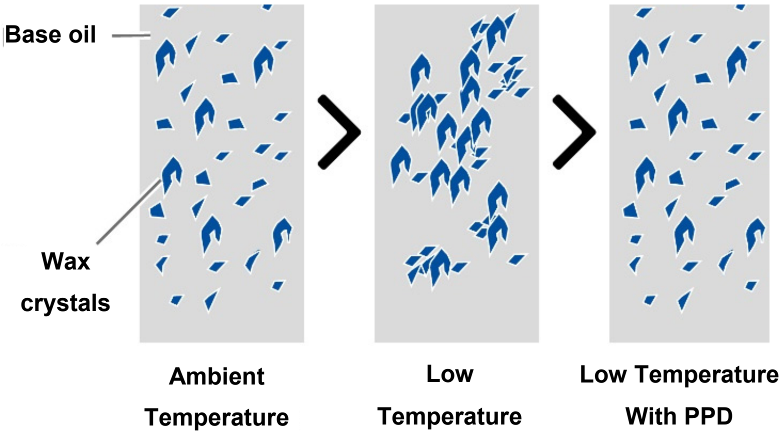


Figure 2.16. The mechanism of action of pour point depressants. Adapted from [44].

Pour point depressants control the wax-crystal phenomenon in two different ways. Generally, two types of pour point depressants are used: polymethacrylates and alkylaromatic polymers. The polymethacrylates are the most widely pour point depressants and act by co-crystallizing with the wax, which delays the crystal formation to significantly lower temperatures. The alkylaromatic polymers adsorb onto the surface of the crystals as they form, interrupting the lateral crystal growth. These additives do not completely inhibit wax crystal growth, but are able to significantly lower the temperature at which crystals are formed [2,34].

Pour point depressants are used in most mineral lubricants that must be able to flow at low temperatures such as engine oils, automotive gear oils, automatic and power transmission fluids, tractor fluids, hydraulic fluids, among others [31].

Information on the typical composition of lubricating oils and the quantity of each additive commonly used is shown in Table 2.9.

Table 2.9. Typical composition of fresh lubricant oils [7].

Compound	% w/w
Base oil	71.5 - 96.2
Detergents	2.0 - 10.2
Dispersants	1.0 - 9.0
Zinc dithiophosphates	0.5 - 3.0
Antioxidants/antiwear	0.1 - 2.0
Friction modifiers	0.1 - 3.0
Pour point depressors	0.1 - 1.5
Antifoam	2 - 15 ppm

2.2. WASTE LUBRICANT OIL

Waste lubricating oil (WLO) is any lubricant oil, whether mineral or synthetic based oil, which after a certain period of useful life has become contaminated, and must be replaced by a fresh one.

In this sub-section, the main contaminants present in WLO are described. The impact of the handling, storage by the producers on the treatment and disposal routes are also addressed. The knowledge on the characteristics of the WLO is a step forward in understanding the nature of the impurities and, therefore, the steps that will be needed to regenerate the waste.

2.2.1. MAIN CONTAMINANTS

Lubricant oils can be contaminated with several compounds and elements (Table 2.10), which varies with the type of application and increases with the service time, and depends on the original base oil, the refining process, the additives package, etc. The most relevant contaminants found in waste oils are:

- **Water** – may be in three forms: dissolved, emulsified and free, depending on the temperature, pressure and the type of oil. Water may arise from several sources, including rain leakage, infiltrations, condensation of air, cooling system leaks, antifreeze agents, fuel combustion by-product or process water, etc. [76]. The concentration of water in the WLO can vary up to 15 wt.% [45].
- **Chlorine** – is part of some metalworking, hydraulic, insulating or heat transfer fluids as chlorinated hydrocarbons or esters which specific characteristics such as chemical stability and fire-resistance [43]. A special concern is the contamination with organochlorides, such as polychlorinated biphenyls

(PCB), which arise mainly from transformer oils. The use of PCB have been banned in most countries due to their toxic and persistent properties [77].

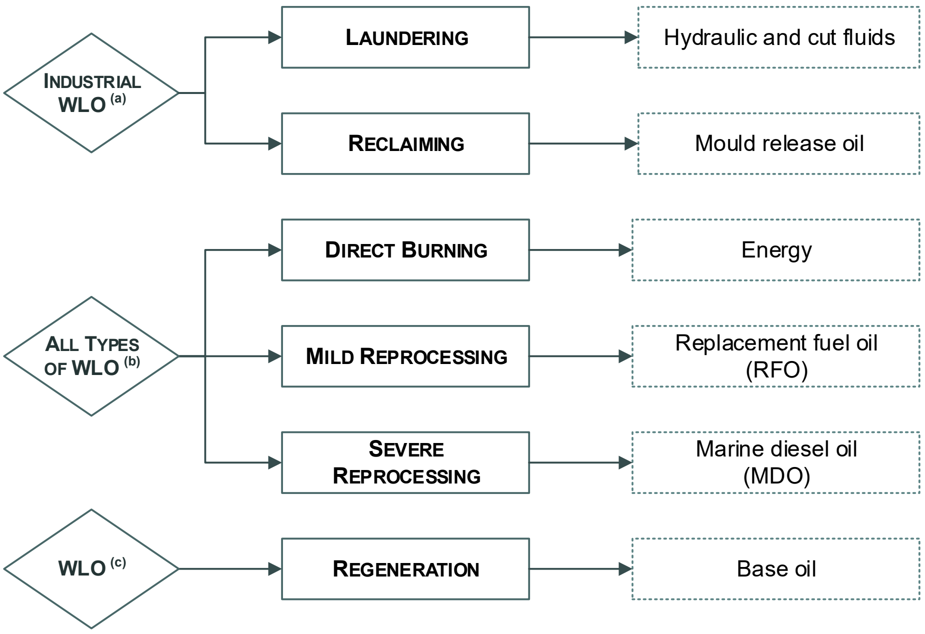
- **Polycyclic aromatic hydrocarbons (PAH) –** can be present in transformer oils which absorb potentially explosive gases produced during transformer operation and extends oil lifetime by acting as natural oxidation inhibitors [78]. PAH can derive from mineral base oils which were not removed during crude refining, and can be formed by the combustion of fossil fuels. Concentration of PAH in used crankcase oil may be 3 times higher than that in fresh oil [79].
- **Metals** – from the additives, the wear of metal, such as engine bearing or bushings, and from contamination with fuel containing metals. Metal are found in WLO as particulate or elemental form [7].
- **Other contaminants –** WLO can be contaminated with many other compounds: i) soot and carbon, which are responsible for the characteristic black color of WLO and are a result of incomplete combustion; ii) oxidation products that form sludge and varnish, as well as corrosive organic acids; iii) unburnt fuel that leaks into the lubricant; iv) dust and dirt composed from silicates from the surrounding environment; v) solvents, antifreeze agents, coolants, brake fluid that result from mishandling of the WLO producer; vi) remaining additives that were not depleted during use, etc. [80].

Table 2.10. Main contaminants and their sources [80].

Element	**Conc. (ppm)**	**Contamination from Additives**	**External Contamination**
Al	5 - 30	Grease	Piston wear (Al-Sb alloy)
Ca	2000 - 3000	Detergents, antioxidants, anticorrosion and grease	Atmospheric dust, cooling water circuit
B	75 - 100	Antiwear agents, extreme pressure, dispersants, friction reducer	Corrosion inhibitor from the cooling water
Cu	25 - 40	Antiwear and antioxidants	Wear and corrosion of bearings and Cu alloys
Cl	300 - 600	Antiwear agents, hydraulic fluids, insulating, heat transfer fluid, high pressure fluid	---
Fe	50 - 100	---	Wear and corrosion of steels
Mg	100 - 300	Detergents	Wear and corrosion caused by Mg alloy
Mo	5 - 20	Antiwear and extreme pressure agents	---
Na	50 - 100	Antirust, soap grease	Presence of salt in the NaCl form
Ni	3 - 5	---	Wear and corrosion of some steel alloys
P	800 - 1200	Antiwear agents, antioxidants, anticorrosion	Wear and corrosion of engine and segments
Pb	50	Extreme pressure additives, soap grease	Dilution by fuel, wear and corrosion coatings bearing
Si	30 - 120	Silicon base oils and antifoam agents	Atmospheric dust, wear and corrosion of alloy steel/silica, anti-corrosion of cooling water
S (%)	0,7 - 0,9	Detergents, antiwear, extreme pressure, antioxidants	---
Zn	1000 - 1200	Antiwear agents, antioxidants, anticorrosion	Cooling water anti-corrosion additive

2.2.1. TREATMENT AND DISPOSAL ROUTES

Due to the increasing need of environmental protection and stricter environmental legislation, the treatment of WLO has become increasingly important [46]. There are several routes for the treatment and disposal of WLO, each subject to local regulations. Currently, the main disposal routes available worldwide are laundering, reclaiming, direct burning, mild and severe reprocessing, and regeneration (Figure 2.17). Recycling is a generic term that may comprise laundering, reclaiming, reprocessing, and regeneration of WLO.



(a) Hydraulic and cutting fluids
(b) Especially heavy polluted oil
(c) With restrictions on chlorine, PCB and saponification number

Figure 2.17. Treatment and disposal routes currently adopted worldwide. Adapted from [47].

Laundering and reclaiming are suitable treatments for clean industrial lubricants. *Laundering* is a closed-loop system especially applied for hydraulic and cut fluids. The process involves the removal of solids by filtration, de-watering by vacuum distillation and the addition of additives. The treated oil is then returned to the same company for reuse [48]. Hydraulic fluids can also be treated by *reclaiming*. The lubricant is simply centrifuged and/or filtered and then reused, for instance, as mould release oil or base oil for the production of chain saw oil [47].

Direct burning of WLO without any pre-treatment can be employed for energy recovery. The selection of this route depends greatly on local regulations and varies in popularity across Europe. The combustion can occur in cement kilns, space heaters or waste incinerators [6].

Mild reprocessing is a simple cleaning process to remove water and sediments from heavy polluted WLO. After this treatment the oil can still contain metals, halogen and sulfur but can be further used as replacement fuel oil (RFO) for combustion in road stone plants, blended into fuel oil or in power stations [47].

Severe reprocessing aims at separating the combustible portion of heavy polluted WLO from less desirable bottom fractions containing metals, non-combustible ash, and dirt. Chemical or thermal treatments are applied to produce a de-metallized heavy fuel oil, also called heavy distillate, which can then be used as marine diesel oil (MDO), fuel for heating plants, etc. [45].

Regeneration involves the production of base oils from WLO after the removal of contaminants, oxidation products, and additives, for further manufacture of lubricant products. The process is more complex than those described above and involves several treatment technologies to achieve a lubricant base oil with similar quality to those from crude oil refining [24]. Depending on local regulations, WLO contaminated with chlorine, PCB or with a chemical composition that hinders the treatment by regeneration must be managed using other treatment or disposal route.

The legislative framework regarding the management of WLO clearly identifies the preference for regeneration over other forms of recycling/recovery. This decision depends on the compliance of the characteristics of WLO with the established technical specifications. The key elements that determines the treatment option of WLO is its chemical composition, including type and level of contamination, base oil properties and energy value (calorific power).

2.2.1. HANDLING, STORAGE AND COLLECTION

The handling and storage of WLO by the producers is of paramount importance for the management of this hazardous waste. Besides the correct storage in proper containers to prevent leakage and spills, it is necessary to ensure that other types of waste (water, solvents, gasoline, antifreeze, etc.) are not mixed with WLO. The mixture will decrease the potential of WLO for regeneration due to contamination with non-lubricant components. In many cases, external contaminations cause the non-compliance of WLO with technical specifications (see Table 1.2) in terms of water, sediments, chlorine, PCB or glycol.

A detailed overview of the waste management systems of WLO implemented in European countries, with special focus on the Portuguese case will be presented in Section 5. Nevertheless, Figure 2.18 illustrates the typical steps of lubricants life cycle, from their production from base oil and additives, generation of waste, handling, storage, collection and treatment. After use, the waste oil generated should be stored by the producers in containers, which in general are not segregated according to the type of waste oil. The management system includes a network of collection operators that provide the collection from producers across national territory and transport to treatment units. Prior to collection and before deciding the final destination of the oil, a quality control is carried out to ensure that the technical requirements for the several destinations imposed by the legislation are met [49]. In Portugal, the disposal routes allowed include: regeneration through vacuum distillation to produce base oils; conversion of WLO into fuel oil by thermal cracking (then used to produce electricity in co-generation engines); production of light expanded clay aggregate (LECA) where WLO is used as expansion agent; and incineration.

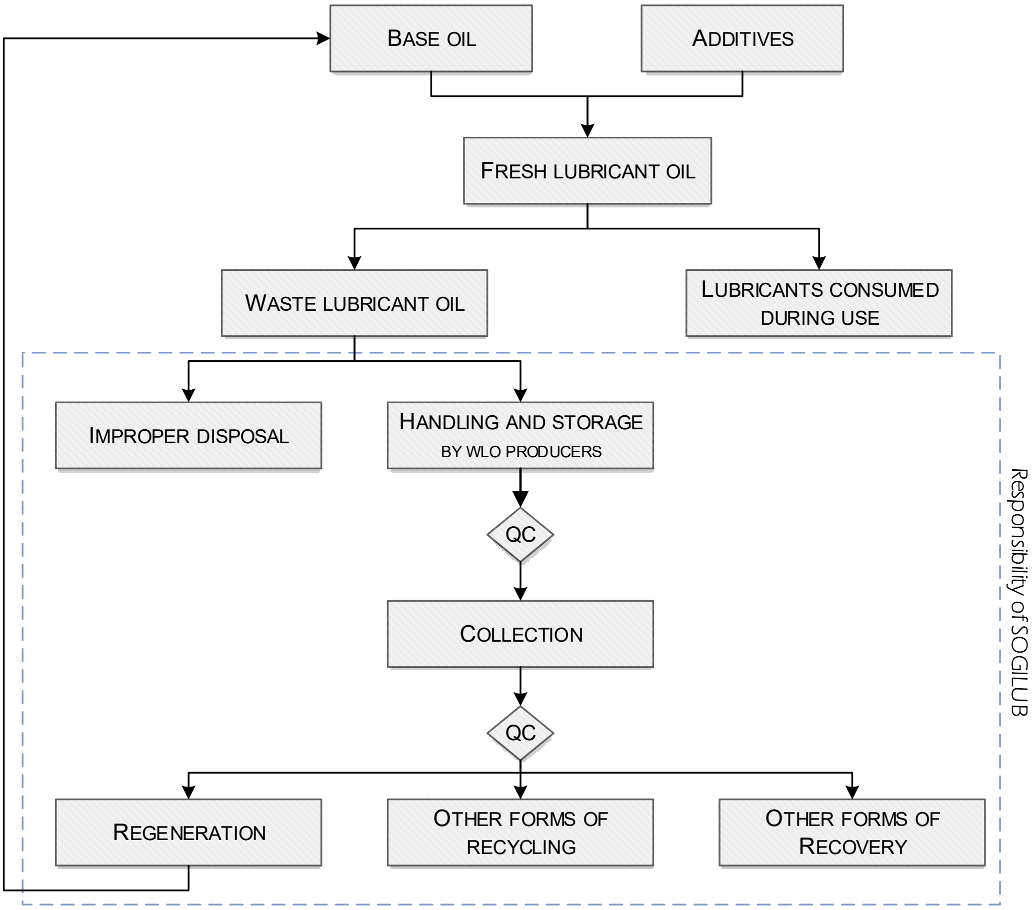


Figure 2.18. Life cycle of lubricants (QC – Quality Control).

If producers do not properly manage WLO, undesired contamination may arise, and regeneration may become unfeasible. In fact, in case of the collection operators receive from a producer a contaminated WLO load, for example with high levels of chlorine (>>2000 ppm), then after checking the quality control (QC), all the tank truck load may be contaminated. Indeed, an entire container contaminated with chlorine content >2000 ppm has to be disposed as chlorinated waste and not regenerated/recovered. If the contaminated load was collected separately, the regeneration potential would be maximized. Thus WLO producers must be alerted to adopt more suitable storage practices of different types of wastes, and for the consequences of non-conformity by the waste management authorities.

In addition to the contamination with other wastes, WLO of different characteristics should not be mixed, if such mixing hinders its treatment. However, to the best of the author’s knowledge, there is no recommendation in the legislation or in the literature on exactly what types of WLO should not be mixed. As aforementioned, there are many types of base oils, blended with different packages of additives depending on the type of application. Even after use, according to the European List of Residues (LoW), there are more than 30 entries for WLO, which makes impossible to segregate the different types of WLO during storage and collection phases.

One opportunity for the improvement of the collection system is a more in-depth knowledge of the physico-chemical characteristics of the WLO generated by national producers. More specific indications could be given to the producers on the correct practives for the segregation of WLO. This would allow the improvement of the management system, the fulfillment of the annual targets and the waste hierarchy. These issues will be addressed in detail in Chapter 5.

2.3. PHYSICOCHEMICAL PROPERTIES OF LUBRICANT OILS

There are several physicochemical properties that are often used to describe the quality and performance capabilities of fresh lubricant oils. For waste oils, the characterization is intended to evaluate the level of contamination and to determine the most appropriate treatment.

In Table 2.11 it can be seen set of properties investigated in this work for fresh and waste lubricant oils, which will be briefly described next.

Table 2.11. Physicochemical properties of fresh and waste lubricant oils assessed in this work.

Property	Method/Technique	Fresh oils	Waste oils
Density (kg/m^3)	ASTM D1298	✓	✓
Viscosity (cSt)	ASTM D445	✓	✓
Viscosity Index	ASTM D2270	✓	
TAN (mg KOH/g)	ASTM D664	✓	✓
Saponification (mg KOH/g)	ASTM D94	✓	✓
Paraffinics (%)	IS 13155	✓	
Naphthenics (%)	IS 13155	✓	
Aromatics (%)	IS 13155	✓	
Water (%)	ASTM D6304		✓
Sediments (%)	ASTM D893		✓
Elemental content (ppm)	EDXRF		✓
Surface tension (mN/m)	Wilhelmy plate		✓

DENSITY

Density is the ratio of the mass to the volume of a substance. The density of lubricants increases with viscosity, boiling range, aromatic and naphthenic content, and decreases as the saturated compounds levels, such as iso-paraffin, increases. As a general rule, the higher the density the lower the viscosity index for a certain lubricant. Moreover, high values of density in WLO can be an indicator of contamination with oxidation products, carbon residues, soot, sulfur, chlorine, solid particles, or metals.

VISCOSITY AND VISCOSITY INDEX (VI)

Viscosity is one of the most important properties of lubricants [8]. It is a measure of the resistance of a fluid when undergone to gradual deformation due either shear stress or tensile stress. Viscosity can be explained with a model of adjacent layers of fluid which, when a shear stress (τ) is applied, the individual layers move parallel to each other in the direction of the shear force with different velocities (V_1 different than V_2). Molecular forces create a resistance to movement between layers which cause the upper layers to move faster than the lower layers (Figure 2.19).

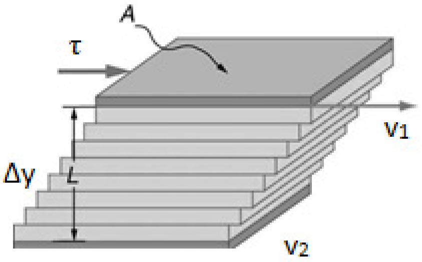


Figure 2.19. Laminar flow of a fluid between two plates. Adapted from [2].

This resistance to movement is called dynamic viscosity (η).

$$\eta = \frac{\tau}{S} \ [\mathrm{cP}] \tag{2.1}$$

The velocity difference between two fluid layers, in relation to their linear displacement, is the shear rate, $S = dv/dy$. The applied force per unit of area of the plates is the shear stress (τ) is proportional to the velocity gradient in Newtonian fluids. The ratio between dynamic viscosity (η) and density (ρ) of the fluid is the kinematic viscosity (ν).

$$\nu = \frac{\eta}{\rho} \ [\mathrm{mm}^2/\mathrm{s}] \text{ or } [\mathrm{cSt}] \tag{2.2}$$

Different oils have different rates of change of viscosity with temperature. The viscosity index (VI) was developed to express numerically the viscosity behavior to temperature changes. This method is based on the comparison of the viscosity variations of "standard" oils that differ widely between each other. Thus, a reference naphthenic oil whose temperature has a high influence on viscosity, was arbitrarily assigned to zero VI, while a reference paraffinic oil, whose temperature has little effect on viscosity, was assigned a VI of 100. With the accurate viscosity data on these two oils, the VI of any oil could be determined as a percentage factor relating the viscosities at 40 °C and 100 °C of the test oil, the zero VI oil and the 100 VI oil [2]. This concept is illustrated in Figure 2.20 and the VI can be calculated using Eq. (2.3),

$$VI = \frac{L - U}{L - H} \times 100 \tag{2.3}$$

where, L is the viscosity of the zero-VI oil at 40 ºC, H is the viscosity of the 100-VI oil at 100 ºC, and U is the viscosity of the test oil at 40 ºC.

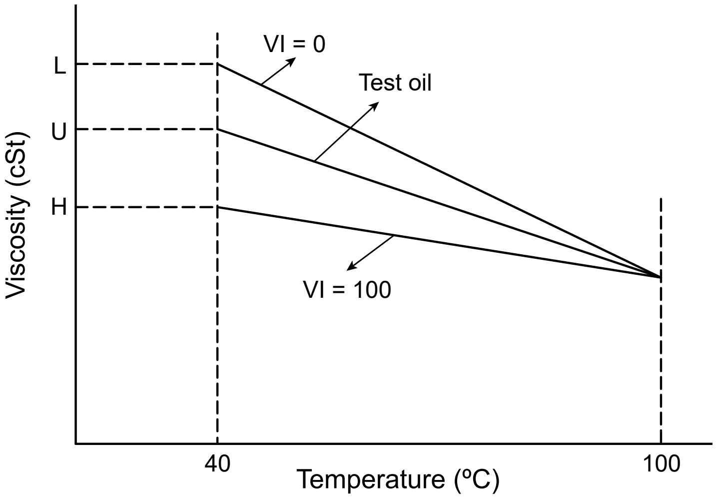


Figure 2.20. The viscosity index (VI) concept.

Generally, lubricants with high VI are preferred since they indicate a relative low viscosity change with temperature, whereas low VI indicates a relatively high rate of change of viscosity with temperature.

TOTAL ACID NUMBER (TAN)

A measure of acidic constituents in a lubricant may be expressed by TAN, which is a useful parameter to estimate its remaining useful life. The acidity of fresh oils is generally derived from special additives such as the antioxidant and antiwear zinc dialkyl dithiophosphate (ZDDP). As the lubricant ages the additives are depleted, reducing the acidity created by these components. For WLO, the TAN is of interest since provides information about of the extent of oxidation in the oil [50]. TAN corresponds to the weight in milligrams of KOH required to neutralize 1 g of the constituents of the oil that react with KOH under specific test conditions. This property is usually determined by titration and the end point corresponds to the most distinct inflection of the titration-curve.

SAPONIFICATION NUMBER (SN)

The saponification value gives an indication of the fatty compounds present in the oil that will saponify under certain conditions, such as organic acids and esters. The saponification number (SN) of fresh oils is usually associated with acidic additives, while in waste oils is related to oxidation products, additives or ester-based oils. In waste oils, the SN is a very important parameter for avoiding plugging of equipment and piping due to soap formation at high temperatures in regeneration plants. The saponification number is defined as the milligrams of KOH required to saponify fatty material present in one gram of fat or oil.

PARAFFINIC, NAPHTHENIC AND AROMATIC CONTENTS

The determination of the aromatics, paraffinics, and naphthenics fractions in fresh lubricant oils is of interest in providing a "fingerprint" of the oil composition. It can also provide an indication of the potential stability, reactivity and solvency of the oil. The determination of those constituents can be achieved by FTIR spectroscopy.

WATER AND SEDIMENTS

Information about water and sediment content in lubricant oils is important in regeneration of WLO to ensure that the limits for collection and pre-treatment comply with local regulations (Table 1.2). In addition, measurement of water and sediments are useful in predicting the quality and performance characteristics of the products. As aforementioned, water can arise from infiltration, combustion by-product, antifreeze, etc. Sediments can result from external contamination, carbonaceous particles, oxidation products, oil and additives degradation, or engine wear and corrosion materials. Sediments in lubricant oil can lead to system malfunctions in critical applications, and thus determination of the amount of sediments is imperative.

ELEMENTAL CONTENT

The elemental content corresponds to the amount and type of elements in the oil. The elements of interest in WLO include several metals from surface wear and from some additives, such as phosphorous, chlorine, sulfur and silicon. As mentioned in Table 2.10, the elements found in WLO can provide an indication on the source of the contamination. It is important to refer that for example the elemental chlorine content is limitative of regeneration process. Regarding sulfur, the base oil API classification depends on the sulfur content.

SURFACE TENSION

Surface tension is the contractile force which makes the material acquire the smallest surface area possible. In lubricant oils, the surface tension can be strongly dependent on the presence of additives such as antiwear, extreme pressure, rust inhibitors, dispersants and detergents. Surfactants or other additives alter the balance of intermolecular forces in the liquid-gas interface [51].

The condition of lubricating oils can, to a large degree, be measured by interfacial tension. Changes in the surface tension can be the earliest sign of contamination, sludge potential and oxidation [52]. As the additives start depleting, the oil degrades by oxidation and become contaminated, and the surface tension decreases (Figure 2.21). Many of the contaminants and oxidation products formed can alter the surface tension of the lubricant before there is any noticeable change in the TAN or viscosity.

Moreover, surface tension also influences oil cooling capacity by affecting spreadability. Poor wettability may reduce heat-transfer due to vapor phase formation [30].

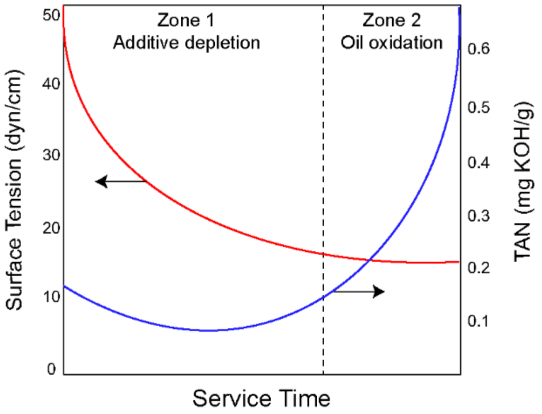


Figure 2.21. Surface tension and TAN of lubricants over the service time. Adapted from [53].

2.3.1. PREDICTION OF PROPERTIES USING ADVANCED STATISTICAL ANALYSIS

The monitoring of physicochemical characteristics is essential to ensure proper quality of lubricant products. Most of the properties mentioned before are determined based on traditional routine measurements (ASTM standards) that are expensive and time consuming methods, and require specific equipment. Currently, infrared spectroscopy (IR) combined with advanced regression techniques (chemometrics) have emerged as powerful alternative methodology to the classic analytical methods.

Predictive analytical methods are used for the development of mathematical models that generate reliable predictions of properties (e.g. density, viscosity, TAN, etc.) from a number of predictor variables (such as the wavenumbers from a IR spectra), as illustrated in Figure 2.22 [54]. Developing the models includes stating the objective of the study, designing the experiment, choosing the type of model, estimating its parameters and validation of the predictions [55].

A large variety of regression methods are currently available for predictive modelling. Each of these methods is based on specific assumptions regarding the nature of the (input variables, represented by X_j's), the response variable (Y) and the data generating mechanism (i.e., the underlying system) [56].

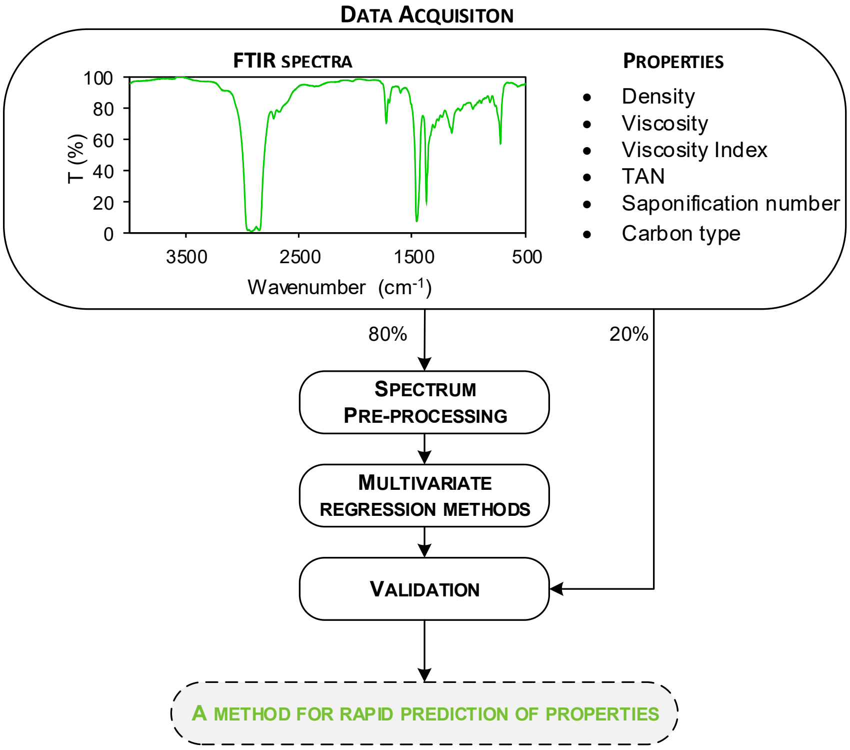


Figure 2.22. Methodology for the prediction of properties using chemometrics. Adapted from [57]

Advanced predictive analytics using IR spectroscopy have been applied for the prediction of the aforementioned properties in crude, lubricant and vegetable oils. Table 2.12 lists some of studies reported in the literature.

Many of the literature papers develop prediction models for a set of samples for the same application and/or with similar composition. The models are applicable in the range of calibration, which is related to the type of samples selected to train the models. Therefore, it would be interesting to develop robust models for analyzing a set of lubricants for different applications. This would allow, for example, a lubricant plant to quickly assess the properties of the different oils produced. This topic will be addressed in more detail in Chapter 3.

Table 2.12. Prediction of properties using chemometrics and infrared spectroscopy.

Analyte	Properties	Regression methods	Observations	Ref.
Engine oil	Viscosity	PCR, PLS	114 diesel engine oil (15W40) in different stages of use. PLS more accurate than PCR. $RMSE_P$ of 3.8 cSt and a relative error of 3.2%.	[58]
Engine oil	Viscosity index	PLS	1085 engine oil samples from 81 different producers. $RMSE_C$ 6.4 and a relative error of 5.2%.	[59]
Engine oil	Viscosity index Base number	PLS, CLS and PCR	350 samples of virgin motor oils and recycled motor oil. PLS showed better performance than CLS and PCR.	[60]
Gas engine oil	Total acid number (TAN)	PLS	69 oil samples from gas engines (sewage and wood gas) for energy production. Standard error of prediction of 0.07 mg KOH/g.	[61]
Base oil	Viscosity at 40 °C Viscosity index Carbon type	PLS	60 base oils produced through different processes, (hydrofinished/conventional, severely hydrofinished, hydrocracked and wax isomerized.	[62]
Lubricants	Water	PLS	Polyalphaolefin (PAO) base oil, fresh and waste lubricating oils. Average standard error of prediction ~80 ppm.	[63]
Aviation engine oil	Total acid number (TAN)	PC, PLS	176 synthetic polyol esters aviation engine oils. $RMSE_P$ of 0.060 mg KOH/g for PC and 0.048 mg KOH/g for PLS.	[64]
Base oil	Density Carbon type Flash point	PLS	88 paraffin base oil samples. $RMSE_P$ for density, aromatics, naphthenics, paraffinics and flash point were 0.0005 g/cm^3, 0.5%, 1.0%, 1.4% and 9.5 ºC, respectively.	[65]
Crude oil	Density	PLS	110 crude oil samples comprising more than 30 types of crude oils originating from more than 12 countries. $RMSE_P$ of 0.0022	[66]
Marine engine oil	Water	MLR, PLS	29 samples were prepared by adding water (from 0.1 and 3.7%) to marine engine oil. Both regression methods gave similar results, with errors of prediction less than 2%.	[67]
Vegetable oil	Saponification number	PLS	Red fruit oil sample was considered. Coefficient of Determination (R^2) of 0.998 and Standard Error of Calibration (SEC) was 0.79%.	[68]
Vegetable oil	Saponification number	PLS	61 samples of a variety of edible oils (soybean, rapeseed, coconut oil, soybean oil, olive oil, canola oil, corn oil and sunflower oil). Standard deviations of the differences (SDD) of 1.074.	[69]
Waste lubricant oil	Ethylene glycol Water Gasoline	iPLS	Samples were prepared from automotive lubricating oil and artificially contaminated with water (n=20), ethylene glycol (n=34) and gasoline (n=24). $RMSE_P$ of 0.34% for gasoline, 0.037% for ethylene glycol and 0.023% for water.	[70]

CLS – Classical Least Squares; MLR – Multilinear Regression; PC – Principal Component; PCR – Principal Component Regression; PLS – Partial Least Squares; iPLS – interval Partial Least Squares.

2.3.2. CORRELATION OF THERMOPHYSICAL PROPERTIES

Another approach to obtain physicochemical properties more quickly and less costly, is to use correlations between properties. Several correlations have been developed for the estimation of physical properties for petroleum fractions [71]. For lubricant oils in particular, correlations and regression analysis has been performed to ascertain relationship among physicochemical and tribological parameters [72]. In this study, the temperature dependence of viscosity will be explored using different correlations, as listed in Table 2.13. The relationship between the glass transition temperature T_g, the dynamic crossover temperature, T_x, and the viscosity-temperature characteristics of lubricants will be also addressed. In addition, different correlations were evaluated to predict viscosity and surface tension starting from properties easily obtained such as density.

These correlations will be explored in Chapter 4.

Table 2.13. Correlations for the temperature dependence of viscosity, between the density and viscosity, and between density and surface tension.

Correlation	**Parameters**	**Ref.**
Temperature dependence of viscosity		
$\eta = \mathrm{A} \exp\left(\frac{\mathrm{E_a}}{\mathrm{RT}}\right)$	A	[73]
$\ln \alpha_T = \frac{-C1(T-T_r)\ln(10)}{C2+(T-T_r)}$	$C1$, $C1$, T_r	[74]
$\ln \eta = A + \left(\frac{B}{T}\right) e^{(C/T)}$	A, B, C	[75]
$\eta = \eta_0 \times \left(\frac{T-T_x}{T_x}\right)^{-\gamma}$	η_0, T_x, γ	[76]
$\left(\frac{1}{\eta}\right)^{\phi} = a + b \times T$	a, b	[77]
Correlations between density and viscosity		
$\rho = A + \frac{B}{\eta^{0.5}}$	A, B	[78,79]
$\ln \eta = A + \frac{B}{T} + C\rho^2 \ln \rho$	A, B, C	[80]
Correlations between density and surface tension		
$\ln \sigma = c - \frac{1}{2} \ln \kappa_T + \frac{1}{2} \ln \rho$	c, κ_T	[81]

2.4. REGENERATION PROCESS

According to the Waste Framework Directive 2008/98/EC, regeneration "means any recycling operation whereby base oils can be produced by refining waste oils, in particular by removing the contaminants, the oxidation products and the additives contained in such oils". The obtained base oil has excellent potential to produce fresh lubricating oils with similar or even better properties as virgin base oils [82].

The earliest and widely adopted technology in the past for the regeneration of WLO was the acid/clay process. The treatment involved mixing the waste oil with concentrated sulfuric acid as an extraction medium for the removal of undesired contaminants, forming acid sludge. The acid treated oil was then mixed with clay and filtered [83]. Good quality base stocks were produced by this simple technology. However, problems associated with secondary pollution as the disposal of spent clay and acid sludge and low yield (45–65%) discouraged the use of this process by environmental regulators, which was banned since the early 1970s [82,84].

Alternative technologies to the acid/clay treatment were developed. In general, the regeneration processes are based on the same separation techniques as the refining of crude oil for base oil production. Thus, these processes includes a pretreatment, dewatering and defueling, deasphalting, finishing and fractioning steps [9,16,26,85]. Figure 2.23 shows a simplified block diagram illustrating the main regeneration steps and the different technologies that can be applied in each step.

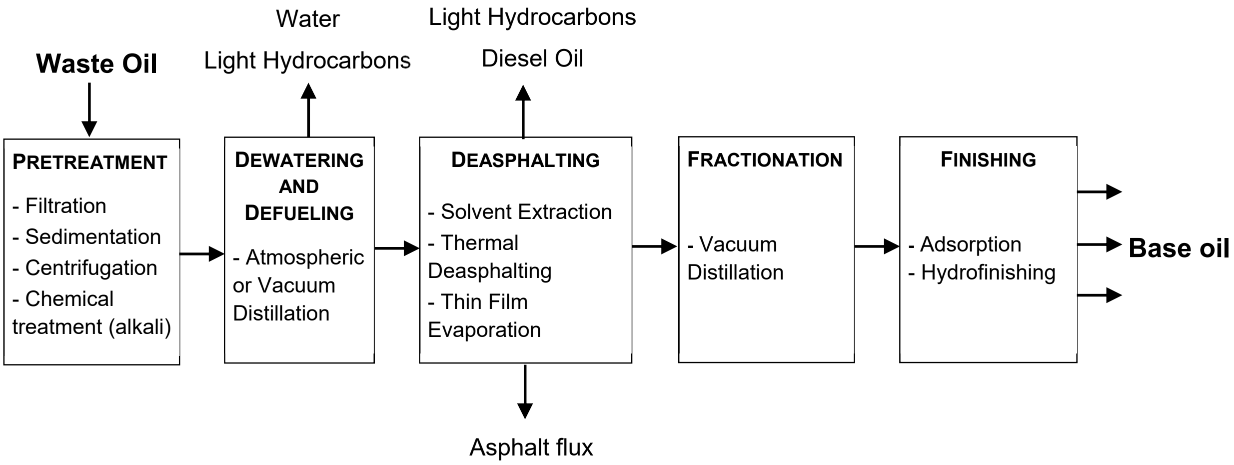


Figure 2.23. Typical regeneration process steps. Adapted from [86].

PRETREATMENT

A chemical and/or physical pretreatment is usually required to remove large contaminants such as polymeric compounds that become unstable when heated, which accelerate fouling and coking of equipment in the subsequent steps [24].

The physical pretreatment typically involves simple operations such as sedimentation, filtration or centrifugation. Sedimentation is used to remove large impurities, which settle from the oil due to solubility or density effects. Filtration or centrifugation are frequently used for the removal of free and emulsified water, suspended matter and heavy impurities [87]. Water and suspended contaminants may not settle easily due to the dispersive action of additives and could require further treatment.

A common chemical pretreatment involves the addition of a strong base such as sodium or potassium hydroxide. The alkali is an effective agent in neutralizing acids and free or bounded chlorine, also causing an extensive demetallization by precipitation of metals and additives. The hydroxide also saponifies the fatty acids present in the oil. The potassium form has been reported to yield better results than the sodium form [6].

DEWATERING AND DEFUELING

The next step involves the dehydration and defueling of the pretreated oil by atmospheric or flash distillation which is effective to remove any dissolved water, low boiling point hydrocarbons and contaminants such as gasoline, naphtha, glycol and solvents [87].

DEASPHALTING

In order to achieve the desirable purity required for the reuse as base oil, the resultant dewatered and defueled oil has to be further processed to remove heavier contaminants [24,84]. The residue (asphalt stream) obtained in this step might be suitable as an asphalt additive for road paving [6]. There are two main technologies for the deasphalting step – vacuum distillation and solvent extraction.

Vacuum distillation involves the distillation of oils under sub-atmospheric pressure, which lowers the necessary operating temperature and minimizes the occurrence of thermal breakdown. The efficiency of contaminants removal can be over 98 % for ash, and heavy metals, and over 95 % for carbon residue. Furthermore, other qualities can be improved such as sulfur content and viscosity [88].

One of the main problems associated with distillation processes for treating WLO is the formation of deposits and hot-spots, arising from resinous material. This can cause coking and fouling of the internal surfaces of columns, which makes continuous operation difficult and low-quality base oils (poor stability, color, and odor). To overcome this problem, the application of column distillations with special characteristics such as the wiped/thin film evaporators (TFE) [82] and thermal deasphalting (TDA) units have been suggested [89]. However, these units operate at high temperature and very high vacuum, requiring high investment and operating costs. They are economically viable for high-capacity plants, usually with processing more than 60 000 tonnes/year [90].

Solvent extraction emerges as an alternative process for the removal of degraded additives, carbonaceous particles and polymeric compounds from WLO [91]. Compared to vacuum distillation solvent extraction is a cost-effective technology with low energy consumption that has been studied as an alternative by several researchers [87,92].

FINISHING

The finishing step aims to improve the base oil color, odor, oxidation stability and increase the useful life of lubricants. There are two main technologies commonly used as finishing step – adsorption and hydrotreatment [6].

Adsorbents such as silica gel, bauxite and natural or activated clay based on magnesium or aluminum silicates (e.g. montmorilonites, atapulgites, sepiolites and bentonites) have been used to selectively remove polar compounds (acids, alcohols, aldehydes, thiols, ketones, esters, etc.), organic residues, asphaltic and resinous materials, heavy metals, or sulfur containing compounds [93–95]. Battalova and Likerova showed that activated bentonite is the most efficient material used to remove polar compounds from WLO [96]. Adsorption is still widely used due to the simplicity of operation and satisfactory quality of the base oil [24].

The hydrotreatment process allows the removal of chlorine, sulfur, oxygen and nitrogen compounds (p.e. mercaptans), trace metals, and the hydrogenation of unsaturated moieties [9,26]. The oil is combined with high-purity hydrogen in the presence of a solid catalyst, such as nickel, or most often cobalt and molybdenum oxides supported on an alumina base, under controlled pressure (5 to 200 bar) and temperature (260 to 425°C) in a catalytic reactor. The sulfur and nitrogen are combined with hydrogen producing hydrogen sulfide (H_2S) and ammonia (NH_3), which are then removed by absorption. The metals stay on the catalyst surface. The aromatic and unsaturated compounds become saturated and remain in the oil [6]. Hydrotreatment has also demonstrated to be efficient in the destruction of PCB [97].

Compared with clay treatment, the hydrotreatment process requires high operation and investment costs, although higher quality base oils are obtained [87]. For small capacity plants (< 12 000 tons/year), a clay adsorption treatment is more suitable, whereas hydrotreatment is typically used in high capacity plants (> 30 000 tons/year) [24].

FRACTIONATION

Finally, a fractionation step by vacuum distillation is used to separate the different base oil grades. The fractions obtained are typically a light cut of vacuum gas oil or spindle base oil, a medium cut of light base oil, and heavy base oil [6].

In Europe, the regeneration plants are based on the combination of several sequential treatment processes using different operating conditions, and producing a large diversity of base oils. Modern regeneration technologies produce high quality base oils that correspond to group I or even group II according to the API classification of base oils [98]. In 2016, the European regeneration industry comprised 28 plants treating waste oil, as illustrated in Figure 2.24.

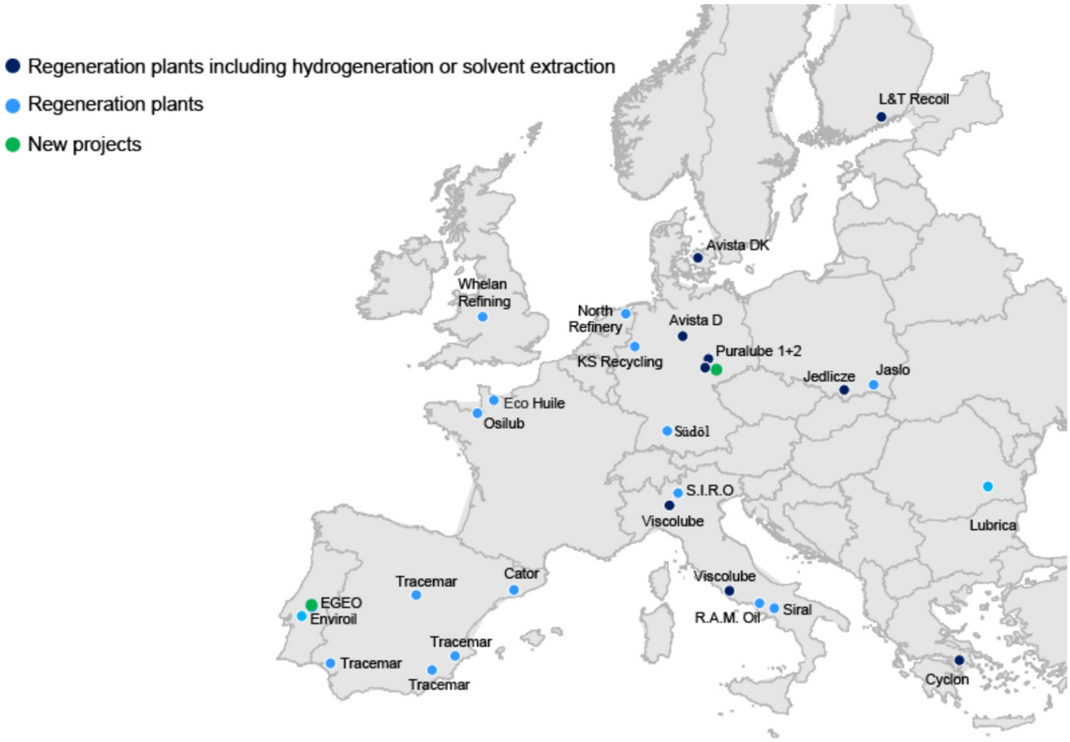


Figure 2.24. Regeneration industries in Europe, 2016. Adapted from [99].

Nowadays, the several regeneration technologies differ from each other mainly with respect to the deasphalting and finishing steps [84].

Table 2.14 shows an overview of the regeneration technologies applied in Europe.

The next sub-sections will explore in more detail the alkaline pre-treatment and the deasphalting step by solvent extraction, which are the stages of the regeneration process that were addressed in this work.

Table 2.14. Waste oil re-refining technologies.

Technology	Process					Yield (%)	Observations	Ref.
	Pretreatment	Dewatering and Defueling	Deasphalting	Fractioning	Finishing			
Acid/clay (Banned)	Filtration	Flash or vacuum distillation T=120-180 °C, P=0.7 bar	Sulfuric acid (7 wt%, T=40 °C); Absorption clay (6 wt%, T=270-300 °C)	Vacuum distillation	---	60-65	Low quality of produced base oil (API I). The product oils are dark in color and tend to have a noticeable odor.	[24,83]
MRD Process (Germany)	Aqueous KOH (conc. 5-50%)	Vacuum distillation T= 140 °C, P=0.6 bar and Multistage distillation T= 260 °C, P=60 mbar	Thin Film Evaporation (TFE) T= 385°C, P=3 mbar	Optional vacuum distillation T= 280 °C, P=80 mbar	Solvent Extraction (NMP) T=80°C, Solvent/oil ratio= 1.5:1	84-92	Good quality base oil. Quantitative elimination of PAHs and PCBs. Preservation of the synthetic oils (PAO). Feedstock can contain up to 5% vegetable oils.	[100]
Interline (UK, Spain)	Aqueous KOH (conc. 45%), and NH_4OH T<93 °C	Atmospheric distillation	Liquid Propane Extraction T=32-43 °C, Solvent/oil ratio=3-10:1	Vacuum distillation	---	~79	Low quality base oil (API Group I).	[101]
Enprotec or Vaxon (Denmark, Spain)	Filtration and addition of Aqueous KOH T= 80 °C	Vacuum distillation (Cyclonic) 1st stage: T=160-180 °C, P=0.4 bar 2nd stage: T=260-290 °C, P=40-100 mbar	Vacuum distillation (Cyclonic) 3rd stage: T=290-330 °C, P=15-25 mbar 4th stage: T=320-345 °C, P=5-15 mbar			65-70	Medium quality of the produced oil. The final stage does not allow the production of high quality base oil Virtually all PAH removed.	[24,47,102]
EcoHuile or Sotulub (France)	Filtration and addition of 1-3 wt.% Aqueous NaOH and/or KOH, T= 140-160 °C	Flash distillation and Gas Oil Stripping T=280 °C	Vacuum distillation and Thin Film Evaporation (TFE)	Vacuum distillation	Optional addition of aqueous NaOH and/or KOH	82-92	Low quality base oil produced	[24,86]

Table 2.14 (cont.). Waste oil re-refining technologies.

Technology	Process					Yield (%)	Observations	Ref.
	Pretreatment	**Dewatering and Defueling**	**Deasphalting**	**Fractioning**	**Finishing**			
CEP process (Finland)	Aqueous KOH (conc. 30%), T= 120-140 °C	Vacuum Distillation P=0.3 bar	Thin Film Evaporation (TFE)	Vacuum distillation	Hydro-treatment T=315 °C, P=90 bar	~70	High-quality base oils (API Group II).	[103]
Revivoil (Italy)	---	Atmospheric distillation T=140°C	Vacuum Distillation (TDA) T=360 °C		Hydro-treatment T=300 °C, P=100 bar	74-77	Products quality comparable to virgin base oils. Possibility to achieve API Group II requirements.	[24]
KTI Process (Greece)	Filtration	Atmospheric distillation or Vacuum distillation T=220 °C, P=20 mbar	TFE T=345 °C, P=20 mbar	Vacuum distillation T=200 ºC, P=30 mbar	Hydro-treatment T=320 °C, P=60 bar	82-95	Excellent product quality	[104]
Snamprogetti (Italy)	---	Atmospheric distillation T=180-230 °C	Propane Deasphalting 1st stage: T=30 °C, P= 24.5-49 bar, Solvent/oil ratio=3-10:1 2nd stage: T=30°C, P= 24.5-49 bar, Solvent/oil ratio=5-20:1	Vacuum distillation T=300 ºC	Hydro-treatment T=250-420 °C	85-90	Improved oil quality. High-pressure extraction equipment	[105]
Viscolube (Italy)	Addition of aqueous KOH (conc. 30%)	Vacuum Distillation T=120-140 °C, P=0.27 bar	Settling and Vacuum Distillation (TDA) T=360 °C, P=13-27 mbar		Clay T=275 ºC, 8 wt.% or Hydrotreatment P=100 bar	~74	Good product quality (if hydrotreated) Significant amount of byproducts to discart (if clay treated)	[89]
Enviroil (Portugal)	Filtration, Sedimentation Centrifugation Addition of aqueous KOH	Atmospheric distillation	Vacuum distillation T = 365 ºC P<50 mbar	Vacuum distillation	Clay treatment	65-75	Good quality product	[106]

2.4.1. ALKALINE TREATMENT

As shown in Table 2.14, most of the technologies include a pretreatment using an alkaline solution such as NaOH or KOH. This step is usually required to remove impurities to avoid plant plugging [24]. In addition, the alkalis saponify the fatty acids and neutralize the chlorine present in both bound and free forms [89]. The saponification of the fatty acids facilitates their elimination by settling and prevents vaporization during distillation and contamination of the distilled base oil. Moreover, the elimination of the chlorine has beneficial effects in reducing corrosion in the plant. The alkaline agent can be added to the WLO during the pretreatment before the sedimentation or centrifugation or before the deasphalting step.

One aspect that is seldom addressed in the literature is the influence of the type of WLO in the alkaline pretreatment. The regeneration industry has been struggling with the fact that after the alkaline treatment and in stages that require a substantial temperature increase such as distillation, some WLO form a gel type oil that can cause plugging of the plant. As aforementioned, the overall composition of WLO can vary widely, depending on the original oil, type of usage and contamination level. The knowledge of the compounds that cause this undesirable effect would be of paramount importance. It would allow the segregation of certain types of WLO at the source and reduce the contamination of other WLO by avoiding the mixing of wastes that hamper the treatment by regeneration.

This topic will be addressed and explored in more detail in Chapter 6.

2.4.2. SOLVENT EXTRACTION

The basic principle of the solvent extraction process consists in the different solubility of waste oil constituents in the solvent. As illustrated in Figure 2.25, the feed is mixed with the solvent, which should have greater affinity for the oil fraction. The aggregation and flocculation of insoluble particles occurs, and their separation is possible. The settling of heavier components allows the formation of a lighter phase, which consists in the base oil dissolved in the solvent, and a heavier phase containing the asphaltic components with some solvent (asphalt flux). The two phases are separated and the solvent recovered by distillation [84].

The application of several low molecular weight compounds such as hydrocarbons, alcohols, and ketones as solvents for the regeneration of WLO has been intensively studied. As in the case of the production of base oil from crude, propane has generally been found to perform well in the removal of degraded additives and contaminants. The operation occurs at high pressure (> 10 atm), and the majority of propane can be recovered by distillation [6,107].

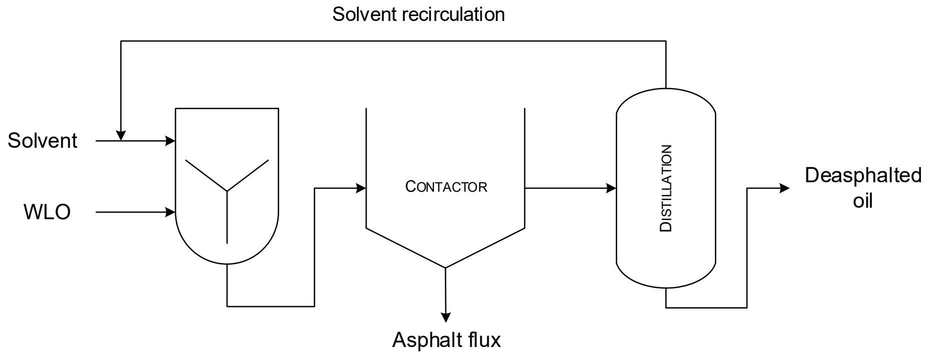


Figure 2.25. The solvent extraction process. Adapted from [84]

As an alternative, the deasphalting process by solvent extraction has also been studied using polar solvents such as hexane, alcohol, and ketones, at ambient pressure [24]. Mohammed and coworkers studied the performance of six solvents, showing that 1-butanol achieved the best percent sludge removal, followed by n-hexane, petroleum ether, 1-hexanol, carbon tetrachloride, and acetone [108]. Martins proposed a mixture of 0.25 waste oil/0.35 n-hexane/0.40 polar compound (80% 2-propanol + 20% 1-butanol) as an effective ternary solvent for the removal of contaminants [109]. Elbashir and coworkers highlighted the performance of three extracting solvents in recycling waste oil, showing that methyl ethyl ketone (MEK) achieved the lowest percent oil losses, followed by 2-propanol and 1-butanol [110]. In addition, N-methyl-2-pyrrolidone has also been used to separate aromatic hydrocarbons and hetero-organics from the base oil [107]. The main process variables include the solvent/oil ratio, the temperature, flocculation agent dosage, settling time, mixing time and mixing speed.

Table 2.15**Table 2.15** presents an overview of the solvents and conditions studied for the treatment of WLO by solvent extraction. Technologies based on extraction use materials that are responsible for creating human health impacts, process safety risks, and multiple impacts to the environment. Therefore, it is becoming imperative to find systems more efficient, environmentally friendly, and at the same time economically feasible.

Nowadays, the increasing awareness for environmental protection and strict environmental legislation, has led to the adoption of measures to boost sustainable development and help to make the transition towards a circular economy. The choice of solvents used for the regeneration of WLO will contribute to both the economic viability and environmental sustainability of the process. Given the need for early consideration of solvent impacts during process design, it is important to develop tools that allow to make informed decisions during solvent selection. There has been several remarkable research in this field that attempt to provide guidance on choosing solvents based on environmental, human health and safety metrics [111–113]. These guides include many conventional solvents and highlight "greener" solvent alternatives.

Table 2.15. Overview of solvent extraction studies for the regeneration of WLO.

Solvents	Operating conditions	Main conclusions	Ref.
Propane	T = 20–140 °C P = 30–60kg/cm^2 t = 0–5 h Propane flowrate = 1, 2, 3 4 L/min Mass of oil = 25, 50, 75, 100 g	The yield is not dependent on the pressure The increase on the temperature increases the removal of oxidation products Optimal conditions are P = 30 kg/cm^2, T = 90 °C and t = 4.5 h	[90]
N-methyl-2-pyrrolidone (NMP) water used as co-solvent	- Water conc. = 0, 1, 3 (%, w/w) - Solvent/oil ratio = 0.5:1 – 1:1 - T = 40 – 90 °C	Moderate extraction temperature, 1% water in NMP and a low solvent/oil ratio (0.5:1) revealed to be the optimum operating conditions	[92]
MEK	- Solvent/oil ratio = 3:1 – 7:1 - Settling time = 24 – 48 h	Best results obtained with a solvent/ oil ratio = 5:1 and 24 h settling time	[94]
n-hexane **1-butanol** **1-hexanol** **carbon tetrachloride** **petroleum ether** **acetone** **KOH as flocculant**	- Solvent/oil ratio = 1:1 – 4:1 - KOH dosage: 1 – 3 g/L	1-butanol achieved the best sludge removal followed by n-hexane, petroleum ether, 1-hexanol, carbon tetrachloride, and acetone	[108]
Mixture of n-hexane/ 2-propanol/ 1-butanol and KOH (used as flocculant)	- Solvent/oil ratio = 2:1 – 8:1 - 2-propanol in the solvent = 60 – 90% - KOH dosage = 3 g/L	Optimal conditions at the composition of 0.25 waste oil, 0.35 n-hexane, and 0.40 polar compound (80% 2-propanol + 20% 1-butanol with 3 g/L KOH).	[109]
2-propanol **1-butanol** **MEK**	- T=20; 28; 50 ºC - Mixing speed = 275 rpm - t = 15 min	MEK has the best performance relatively to oil loss Minimum oil loss achieved at 50 ºC	[110]
1-butanol **Sec-butanol** **1-pentanol** **1-hexanol** **Methyl ethyl ketone (MEK)** **Methyl butyl ketone (MBK)** **Methyl isobutyl ketone (MIBK)**	- T= 20 ºC,35 ºC, 50 ºC - Solvent/oil ratio = 1:1–10:1	The greater the solubility parameter difference between the solvent and the impurities, the greater the PSR 1-butanol and MEK show the greatest PSR Optimum PSR achieved at 20 ºC	[114]
2-propanol **1-butanol** **MEK**	- T=25, 28, 50 ºC - Solvent/oil ratio = 1:1 – 9:1	Alcohols produce the best sludge removal, while ketones achieve minimum oil loss.	[115]
2-propanol **2-butanol** **2-pentanol** **MEK, MBK**	- T= 25 – 60 ºC - Solvent/oil ratio = 1:1 – 15:1 - t =: 5 – 60 min	Yield increases with the increase on molecular weight of the solvent Yield and sludge removal increases with solvent/oil ratio up to a point it stabilizes	[116]

Table 2.15 (cont.). Overview of solvent extraction studies for the regeneration of WLO.

Solvents	Operating conditions	Main conclusions	Ref.
Ethane	- P = 40 – 145 kg/cm^2 - T = 25 – 95 ºC	Yield increases with P but impurities removal decreased Yield independent on T at a given P if ethane is liquid, but decreased with T when ethane is supercritical	[117]
n-heptane,n-hexane **MBK, MIBK** **1-butanol, 2-butanol** **benzene, 1-hexanol**	- Settling time = 0 – 50 h - Solvent/oil ratio = 2:1 – 6:1 - T = 15 – 60 °C	1-butanol and MEK achieve the best performance Recovery of base oil with 94% yield	[118]
mixture of 2-propanol/MEK/1-butanol	- 25% 2-propanol, 25% MEK, 50% 1-butanol - Solvent/oil ratio = 2:1 – 6:1	Solvent/oil ratios higher than 6:1 were considered economically infeasible Optimal solvent/oil ratio = 4:1	[119]
1-butanol **2-propanol** **MEK**	- T = 20, 30 e 50 ºC - Solvent/oil ratio = 1:1 – 7:1	MEK achieved the highest sludge removal and the lowest oil loss Oil loss decreases with temperature	[120]
MEK **1-butanol** **2-propanol** **triclorotrifluoretano (CFC-113)** **triclorofluormetano (R-11)**	- T = 23, 30, 40 e 50 ºC - Solvent/oil ratio = 1:1 – 5:1	Lowest oil loss using R-11 Oil loss decreases with temperature Oil loss decreases with the increase of the solvent/oil ratio	[121]
1-butanol **iso-butanol** **Etanolamine (MEA) as flocculant**	- Solvent/oil ratio = 1:1 – 11:1 - Flocculant dosage = 1 – 3 g/kg - t = 5 – 50 min - T= 10 – 50 ºC	Optimal conditions are t = 20 min, T = 30 °C, MEA dosage = 2g/kg, solvent/oil ratio 5:1 Higher extraction yield obtained using iso-butanol/MEA	[122]
Methanol **1- propanol** **1-butanol, iso-butanol** **acetone** **MEK, hexane**	- Solvent/oil ratio = 4:1 – 9:1 - T = 5, 15, 25 min - Mixing speed = 400, 800, 1200 rpm - T = 25, 40, 60 °C	Highest yield obtained with 1-butanol, followed by 1-propanol, and acetone	[123]
1-butanol **MEK**	- Settling time = 10 – 50 h - T = 10 – 60 °C - Solvent/oil ratio: 2:1 – 6:1	The alcohol is superior over the ketone showing better PAH removal and higher sludge removal	[124]
1-butanol **2-propanol** **mixture of 1-butanol/ethanol**	- Solvent/oil ratio = 1:1 – 6:1 - t = 20, 30 min - T = 35, 45, 50 °C.	Mixing time does not highly affect the PSR, instead solvent-oil ratio does it. Best results achieved with 1-butanol with SOR of 3:1.	[125]
Phenol **Furfural** **NMP**	- Solvent/oil ratio = 1:1 – 4:1 - T=40, 60, 80, 100 ºC	Best yield was obtained using furfural at T = 100 ºC and solvent/oil ratio = 4:1	[126]
1-butanol **MEK** **KOH, NaOH, MEA as flocculant**	- Solvent/oil ratio = 1:1 – 4:1 - T= 20, 40, 60 ºC - Mixing speed = 500 – 19000 rpm - Flocculant dosage = 1 – 4 g/kg	Optimum conditions solvent/oil ratio = 2.4 and 3.12 (%, v/v), T = 54 and 18 °C, and mixing speed =569 and 739 rpm for 1-butanol and MEK, respectively Best flocculation agent was MEA with dosage = 2.5 g/kg	[127]

2.5. REFERENCES

[1] S.Q.A. Rizvi, A Comprehensive Review of Lubricant Chemistry, Technology, Selection, and Design, ASTM International, Baltimore, 2009.

[2] T. Mang, W. Dresel, Lubricants and Lubrication, second ed., Wiley-VCH, Weinheim, Germany, 2007.

[3] T. Mang, K. Bobzin, T. Bartels, Industrial Tribology: Tribosystems, Friction, Wear and Surface Engineering, Lubrication, Wiley-VCH, Weinheim, Germany, 2011.

[4] J. Williams, Engineering Tribology, Cambridge University Press, Cambridge, 2006.

[5] F. Gustavsson, Triboactive Component Coatings. Tribological Testing and Microanalysis of Low-Friction Tribofilms, Ph.D. Thesis, Uppsala University, Sweden, 2013.

[6] J.G. Speight, D.I. Exall, Rerefining of Used Lubricating Oils, CRC Press, Boca Raton, 2014.

[7] R.M. Mortier, M.F. Fox, S.T. Orszulik, Chemistry and Technology of Lubricants, third ed., Springer, New York, 2010.

[8] G. Totten, S. Westbrook, R. Shah, Fuels and Lubricants Handbook: Technology, Properties, Performance, and Testing, West Conshohocken, PA, 2003.

[9] P.R. Robinson, Petroleum processing overview, in: C.S. Hsu, P.R. Robinson (Eds.), Practical Advances in Petroleum Processing. Vol. 1, Springer, New York, 2006, pp. 1–76.

[10] L.R. Rudnick, Synthetics, Mineral Oils, and Bio-Based Lubricants: Chemistry and Technology, CRC Press, Boca Raton, 2013.

[11] T.R. Lynch, Process Chemistry of Lubricant Base Stocks, CRC Press, Boca Raton, 2007.

[12] A. Sequeira, Lubricant Base Oil and Wax Processing, Marcel Dekker, Inc., New York, 1994.

[13] D.M. Pirro, E. Daschner, A.A. Wessol, Lubrication Fundamentals, second ed., CRC Press, New York, 2001.

[14] E. Jantzen, The origins of synthetic lubricants: The work of Hermann Zorn in Germany Part 1 Basic studies of lubricants and the polymerisation of olefins, J. Synth. Lubr. 12 (1996) 283–301.

[15] HIS Markit, Synthetic lubricants - Specialty chemicals update program. https://ihsmarkit.com/products/chemical-synthetic-lubricants-scup.html, 2015 (accessed March 13, 2018).

[16] L. Rudnick, R. Shubkin, Synthetic Lubricants and High-Performance Functional Fluids, second ed., CRC Press, Boca Raton, Florida, 1999.

[17] P.M. Lugt, Grease Lubrication in Rolling Bearings, Wiley, New Delhi, 2013.

[18] R. Benda, J. Bullen, A. Plomer, Synthetics basics: Polyalphaolefins — base fluids for high-performance lubricants, J. Synth. Lubr. 13 (1996) 41–57.

[19] S. Ray, P.V.C. Rao, N. V. Choudary, Poly-α-olefin-based synthetic lubricants: A short review on various synthetic routes, Lubr. Sci. 24 (2012) 23–44.

[20] M. Torbacke, A.K. Rudolphi, E. Kassfeldt, Lubricants. Introduction to Properties and Performance, Wiley, West Sussex, United Kingdom, 2014.

[21] N.P. Cheremisinoff, Industrial Solvents Handbook, Revised and Expanded, Marcel Dekker, Inc., New York, 2003.

[22] A. Harnoy, Bearing Design in Machinery: Engineering Tribology and Lubrication, Marcel Dekker, Inc., New York, 2003.

[23] D. Laing, H. Thomas, Food and Pharma Industry Lubrication, in: T. Mang (Ed.), Encyclopedia of Lubicants and Lubrication, Springer-Verlag, Berlin, 2014, pp. 645–679.

[24] F. Audibert, Waste Engine Oils. Rerefining and Energy Recovery, Elsevier Science & Technology Books, Amsterdam, 2006.

[25] S.P. Srivastava, Developments in Lubricant Technology, Wiley, Hoboken, New Jersey, 2014.

[26] J.G. Gary, G.E. Handwerk, M.J. Kaiser, Petroleum Refining: Technology and Economics, fifth ed., CRC Press, Boca Raton, 2007.

[27] E. Cerić, Crude Oil, Processes and Products, Petrolinvest, Sarajevo, 2012.

[28] L.R. Rudnick, Lubricant Additives: Chemistry and Applications, CRC Press, Boca Raton, 2009.

[29] J. Braun, Additives, in: T. Mang, W. Dresel (Eds.), Lubricants and Lubrication, Wiley-VCH Verlag, Weinheim, 2007, pp. 88–118.

[30] V. Štěpina, V. Veselý, Lubricants and Special Fluids, Elsevier, Amsterdam, 1992.

[31] N.S. Ahmed, A.M. Nassar, Lubricating oil additives, in: C.-H. Kuo (Ed.), Tribology - Lubricants and Lubrication, InTech, Shanghai, 2011, pp 249–268.

[32] H.G. Müller, Mechanism of action of viscosity index improvers, Tribol. Int. 11 (1978) 189–192.

[33] M.J. Covitch, K.J. Trickett, How Polymers behave as viscosity index improvers in lubricating oils, Adv. Chem. Eng. Sci. 5 (2015) 134–151.

[34] Z. Pawlak, Tribochemistry of Lubricating Oils, Amsterdam, The Netherlands, 2003.

[35] K.C. Ludema, Friction, Wear, Lubrication, A Textbook in Tribology, CRC Press, Boca Raton, 1996.

[36] C. Kajdas, E. Wilusz, S. Harvey, Encyclopedia of Tribology. Vol. 15, Elsevier, Amsterdam, 1990.

[37] M. Reik, F. Oberli, Contamination of Lubrication Oils, in: T. Mang (Ed.), Encyclopedia of Lubicants and Lubrication, Springer-Verlag Heidelberg, Berlin, 2014, pp. 292–313.

[38] E.R. Booser, CRC Handbook of Lubrication: Theory and Practice of Tribology, CRC Press, Boca Raton, 1993.

[39] D. Johnson, J. Hils, Phosphate Esters, thiophosphate esters and metal thiophosphates as lubricant additives, Lubricants 1 (2013) 132–148.

[40] L.C. Ancho, Oxidation in lubricant base oils, The Filter. 4 (2006) 6–7.

[41] G. Aguilar, G. Mazzamaro, M. Rasberger, Oxidative Degradation and Stabilisation of Mineral Oil-Based Lubricants, in: R.M. Mortier, M.F. Fox, S.T. Orszulik (Eds.), Chemistry and Technology of Lubricants, Springer, New York, 2010, pp. 107–152.

[42] M. Duncanson, Controlling oil aeration and foam. http://www.machinerylubrication.com/Read/255/oil-foam, 2001(accessed March 14, 2018).

[43] J.D. Burrington, J.K. Pudelski, J.P. Roski, Challenges in detergents and dispersants for engine oils, in: C.S. Hsu, P.R. Robinson (Eds.), Practical Advances in Petroleum Processing, Springer, New York, 2006, pp. 579–595.

[44] I. Minami, Ichiro, Molecular science of lubricant additives, Appl. Sci. 7 (2017) 445.

[45] F. Audibert, Waste Engine Oils: Rerefining and Energy Recovery, Elsevier, Amsterdam, The Netherlands, 2006.

[46] W.A. Gorman, Recovering base oils from lubricants, Pet. Technol. Q. 4 (2005) 85–88.

[47] V. Monier, E. Labouze, Critical review of existing studies and life cycle analysis on the regeneration and incineration of waste oils. http://ec.europa.eu/environment/waste/studies/oil/waste_oil.pdf, 2001 (accessed January 15, 2018).

[48] G.E. Totten, V.J. De Negri, Handbook of Hydraulic Fluid Technology, second ed., CRC Press, New York, 2017.

[49] A. Pires, G. Martinho, Life cycle assessment of a waste lubricant oil management system, Int. J. Life Cycle Assess. 18 (2013) 102–112.

[50] M.F. Fox, Z. Pawlak, D.J. Picken, Acid-base determination of lubricating oils, Tribol. Int. 24 (1991) 335–340.

[51] G. Biresaw, K.L. Mittal, Surfactants in Tribology, Volume 3, CRC Press, Boca Raton, 2008.

[52] J. Fitch, The Surface Tension Test - Is it Worth Resurrecting?, Pract. Oil Anal. Mag. (2002).

[53] Machinery Lubrication, The surface tension test for lubricant analysis. http://www.machinerylubrication.com/Read/376/surface-tension-test, 2002 (accessed May 11, 2018).

[54] M. Kuhn, K. Johnson, Applied Predictive Modeling, Springer, New York, 2013.

[55] D.L. Massart, Handbook of Chemometrics and Qualimetrics. Part A, Elsevier, Amsterdam, 1998.

[56] R. Rendall, A.C. Pereira, M.S. Reis, Advanced predictive methods for wine age prediction: Part I – A comparison study of single-block regression approaches based on variable selection, penalized regression, latent variables and tree-based ensemble methods, Talanta. 171 (2017) 341–350.

[57] C.A. Nunes, Vibrational spectroscopy and chemometrics to assess authenticity, adulteration and intrinsic quality parameters of edible oils and fats, Food Res. Int. 60 (2014) 255–261.

[58] A.R. Caneca, M.F. Pimentel, R.K.H. Galvão, C.E. da Matta, F.R. de Carvalho, I.M. Raimundo, C. Pasquini, J.J.R. Rohwedder, Assessment of infrared spectroscopy and multivariate techniques for monitoring the service condition of diesel-engine lubricating oils, Talanta 70 (2006) 344-352.

[59] J.W.B. Braga, A.A.D.S. Junior, I.S. Martins, Determination of viscosity index in lubricant oils by infrared spectroscopy and PLSR, Fuel 120 (2014) 171–178.

[60] M.A. Al-Ghouti, Y.S. Al-Degs, M. Amer, Application of chemometrics and FTIR for determination of viscosity index and base number of motor oils, Talanta 81 (2010) 1096–1101.

[61] Y. Felkel, N. Dörr, F. Glatz, K. Varmuza, Determination of the total acid number (TAN) of used gas engine oils by IR and chemometrics applying a combined strategy for variable selection, Chemom. Intell. Lab. Syst. 101 (2010) 14–22.

[62] M.I.S. Sastry, A. Chopra, A.S. Sarpal, S.K. Jain, S.P. Srivastava, A.K. Bhatnagar, Determination of physicochemical properties and carbon-type analysis of base oils using mid-IR spectroscopy and partial least-squares regression analysis, Energy Fuels 12 (1998) 304–311.

[63] F.R. Van De Voort, J. Sedman, V. Yaylayan, C. Saint Laurent, C. Mucciardi, Quantitative determination of moisture in lubricants by Fourier transform infrared spectroscopy, Appl. Spectrosc. 58 (2004) 193–198.

[64] M.J. Adams, M.J. Romeo, P. Rawson, FTIR analysis and monitoring of synthetic aviation engine oils, Talanta. 73 (2007) 629–634.

[65] F.S.G. Lima, M. a S. Araújo, L.E.P. Borges, Determination of lubricant base oil properties by

near infrared spectroscopy using different sample and variable selection methods, J. Near Infrared Spectrosc. 12 (2004) 159–166.

[66] K. Hidajat, S.M. Chong, Quality characterisation of crude oils by partial least square calibration of NIR spectral profiles, J. Near Infrared Spectrosc. 8 (2000) 53–59.

[67] M. Blanco, J. Coello, H. Iturriaga, S. Maspoch, R. González, Determination of water in lubricating oils by mid- and near-infrared spectroscopy, Mikrochim. Acta. 128 (1998) 235–239.

[68] A. Rohman, L. Triyasmono, S. Riyanto, L. Andina, Rapid determination of saponification value in red fruit oil by infrared spectroscopy and partial least square calibration, Res. J. Med. Plant. 9 (2015) 442–448.

[69] H. Li, F.R. van de Voort, J. Sedman, A.A. Ismail, Rapid determination of cis and trans content, iodine value, and saponification number of edible oils by fourier transform near-infrared spectroscopy, J. Am. Oil Chem. Soc. 76 (1999) 491–497.

[70] A. Borin, R.J. Poppi, Application of mid infrared spectroscopy and iPLS for the quantification of contaminants in lubricating oil, Vib. Spectrosc. 37 (2005) 27–32.

[71] M.R. Riazi, Characterization and Properties of Petroleum Fractions, ASTM International, West Conshohocken, PA, 2007.

[72] P. Thapliyal, G.D. Thakre, Correlation study of physicochemical, rheological, and tribological parameters of engine oils, Adv. Tribol. 2017 (2017) 1–12.

[73] C.-Y. Liu, J. He, R. Keunings, C. Bailly, New Linearized relation for the universal viscosity−temperature behavior of polymer melts, Macromolecules. 39 (2006) 8867–8869.

[74] P. Sopade, P. Halley, B. Bhandari, B. D'Arcy, C. Doebler, N. Caffin, Application of the Williams–Landel–Ferry model to the viscosity–temperature relationship of Australian honeys, J. Food Eng. 56 (2003) 67–75.

[75] J.C. Mauro, Y. Yue, A.J. Ellison, P.K. Gupta, D.C. Allan, Viscosity of glass-forming liquids, Proc. Natl. Acad. Sci. U. S. A. 106 (2009) 19780–19784.

[76] P. Taborek, R.N. Kleiman, D.J. Bishop, Power-law behavior in the viscosity of supercooled liquids, Phys. Rev. B. 34 (1986) 1835–1840.

[77] M.H. Ghatee, M. Zare, A.R. Zolghadr, F. Moosavi, Temperature dependence of viscosity and relation with the surface tension of ionic liquids, Fluid Phase Equilib. 291 (2010) 188–194.

[78] C.M. Rodenbush, F.H. Hsieh, D.S. Viswanath, Density and viscosity of vegetable oils, J. Am. Oil Chem. Soc. 76 (1999) 1415–1419.

[79] B. Esteban, J.-R. Riba, G. Baquero, A. Rius, R. Puig, Temperature dependence of density and viscosity of vegetable oils, Biomass and Bioenergy. 42 (2012) 164–171.

[80] O. Alomair, M. Jumaa, A. Alkoriem, M. Hamed, Heavy oil viscosity and density prediction at normal and elevated temperatures, J. Pet. Explor. Prod. Technol. 6 (2016) 253–263.

[81] I.C. Sanchez, Liquids: Surface tension, compressibility, and invariants, J. Chem. Phys. 79 (1983) 405–415.

[82] C. Kajdas, Re-refining technologies, in: T. Mang (Ed.), Encyclopedia of Lubicants and Lubrication, Springer-Verlag Heidelberg, Berlin, 2014, pp. 1554–1568.

[83] G.S. Dang, Rerefining of used oils: A review of commercial processes, Tribotest. 3 (1997) 445-457.

[84] F. Awaja, D. Pavel, Design Aspects of Used Lubricating Oil Re-Refining, Elsevier, Amsterdam, 2006.

[85] Y.-L. Hsu, C.-H. Lee, V.B. Kreng, Analysis and comparison of regenerative technologies of waste lubricant, WSEAS Trans. Environ. Dev. 5 (2009) 295–309.

[86] A. Kupareva, P. Mäki-Arvela, D.Y. Murzin, Technology for rerefining used lube oils applied in Europe: A review, J. Chem. Technol. Biotechnol. 88 (2013) 1780–1793.

[87] W.T.-C. Fan, Regeneration of Used Petroleum-Based Lubricants and Biolubricants by a Novel Green and Sustainable Technology, Ph.D. Thesis, University of Southern California, 2010.

[88] M. Kim, J. Hwang, H. Kim, Re-refining of waste lube oils by vacuum distillation with petroleum atmospheric residuum, J. Environ. Sci. Heal. . Part A Environ. Sci. Eng. Toxicol. 32 (1997) 1013–1024.

[89] J. Minana, R. Schieppati, F. Dalla, Process to re-refine used oils, EP Patent 0618959 A1, 1994.

[90] J. Rincón, P. Cañizares, M.T. García, I. Gracia, Regeneration of used lubricant oil by propane extraction, Ind. Eng. Chem. Res. 42 (2003) 4867–4873.

[91] M.A. Reis, Waste Lubricating oil rerefining by extraction–flocculation. 3. A Pilot plant study, Ind. Eng. Chem. Res. 30 (1991) 2449–2456.

[92] J. Lukić, A. Orlović, M. Spiteller, J. Jovanović, D. Skala, Re-refining of waste mineral insulating oil by extraction with N-methyl-2-pyrrolidone, Sep. Purif. Technol. 51 (2006) 150–156.

[93] L. Moura, J. Filho, A. Ramos, Recovery of used lubricant oils through adsorption of residues on solid surfaces, Brazil. J. Pet. Gas. 4 (2010) 91–102.

[94] E.A. Emam, A.M. Shoaib, Re-refining of used lube oil, i-by solvent extraction and vacuum distillation followed by hydrotreating, Pet. Coal. 55 (2013) 179–187.

[95] M.A. Araújo, A.S. Telles, Adsoption of oxidation products from lubricating oils using commercial adsorbents, Brazil. J. Chem. Eng. 12 (1995) 98–105.

[96] S.B. Battalova, A. Likerova, Influence of strength of acid centers of adsorbents on degree of finishing of lubricating oils, Chem. Techno. Fuels Oils. 22 (1968) 191–194.

[97] D.W. Brinkman, J.R. Dickson, D. Wilkinson, Full-scale hydrotreatment of polychlorinated biphenyls in the presence of used lubricating oils, Environ. Sci. Technol. 29 (1995) 87–91.

[98] I. Madanhire, C. Mbohwa, Mitigating Environmental Impact of Petroleum Lubricants, Springer, Johannesburg, South Africa, 2016.

[99] GEIR, Waste Framework Directive revision: European waste oil re-refining industry position, (2016).

[100] J. Pöhler, M. Mödler, D. Bruhnke, H. Hindenberg, Method for reprocessing waste oils, base oils obtained according to said method and use thereof, US Patent 6712954 B1, 2004.

[101] M.R. Williams, J. Krzykawski, Method for obtaining base oil and removing impurities from used oil products, US Patent 6174431 B1, 2001.

[102] K.J. Kentonm, Oil re-refining method and apparatus, US Patent 5814207A, 1998.

[103] L.M. Magnabosco, W.A. Rondeau, Improved process for the production of base stock oils from used oil, EP Patent 0574272 A2, 1993.

[104] L. Mannetje, A. Laghate, Process for re-refining spent lube oils, US Patent 4941967 A, 1990.

[105] M. Borza, S. Leoncini, A. Modenesi, Spent oil recovery process, US Patent 4406778 A, 1983.

[106] C. Cardoso, Regeneração de óleos usados em portugal - Enviroil II. Departamento De Engenharia Química - FCTUC. https://www.uc.pt/fctuc/deq/ciepqpf/research_seminars/

seminars_pdf/regeneracao_oleos_usados_em_Portugal.pdf, 2012 (accessed March 11, 2018).

[107] A.L. Compere, W.L. Griffith, Third party evaluation of petrotex hydrocarbons LLC regen lubricating oil re-refining process. https://www.osti.gov/biblio/950809-third-party-evaluation-petro-tex-hydrocarbons-llc-regen-lubricating-oil-re-refining-process, 2009 (accessed March 1, 2018).

[108] R.R. Mohammed, I.A.R. Ibrahim, A.H. Taha, G. McKay, Waste lubricating oil treatment by extraction and adsorption, Chem. Eng. J. 220 (2013) 343–351.

[109] J.P. Martins, The extraction-flocculation re-refining lubricating oil process using ternary organic solvents, Ind. Eng. Chem. Res. 36 (1997) 3854–3858.

[110] N.O. Elbashir, S.M. Al-zahrani, M.I.A. Mutalib, A.E. Abasaeed, A method of predicting effective solvent extraction parameters for recycling of used lubricating oils, 41 (2002) 765–769.

[111] K. Alfonsi, J. Colberg, P.J. Dunn, T. Fevig, S. Jennings, T.A. Johnson, H.P. Kleine, C. Knight, M.A. Nagy, D.A. Perry, M. Stefaniak, Green chemistry tools to influence a medicinal chemistry and research chemistry based organisation, Green Chem. 10 (2008) 31–36.

[112] C.M. Alder, J.D. Hayler, R.K. Henderson, A.M. Redman, L. Shukla, L.E. Shuster, H.F. Sneddon, Updating and further expanding GSK's solvent sustainability guide, Green Chem. 18 (2016) 3879–3890.

[113] D. Prat, A. Wells, J. Hayler, H. Sneddon, C.R. McElroy, S. Abou-Shehada, P.J. Dunn, CHEM21 selection guide of classical- and less classical-solvents, Green Chem. 18 (2016) 288–296.

[114] M.A. Reis, M.S. Jeronimo, Waste lubricating oil rerefining by extraction-flocculation. 1. A scientific basis to design efficient solvents, Ind. Eng. Chem. Res. 27 (1988) 1222–1228.

[115] O.M. Nimir, M.I.A. Mutalib, R.Adnan, Recycling of used lubrication oil by solvent extraction — a guideline for single solvent design, in: Regional Symposium on Chemical Engineering in conjunction with 13th Symposium of Malaysian Chemical Engineers, October 13-15, Johor, Malaysia, 1997, pp. 420–427.

[116] J. Rincón, P. Cañizares, M.T. García, Regeneration of used lubricant oil by polar solvent extraction, Ind. Eng. Chem. Res. 44 (2005) 4373–4379.

[117] J. Rincón, P. Cañizares, M.T. García, Regeneration of used lubricant oil by ethane extraction, J. Supercrit. Fluids. 39 (2007) 315–322.

[118] A. Kamal, F. Khan, Effect of extraction and adsorption on re-refining of used lubricating oil, Oil Gas Sci. Technol. - Rev. l'IFP. 64 (2009) 191–197.

[119] A.-E. Sterpu, A.I. Dumitru, M.-F. Popa, Regeneration of used engine lubricating oil by solvent extraction, Ovidius Univ. Annals Chem. 23 (2012) 149–154.

[120] H.A.L.I. Durrani, M.I. Panhwar, R.A. Kazi, Determining an efficient solvent extraction parameters for re-refining of waste lubricating oils, Mehran Univ. Res. J. Eng. Technol. 31 (2012) 265–270.

[121] S.M. Al-Zahrani, M.D. Putra, Used lubricating oil regeneration by various solvent extraction techniques, J. Ind. Eng. Chem. 19 (2013) 536–539.

[122] X. Yang, L. Chen, S. Xiang, L. Li, D. Xia, Regeneration of waste lubricant oil by extraction-flocculation composite refining, Ind. Eng. Chem. Res. 52 (2013) 12763–12770.

[123] M. Hussein, A.A. Amer, A.S. Gaberah, Used lubricating oils re-refining by solvent extraction, Am. J. Environ. Eng. Sci. 1 (2014) 44–50.

[124] M.A. Kamal, S.M.D. Naqvi, F. Khan, Optimized liquid-liquid extractive rerefining of spent

lubricants., Sci. World J. 2014 (2014) 1–10.

[125] M. Omolara, D. Olurotimi, O. Olatunji, Regeneration of used lubricating engine oil by solvent extraction process, Eur. Am. Journals. 3 (2015) 1–12.

[126] E. Epelle, Y. Lukman, A.J. Otaru, A comparative study of the solvent powers of phenol , furfural and NMP in improving the viscosity index of spent lubricating oil, Int. Res. J. Eng. 3 (2016) 8-24.

[127] G.R. Daham, A.A. AbdulRazak, A.S. Hamadi, A.A. Mohammed, Re-refining of used lubricant oil by solvent extraction using central composite design method, Korean J. Chem. Eng. 34 (2017) 2435–2444.

PART B – CHARACTERIZATION OF FRESH LUBRICANT OIL

The Parte B of the thesis is composed by Chapter 3, which is devoted to the determination and prediction of the physicochemical properties of fresh lubricant oils. Indeed, monitoring the physicochemical properties is essential to ensure proper quality of lubricant oils. Advanced statistical analysis coupled with infrared spectroscopy will be assessed for the rapid and low cost prediction of properties. In addition, the knowledge of the properties of fresh lubricant oil that are placed on the Portuguese market and which will then give rise to waste is of paramount importance for the correct segregation of WLO and treatment.

3. ASSESSMENT AND PREDICTION OF LUBRICANT OIL PROPERTIES USING INFRARED SPECTROSCOPY AND ADVANCED PREDICTIVE ANALYTICS

The present work focuses on the comparison of the predictive ability of four classes of analytical methods: regression with variable selection, penalized regression, latent variable regression and tree-based ensemble methods. A dataset of 62 lubricant samples for different applications was collected in Portugal. Assessed lubricant properties included kinematic viscosity (at 40 and 100 ºC), viscosity index, density, total acid number (TAN), saponification number and percentage of aromatics, naphthenics and paraffinics. This work showed that there is no overall superior regression method and the choice is dependent on the predicted property. Density, percentage of aromatics, naphthenics and paraffinics were well predicted (correlation between predicted and observed of 0.97-0.98). Finally, it can be concluded that the adopted methodology is highly relevant in the field of prediction of lubricant oil properties.

KEYWORDS

Lubricant oil properties; FTIR; variable selection; latent variable; penalized regression; tree based ensemble methods.

This chapter is based upon the publication:

C.T. Pinheiro, R. Rendall, M.J. Quina, M.S. Reis, L.M. Gando-Ferreira. Assessment and prediction of lubricant oil properties using infrared spectroscopy and advanced predictive analytics, Energy Fuels 31 (2017), 179–187. doi: 10.1021/acs.energyfuels.6b01958

3.1. INTRODUCTION

Lubricants are products applied on mechanical moving parts, forming a protective film that reduce friction and wear of machinery, protect against corrosion and reduce energy consumption. Their function may also include the removal of debris and cooling of surfaces [1]. A diverse variety of lubricants are designed and manufactured to operate over a wide range of temperatures, loads, sliding speeds and operating environments, leading to different physicochemical properties that must be properly monitored and controlled.

Monitoring physicochemical properties (density, viscosity, total acid number, etc.) is essential to ensure proper quality of the lubricant oils placed on the market. Traditionally, routine measurements of petroleum products properties are based on the American Standards for Testing and Material (ASTM) procedures. However, such methods can be quite complex to perform, time and reagent consuming and require large sample sizes and specific equipment. Infrared spectroscopy (IR) combined with advanced multivariate analysis has been proposed as a powerful alternative to the classic ASTM methods, given the fast implementation and low associated unit cost, requiring only one sample drop and avoiding the use of toxic reagents as well as the generation of undesirable wastes [2].

Several studies have been conducted on the prediction of gasoline, diesel and biodiesel properties based on IR spectroscopy [3–8]. Regarding lubricating oils, Sastry et al. determined physicochemical properties (viscosity index and pour point) and performed carbon type analysis (paraffins, isoparaffins, naphthenes, aromatics and heteroaromatics) of base oils using IR spectral features and Partial Least Squares (PLS) [9]. Braga et al. developed a method for determining the viscosity index of lubricant oils based on vibrational spectroscopy and PLS. This method was applied to 81 different producers/brands, from different kinds of lubricating oils and origin of the base oils (mineral or synthetic), as well as covering different API and SAE classifications10. IR spectroscopy has also been used for the prediction of contaminants, oxidation products and additives, typically employing Principal Component Regression (PCR), PLS and interval-PLS (iPLS) [9–12]. The determination of total acid and base number to evaluate the lubricant condition in service has been also reported in the literature [11–13]. The determination of moisture content by infrared spectroscopy in lubricants was described by Voort et al. [14]. Borin et al., investigated the feasibility of using a narrow spectral range in the MIR region for the determination of contaminants (gasoline, ethylene glycol and water) in lubricating oils using iPLS [15].

Analyzing vibrational spectroscopy works available in the literature, one can verify the existence of a strong preference towards employing standard multivariate methods based on latent variables such as PLS, iPLS and some variants. This is usually a suitable solution, since spectroscopy data is highly collinear, a feature that can be handled by this class of approaches. However, in practical scenarios of quality control and monitoring, one is often interested in obtaining optimal predictive performance and therefore the search space of suitable predictive approaches must be enlarged and enriched with different modeling approaches. The selection of the proper predictive methodology may sometimes be conducted based on prior knowledge regarding the problem under analysis. However, the theoretical information for supporting this decision is often very scarce and the whole procedure is highly prone to bias towards the preferred methods of the researcher. This selection approach is therefore not recommended in general, unless there are sound and well-established reasons to implement it. Instead, the present work recommends the implementation of a robust and rigorous data-driven comparison framework that has the capability to estimate the methods performance as well as the statistical significance of their differences, thus assessing their relative merits in an unbiased and consistent way. This approach was followed in this study, where a rich variety of predictive analytical methods was considered for the prediction of nine lubricant oil properties of paramount importance for characterizing their quality.

In this context, this work is focused on the evaluation of the ability of different predictive analytical methods and on the identification of those with high potential to predict the desired oil properties. Methods were selected from four distinct classes of modeling approaches: regression with variable selection, penalized regression, latent variables regression and tree-based ensembles. These methods were included in the comparison study since they cover different prior assumptions regarding the underlying data structures and allow for the analysis of the suitability of different modelling formalisms in characterizing the relationship between predictors and response variables. The typical procedure for model validation consists in a single split between training and test sets. The former is used to build models while the latter allows the assessment of the methods' prediction ability and check for overfitting. This procedure is robust but the effect of different data splits is not properly taken into account. To overcome this drawback, a double cross-validation procedure was adopted in this work, allowing for a better and more conservative estimate of the methods' true prediction ability. This feature is highly recommended but not often (even rarely) employed in comparison studies. The number of predicted oil properties and prediction methods considered, and also the double-cross validation procedure employed, makes this work, to the best of our present knowledge, one of the most extensive and thorough analysis in the prediction of oil properties.

3.2. MATERIALS AND METHODS

3.2.1. SAMPLES DESCRIPTION

Lubricant samples were selected based on the most representative lubricants currently available in the Portuguese market. In this work, we studied oils from a variety of applications (including brake fluids), chemical compositions and oil brands. The entire dataset is composed by 62 samples collected in 2015, from 13 different producers, classified according to the categories indicated in Table 3.1. The highest number of analyzed samples were from engine category (31), in which 44% were synthetic base oil type, 30% semi-synthetic and 36% mineral.

Table 3.1. Classification categories of lubricant oil samples

Classification Categories	Number of Samples	Sample Reference
Cutting fluid	2	1-2
Gear	11	3-13
Brake fluid	6	14-19
Hydraulic	4	20-23
Engine	31	24-54
Marine	2	55-56
Others	6	57-62

3.2.2. PHYSICOCHEMICAL CHARACTERIZATION

Lubricating oil properties were determined using reference ASTM methods. Kinematic viscosity was obtained at 40 and 100°C according to ASTM D7042, using an Anton Parr-SVM 3000 Stabinger Viscosimeter. Viscosity Index was calculated following ASTM D2270. The density was determined according to ASTM D4052, using a digital densimeter, Mettler Toledo DM40. Total acid number (TAN) was determined by potentiometric titration according to ASTM D664. Titrations were carried out using a solution of alcoholic potassium hydroxide (0.1 M) to neutralize the lubricant acidic components. A mixture of toluene, isopropanol and water (50, 49.5 and 0.5% v/v, respectively) was used as titration solvent. TAN was expressed in milligrams of KOH required to neutralize the acidic constituents per gram of oil. Saponification number (SN) was determined by potentiometric titration following ASTM D94. Oil samples are dissolved in a mixture of a KOH alcoholic solution (0.5M) and butanone (50 mL each). Taking into account the difficulty to dissolve organic samples such as lube oil and some additives in these solvents, it was necessary to add 25 ml of White Spirit solution. The mixture is heated in total reflux for 30 min, and the condenser washed with 50 mL of naphtha to remove any remaining sample. Finally, the titration was performed with HCl (0.5M). The Saponification number corresponds to the milligrams of KOH required to saponify fatty material present in one gram of oil.

FTIR spectra were recorded in transmittance mode using potassium bromide (KBr) pellets, prepared using a pneumatic press. One drop of lubricant was placed on the top of one pellet, creating a thin film, which was placed into an appropriate sample holder and immediately analyzed in a Jasco FT/IR – 4200. 64 scans/sample with a resolution of 4 cm^{-1} were carried out in the 4000-500 cm^{-1} range. Every analysis was performed using a different pellet and before each measurement a background spectrum was obtained using one clean pellet without lubricant. The determination of aromatic (arom.), paraffinic (paraff.), and naphthenic (napht.) carbon was based on the Indian Standard Method 13155.

3.2.3. PREDICTIVE ANALYTICAL METHODS AND COMPARISON FRAMEWORK

In order to explore the potential of different modeling approaches for predicting lubricant oil properties based on FTIR, the available methods were first grouped in four classes: variable selection, penalized regression, latent variables and tree-based ensembles. Then, from each class, representatives with high potential interest were selected and used in this study. Each class will be briefly described next, followed by the comparison framework used to assess the performance of the selected methods.

VARIABLE SELECTION METHODS

The main assumption of this class of methods is that only some predictor variables carry relevant information regarding the response (the sparsity assumption). Thus, in order to reduce model complexity and avoid overfitting, there is a first stage of screening where potentially important variables are selected, discarding others which do not contribute to predict the response or do not bring an additional significant advantage in this regard. In this class of methods, Forward Stepwise Regression (FSR) was the regression method included in the comparison study [16]. Briefly, FSR starts with a model that has no predictors and gradually includes those that are deemed significant to predict the response. Variables already included in the model may be removed in a later stage, if they are found to be redundant after the inclusion of others. The p-value of the partial F statistical test is used to assess the predictors' significance and a Multiple Linear Regression (MLR) model structure is adopted to relate the selected predictors with the response variables.

PENALIZED REGRESSION METHODS

The class of penalized regression methods is characterized by imposing a certain penalty to the values of the regression coefficients in a least squares formulation, resulting in biased versions of the MLR method, but presenting smaller variances and therefore lower expected errors. The decrease in variance usually overcomes the increased bias, improving the prediction results. In this class, four methods were included in the study: Ridge Regression (RR), Least Absolute Shrinkage and Selection Operator (LASSO), Elastic Nets (EN) [17, 18] and Support Vector Regression (SVR) [19, 20]. EN is a general approach that contains both RR and LASSO as particular cases. The regression coefficients for an EN model $\hat{\mathbf{b}}_{\mathbf{EN}}$, are obtained by solving Eq. (3.1):

$$\hat{\mathbf{b}}_{\mathbf{EN}} = \underset{b=[b_0 \dots b_p]^{\mathrm{T}}}{\arg\min} \left\{ \sum_{i=1}^{n} \left(y(i) - \hat{y}(i) \right)^2 + \gamma \left(\alpha \sum_{j=1}^{p} \left| b_j \right| + \frac{1-\alpha}{2} \sum_{j=1}^{p} b_j^2 \right) \right\} \tag{3.1}$$

where, α ($\alpha \in [0,1]$) is an hyper-parameter that weights the squared penalty and the norm penalty and γ controls the bias-variance tradeoff. Both hyper-parameters are selected by cross-validation. The RR solution is obtained for $\alpha = 0$ and LASSO for $\alpha = 1$.

LATENT VARIABLE METHODS

The third class of regression methods takes advantage of the correlation structure in both predictors and response variables. In particular, it assumes that the observed variability is governed by a few underlying variables (also known as latent variables), which are not directly measured or observed, but may be estimated using linear combinations of the original measurements. The general model for the latent variable methods [21] is presented in Eqs. (3.2) and (3.3):

$$\mathrm{X} = \mathrm{TP}^{\mathrm{T}} + \mathrm{E} \tag{3.2}$$

$$\mathrm{y} = \mathrm{Tc}^{\mathrm{T}} + \mathrm{f} \tag{3.3}$$

where P is a $p \times a$ matrix of loadings, T is a $n \times a$ score matrix, c is a $1 \times a$ vector that relates the latent variables scores and the response and E and f are assumed to be random errors with dimensions $n \times p$ and $n \times 1$, respectively. In this class of methods, four approaches were considered: Principal Component Regression (PCR) [22], Principal Component Regression with a Forward Stepwise procedure (PCR_FS) [23], Partial Least Squares (PLS) [24,25] and interval PLS (iPLS) [26].

TREE-BASED ENSEMBLES

The last class of methods is based on ensembles of regression trees [18, 27-29], from which three approaches were selected: Bagging of Regression Trees (BRT), Random Forests (RF) and Boosted Trees (BT). BRT uses bootstrapping to generate training datasets, which are used to build many regression trees and the predicted response is the average prediction from all trees in the ensemble. RF is similar to BRT but each tree only considers a randomly selected subset of the predictor variables so that the predictions of the trees in the ensemble are more uncorrelated. Both BRT and RF often use a high number of trees to stabilize the variance of predictions and this number may be selected by cross-validation. Lastly, BT [30-32] uses weak learners in order to iteratively approximate the relationship between predictors and response.

COMPARISON FRAMEWORK

The comparison framework used is based on a double cross-validation procedure with an inner and outer validation loop, providing a more conservative approach than traditional cross-validation followed by model validation in a test set. The procedure starts by randomly splitting the complete dataset in a training set, containing 80% of the samples and a left-out set containing the remaining 20%. The training set is used for model building and usual cross-validation can be employed to select an appropriate hyper-parameter (this cross-validation constitutes the inner loop of the comparison framework). After model building, the models are used to predict the left-out set and the quantification of the prediction errors characterize the performance of the regression methods. The outer loop of the double cross-validation procedure consists in generating new random splits of the complete dataset, providing a different training and left-out sets which are again used for model building and assessment, respectively. In this work, 40 iterations of double cross-validation were applied and the median value of the correlation between the predictions and measured values in the left out set quantifies the performance of the regression methods while its inter-quartile range (difference between the third and first percentiles) characterizes the variability across different data splits.

3.3. RESULTS AND DISCUSSION

3.3.1. PREDICTION OF PHYSICOCHEMICAL PROPERTIES

In this section, the framework described in Section 3.2.3 will be applied to predict nine physiochemical properties of lubricant oils. Since the number of properties is rather large, the overall results are presented first and the most promising regression methods are identified. Then, a more detailed analysis is conducted on the properties that were successfully predicted.

In a first stage of exploratory data analysis, PCA was applied to the fresh oil properties in order to observe the samples' distribution and assess the degree of collinearity between the different oil properties. The results are presented in Figure 3.1 where the scores of the 1st and 2nd principal components (Figure 3.1(a)) and their respective loadings (Figure3.1(b)) are shown. The presence of clusters is quite clear in Figure 3.1 (a) and can be related to the different oil types (Table 3.1). In particular, one can observe a cluster formed by the brake fluid type (samples 14 to 19) that are significantly distant from the remaining samples and in the case of gear category there is a rather extreme result (sample 7). In terms of oil properties, Figure 3.1(b) shows that the first principal component (1st PC) mainly describes density, TAN, saponification number and the percentage of naphthenics and paraffinics while the second component (2nd PC) describes the different viscosity measures, which are, as expected, correlated to each other and therefore are close to in the loadings plot. Nevertheless, the properties do not present a high collinear structure because the PCA results showed that in order to describe 90% of the dataset, 4 principal components are needed. Compared with the total number of properties (9), this is a rather low compression ratio and suggests that each property should be better predicted individually.

In a first preliminary study, although some samples could be considered outliers, none was removed from the dataset and the comparison framework was applied to assess the performance of the regression methods. However, the results obtained showed that some samples (with reference 7, 57 and 59) presented systematically higher prediction residuals for all properties and had a high influence on the model (these results are presented in the Annex A1). This observation can be explained by the chemical composition of these samples which is very different from the commonly used mineral or synthetic oils. Sample 7 is a polyalkylene glycol synthetic oil, applied in gears working under severe conditions. Samples 57 and 59 are used for compressors lubrication and cooling, containing diester and alkyl-benzene synthetic oils, respectively.

The results from the regression trees-based ensemble methods (BRT, RF and BT) showed systematically poorer prediction performances in this case, so they were suppressed from further comparisons in order to simplify the analysis of results. This fact can be partially justified by the presence of clusters in the measured responses and also by the underlying relationship between FTIR and oil properties, which from a theoretical standpoint is presumably described better by a continuous linear function rather than a step-wise relation. Sample clusters in the predicted properties negatively affect regression trees since their predictions are bounded to be within the response values observed in the training set. If during the random split, no samples from a given cluster are included in the training data, the ensemble will fail to extrapolate to the new regions.

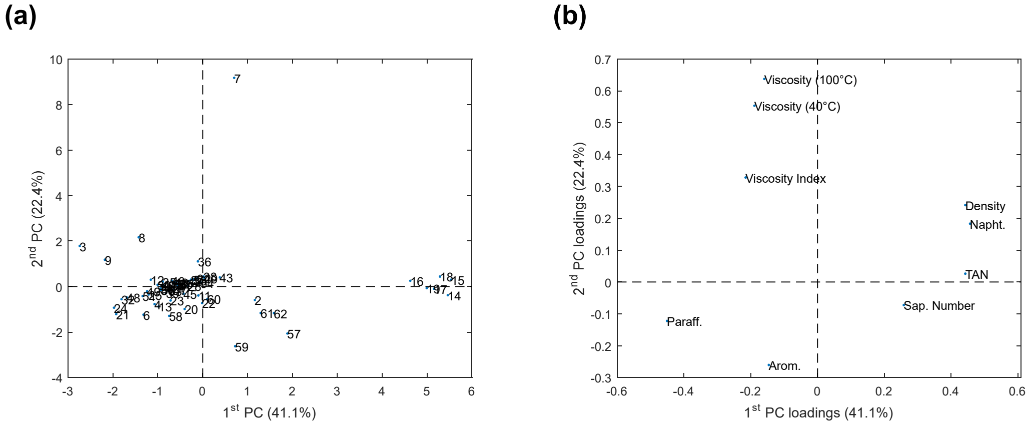


Figure 3.1. PCA results obtained to the nine oil properties: (a) the scores of the 1st and 2nd principal components and (b) their respective loadings.

Following these considerations, a second stage of the comparison was performed, where extreme samples and methods with smaller predictive ability were removed. The overall results are presented in Table 3.2, where the $\tilde{R}^2_{DCV}$ and its interquartile range are reported for each regression method.

The results in Table 3.2 show that not all physicochemical properties are well predicted and the variation in $\tilde{R}^2_{DCV}$ ranges from 0.98, for density or the percentage of paraffinics, to values below 0 (only possible because the R^2 is evaluated by cross-validation). Nevertheless, many properties have high $\tilde{R}^2_{DCV}$ values, suggesting that they can be predicted using a suitable predictive model. In these situations, FTIR measurements could be considered a reliable route instead of the more common chemical/physical quantification. The confidence in the results is assured by the double cross-validation procedure used in the comparison framework which produces a more conservative estimation of the performance of the predictive models under testing scenarios.

Table 3.2. Prediction results for oil properties. *

Oil properties	**Predictive analytical methods**								
	FSR	**RR**	**LASSO**	**EN**	**SVR**	**PCR**	**PCR_FS**	**PLS**	**iPLS**
Density at 15°C (Kg/m$^{3)}$	0.95 (0.04)	0.95 (0.05)	**0.97 (0.03)**	**0.98 (0.03)**	0.91 (0.07)	0.95 (0.07)	0.84 (0.25)	**0.97 (0.04)**	0.92 (0.11)
Viscosity at 40°C (cSt)	<0 (>1)	**0.08 (>1)**	<0 (1)	**0.09 (1)**	<0 (>1)	<0 (0.74)	**0.11 (0.28)**	0 0.84	<0 (>1)
Viscosity at 100°C (cSt)	0.03 (>1)	0.05 (0.91)	**0.45 (0.6)**	**0.45 (0.6)**	<0 (>1)	**0.34 (0.64)**	0.32 (0.47)	0.09 (0.75)	<0 (0.75)
Viscosity Index	0.17 (0.82)	**0.26 (0.7)**	0.14 (0.82)	0.19 (0.98)	<0 (>1)	**0.24 (0.48)**	0.1 (0.02)	**0.27 (0.49)**	0.02 (>1)
TAN (mg KOH/g)	0.85 (0.52)	**0.91 (0.53)**	0.88 (0.46)	0.86 (0.39)	**0.91 (0.5)**	0.88 (0.43)	0.74 (>1)	**0.9 (0.33)**	0.65 (>1)
Sap. Number (mg KOH/g)	<0 (>1)	0.24 (0.99)	**0.36 (>1)**	0.24 (>1)	<0 (>1)	**0.56 (>1)**	0.1 (>1)	**0.4 (>1)**	0.32 (0.82)
Arom. (%)	**0.9 (0.1)**	0.79 (0.29)	**0.83 (0.16)**	0.82 (0.16)	0.79 (0.23)	0.53 (0.51)	0.29 (0.33)	0.82 (0.25)	**0.94 (0.1)**
Napht. (%)	**0.96 (0.03)**	0.94 (0.04)	**0.97 (0.03)**	**0.97 (0.03)**	0.93 (0.04)	0.95 (0.04)	0.71 (0.32)	**0.96 (0.03)**	**0.96 (0.04)**
Paraff. (%)	0.93 (0.06)	0.93 (0.04)	**0.97 (0.04)**	**0.97 (0.04)**	0.91 (0.06)	0.96 (0.04)	0.72 (0.26)	0.95 (0.05)	**0.98 (0.03)**

FSR – Forward Stepwise Regression; RR – Ridge Regression; LASSO – Least Absolute Shrinkage and Selection Operator; EN – Elastic Nets; SVR – Support Vector Regression; PCR – Principal Component Regression; PCR_FS – PCR with Forward Stepwise; PLS – Partial Least Squares; iPLS – interval PLS.

*The value at the top of each cell represents the $\tilde{R}^2_{DCV}$ and the value inside parenthesis is the respective interquartile range. The best 3 regression methods for each property are identified in boldface.

Density and the percentage of aromatics, naphthenics and paraffinics are all well predicted and the best methods obtain $\tilde{R}^2_{DCV}$ above 0.94. TAN is reasonably well predicted and although the $\tilde{R}^2_{DCV}$ is high, the interquartile range is also significant. Lastly, saponification number and properties related to viscosity are poorly predicted and their top $\tilde{R}^2_{DCV}$ is around 0.56. These results provide a first estimate of the suitability of different regression methods and should be viewed in the context of a given practical application, characterized by a desired accuracy. If the prediction errors are below the desired accuracy, a model can be built and used with a high degree of confidence, whereas a wide gap between the methods' performance and the desired accuracy indicates that the regression methods are not capable of modelling the relationships between FTIR and the desired oil property. If the gap is small enough, variants of the methods included in the comparison study (e.g. SVR with non-linear transformations) might improve results.

Another fact worth noting in Table 3.2 is that there is no overall best regression method and the most suitable ones are dependent on the particular physicochemical property under analysis. This was foreseen since the underlying relation between predictors and response variables is not expected to be optimally represented by the same modelling formalism but instead the information content in the predictors combined differently in order to obtain good estimates of the response. As a consequence, the comparison framework adopted in this work is of critical importance in order to find out, in a rigorous and unbiased way, which methods are better and when. Nevertheless, it is interesting to note that LASSO provides consistent predictions and is often one of the top methods for this dataset.

In the next subsections, each successfully predicted physicochemical property is analyzed in detail in order to identify important predictor variables. The results related to density, TAN and the percentage of aromatics, naphthenics and paraffinics are further explored whereas the saponification number and properties related to viscosity will not be discussed. The failure to predict these last properties may arise from different reasons, one of them could be the number of samples collected when one takes into account the different oil types analyzed. As an example, Braga et. al.10 successfully predicted the viscosity index based on 1085 representative samples from the Brazilian market. However, obtaining such a high number of samples is not always possible in practice and no method is able to predict, a priori, the minimum sufficient number of samples. Thus, the number of samples may also be a limiting factor in the development of good prediction models for the aforementioned properties. Another possible reason can be related to the fact that lubricant oils are subject to restrict quality control procedures and should conform to tight specifications. One may therefore argue that the observed variability for these properties is not enough to develop a good predictive model, as it would be if the range of variation of their values was higher.

3.3.1.1. DENSITY

The density of the samples is well predicted and it is desirable to validate the model by analyzing the prediction results and also to identify regions of the spectrum that are more relevant. Since EN was the best predictive method for this property, Figure 3.2 (a-c) presents the observed density values and those predicted by the EN models in the outer loop of the double cross-validation procedure, some typical spectrum from different lubricating oil types and the regression coefficients obtained. In terms of predicted and observed density values (Figure 3.2 (a)), two clusters seem to exist: one centered at approximately 875 kg/m^3 and another at 1075 kg/m^3. The second cluster is composed only of brake fluid samples. The existence of clusters is known to increase the value of the R^2, even when the model fails to predict well within each cluster. Computing the R^2 for the predicted and measured density within each cluster results in a value of 0.72 for the first cluster and 0.14 for the second one. These lower values are different from those obtained in Table 3.2, suggesting that the models are able to discriminate between samples with low or high densities but are less reliable in making inferences within each cluster. In fact, the root mean squared error of double cross-validation ($RMSE_{DCV}$) has a mean value of 10.1 kg/m^3 and a standard deviation of 2.6 kg/m^3, a rather large value when one considers the small ranges spanned by both clusters. Nevertheless, densities in the range from 800-900 kg/m^3 fall close to the 1:1 line and the predictions are generally acceptable. As a general conclusion, the results suggest that the regression models developed to predict the samples' density should be limited to scenarios where only approximate estimates are needed.

The distribution of regression coefficients (Figure 3.2 (c)) is also worth analyzing since spectral regions can be identified that are not being used to predict the response and that can be suppressed to obtain a more parsimonious model. In particular, the region between wavenumbers 1900 cm^{-1} and 2700 cm^{-1} are largely ignored, being almost 0 in most iterations of double cross-validation. Furthermore, the region between 3100 cm^{-1} and 3400 cm^{-1} and also wavenumbers higher than 3700 cm^{-1} are seldom used for model building, which suggests a sparse structure, where penalized regression methods that tacitly implement variable selection may have an advantage. This can be verified by the good performances obtained with LASSO and EN. On the other hand, one can also remove the irrelevant spectral regions and reapply some of the regression methods that do not implement variable selection in order to improve the prediction results. For instance, it is seen that PLS makes very good predictions without explicitly removing the uninformative regions. Thus, one may test if their removal could lead to even better predictions, a scenario often observed in practice.

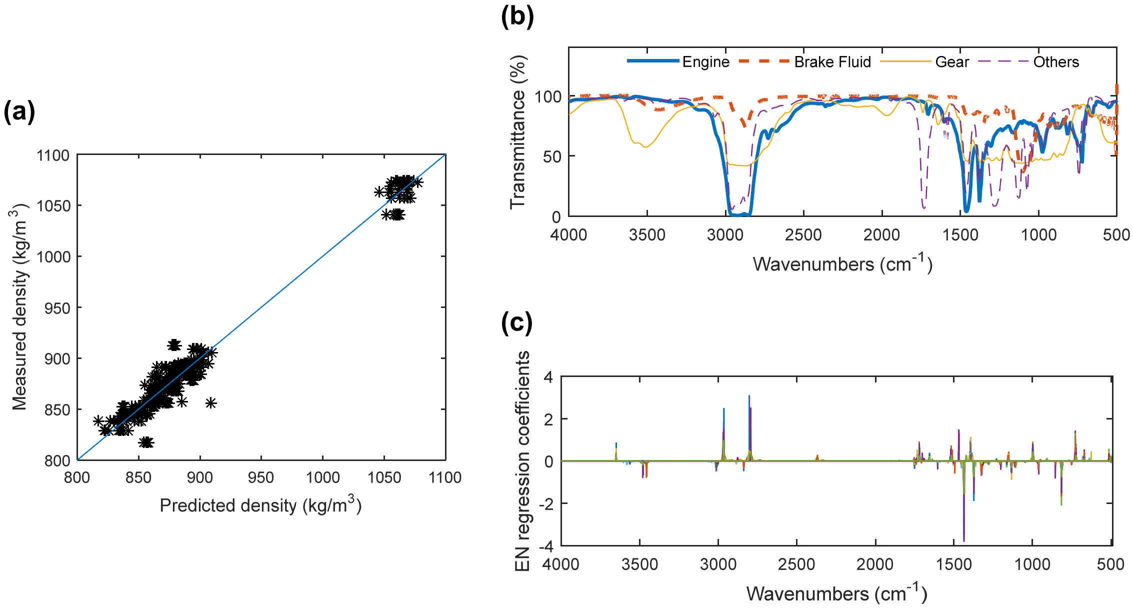


Figure 3.2. Results obtained with EN method to predict density: (a) predicted and measured density values, (b) representative spectrum of different sample classes and (c) EN regression coefficients in the comparison study.

3.3.1.2. TOTAL ACID NUMBER (TAN)

In general, TAN has high $\tilde{R}^2_{DCV}$ but the deviations from the median value are quite substantial. This fact suggests that the performance is highly dependent on the split between training data and the left out fold obtained during the double cross-validation procedure. Figure 3.3(a)-(c) presents the predicted and measured TAN values, the typical spectra and the regression coefficients for the different PLS models obtained during double cross-validation. In Figure 3.3(a) one can see two clusters similar to those found when predicting density. Indeed, the second cluster is formed again by brake fluid samples. One can further compute the R^2 between predicted and measured TAN values for both regions, obtaining a value of 0.94 for the region below 10 mg KOH/g and a value below 0 for the region near 22 mg KOH/g. Furthermore, the $RMSE_{DCV}$ has a mean of 1.5 mg KOH/g and a standard deviation of 0.96 mg KOH/g. This is a clear indication that the developed models are unable to predict TAN reliably and can only provide reasonable estimates. In terms of regression coefficients (Figure 3.3 (c)), one can see a sparse structure where only a few wavenumbers contribute to the final model. The region between 500 and 1800 cm^{-1} and also the region around 3000 cm^{-1} seem to be the more active and the value of the regression coefficients tend to be higher.

In order to improve the prediction results and assess the influence of the brake fluid samples, PLS regression was applied to the dataset with and without the brake fluid samples. The first PLS model, which included the brake fluids, had a minimum $RMSE_{CV}$ of 1.5 mg KOH/g, which is similar to the value obtained with the double cross-validation procedure. However, after discarding the brake fluid samples, the $RMSE_{CV}$ decreased to 0.6 mg KOH/g, which is a significant reduction. This indicates that the brake fluids oil type is not consistent with the remaining oils and can be discarded if they are not expected to be found in a given practical application.

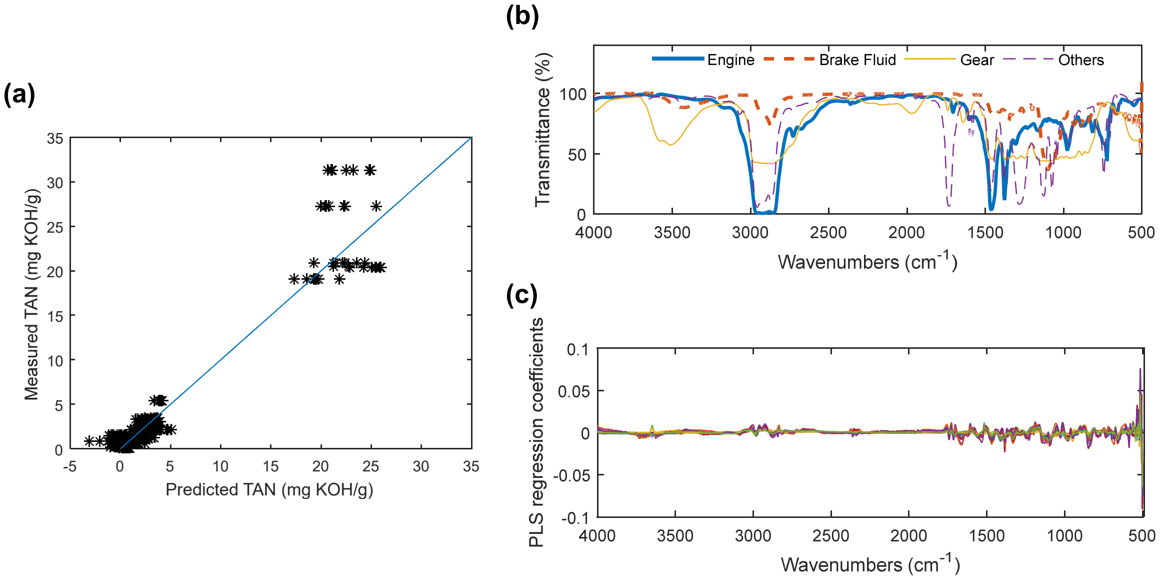


Figure 3.3. Results obtained with PLS to predict TAN: (a) predicted and measured TAN values, (b) representative spectrum of different sample classes and (c) PLS regression coefficients in the comparison study.

3.3.1.3. AROMATICS

The percentage of aromatics can be predicted quite well but a significant gap is observed between the best and worse methods. Figure 3.4 (a-c) presents the predicted and measured percentage of aromatics, some representative spectra from different lubricating oil classes and the number of times each bin was included in the iPLS model (each bin contains 12 wavenumbers). In terms of predicted and measured values (Figure 3.4 (a)), it can be observed that the predictions are close to the straight line, thus the majority of samples seem to be well predicted and the mean $RMSE_{DCV}$ is 0.5% and the standard deviation is 0.24%. Regarding important spectral regions, the bin containing the region 1592-1614 cm^{-1} stands out as it is selected in all 40 iterations of double cross-validation. Furthermore, bins adjacent to this region are selected far more often than the remaining spectrum, which allows to conclude that, overall, the region 1500-1637 cm^{-1} contains relevant predictive information of the percentage of aromatics.

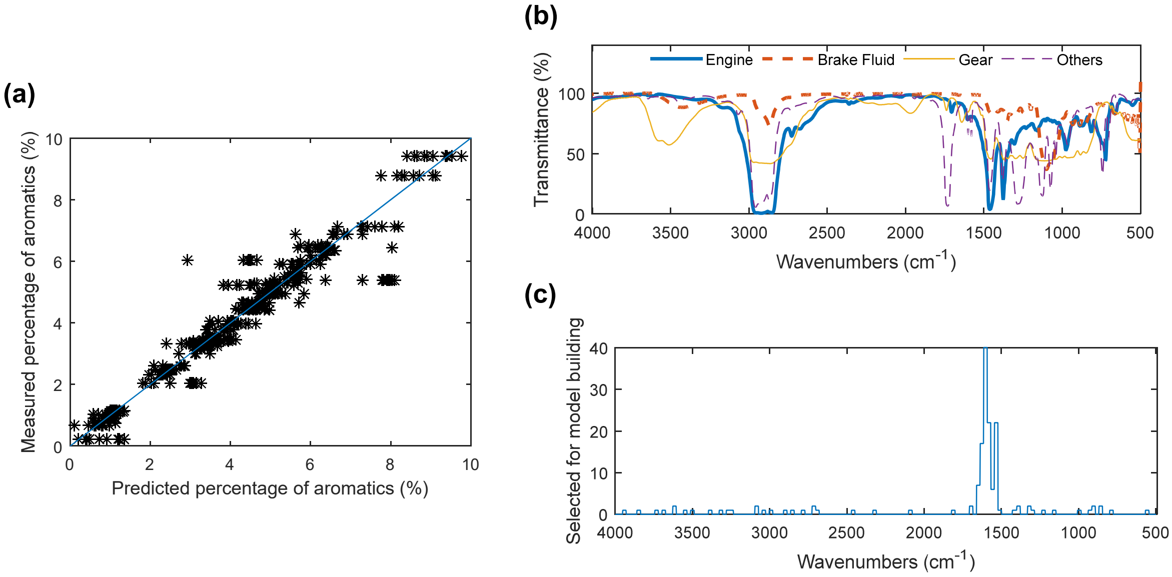


Figure 3.4. Results obtained with iPLS to predict the percentage of aromatics: (a) predicted and measured percentages of aromatics, (b) representative spectra from different sample classes and (c) number of times each bin was included in the regression model.

3.3.1.4. NAPHTHENICS

The $\tilde{R}^2_{DCV}$ for the percentage of naphthenics is high and the variation around the median value is quite small. For this property, LASSO and EN had similarly good performances. Since the solution provided by LASSO is often more sparse, Figure 3.5 (a-c) presents the measured and predicted percentages of naphthenics in the different splits of double cross-validation, some typical spectra and the regression coefficients. The analysis of Figure 3.5 (a) shows that the model is indeed able to predict the response and no clusters are observed. The majority of predictions fall reasonably close to the straight line and the mean $RMSE_{DCV}$ is 2.2 %. In terms of relevant regions, those near 3500 cm^{-1} and between 500 cm^{-1} and 1700 cm^{-1} seem to be important since they had significant regression coefficients.

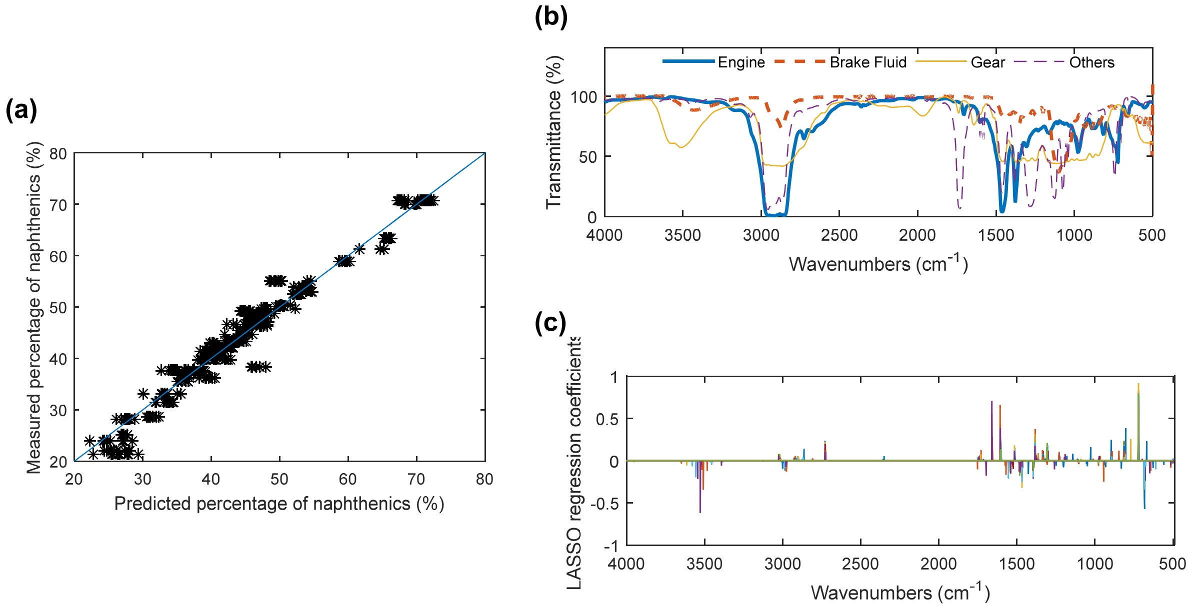


Figure 3.5. Results obtained with LASSO to predict the percentage of naphthenics: (a) predicted and measured percentage of naphthenics, (b) representative spectra for different sample classes and (c) regression coefficients.

3.3.1.5. PARAFFINICS

The last successful predicted property was the percentage of paraffinics. For this property, iPLS, LASSO and EN were the best regression methods. The LASSO regression coefficients or the selected bins in iPLS can be easily analyzed but due to the simpler interpretation of the selected bins in iPLS, its results are presented here (similar conclusions are found when considering the other top methods). Figure 3.6(a) presents the predicted and measured percentage of paraffinics and one can observe that the iPLS models are indeed working as expected. Although there are some large prediction errors when predicting the sample with the lowest percentage of paraffinincs. For higher percentages, the models seem much more reliable. Figure 3.6(b) presents representative spectra from the different lubricant classes while in regards to important spectral bands, Figure 6.c presents the number of times each bin was selected to be included in an iPLS model and one can observe that the bin containing wavenumbers 707 to 728 cm^{-1} is clearly the most important. Out of 40 iterations of double cross-validation, it was selected 36 times to be included in the final model whereas the others were selected at most 5 times. Further investigation showed that the correlation between the transmittance in this bin and the percentage of paraffinics has values as high as 0.98. This is in accordance with previous knowledge regarding the measurement system, which uses a specific wavelength to quantify the percentage of paraffinics. If the estimates provided by the spectrometer are reliable enough, then the developed models will also provide a good indication and can be used in scenarios where the measurement system find limitations.

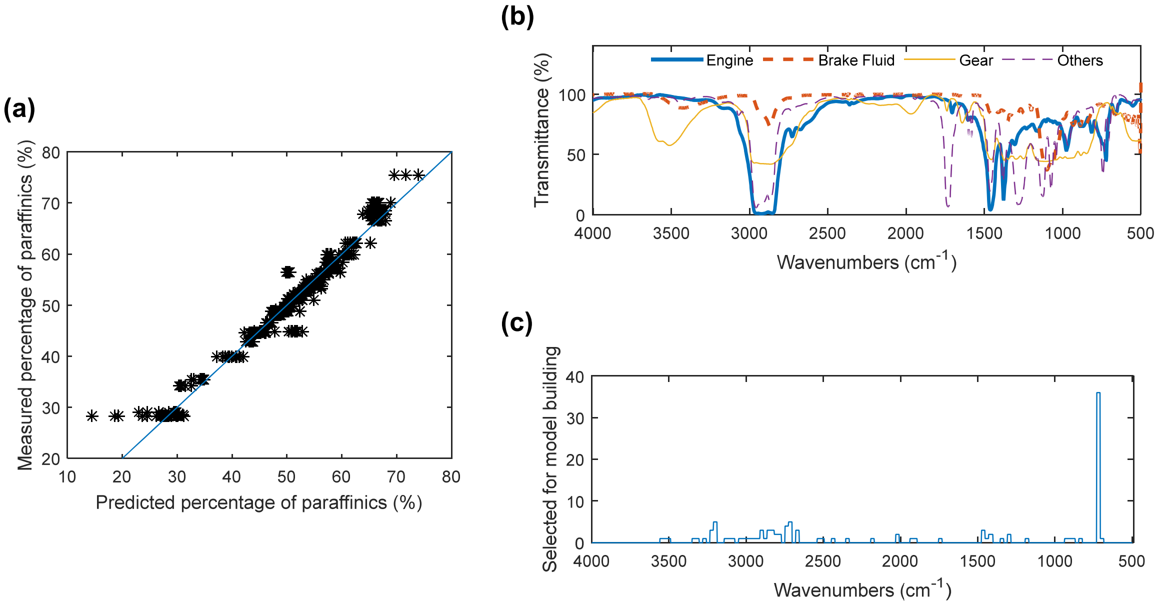


Figure 3.6. Results obtained with iPLS to predict the percentage of paraffinics: (a) predicted and observed response and (b) representative spectra for different sample classes and (c) number of times each bin was included in the iPLS model.

3.4. CONCLUSIONS

A comparison study was carried out in order to predict nine properties of different lubricant oils, namely: density, viscosity at 40 ºC and 100 ºC, viscosity index, TAN, saponification number and the percentages of aromatics, naphthenics and paraffinics. The main goal was to derive robust and accurate models that can predict the desired properties based on FTIR spectra of lubricant oil samples.

A wide variety of regression methods from four different classes, namely variable selection, penalized regression, latent variables and regression tree-based ensembles were tested. One of the main conclusions of this comparison study is that there is no overall better regression method and their optimality is dependent on the property to be predicted. It was found that density and percentage of aromatics, naphthenics and paraffinics can be well predicted and high values of were obtained (0.97-0.98 for the best methods). In general, LASSO method is able to predict these properties. Although better results can be obtained with EN for density and iPLS for aromatics and paraffinics. Nevertheless, some clusters were observed for the density and thus predictions can only be used as rough estimates for this property. Total acid number could be reasonably predicted by RR, SVR and PLS methods, but again some clusters were identified. Indeed, samples belonging to the brake fluid type were rather different. The exclusion of brake fluid samples from the regression analysis allowed the development of more reliable predictive models (RMSECV decreased from 1.5 to 0.6 mg KOH/g). The saponification number and the properties related to viscosity were not satisfactorily predicted, due to the low number of samples available, the diversity of oil types present and the reduced variation in their properties, which is due to the tight specification range they have to meet, making model development harder.

3.5. REFERENCES

[1] T. Mang, W. Dresel, Lubricants and Lubrication, second ed., Wiley-VCH, Weinheim, Germany, 2007.

[2] M.A. Al-Ghouti, Y.S. Al-Degs, M. Amer, Application of chemometrics and FTIR for determination of viscosity index and base number of motor oils, Talanta 81 (2010) 1096−1101.

[3] S. Marinović, M. Krištović, B. Špehar, V. Rukavina, A. Jukić, Prediction of diesel fuel properties by vibrational spectroscopy using multivariate analysis, J. Anal. Chem. 67 (2012) 939−949.

[4] N. Pasadakis, S. Sourligas, C. Foteinopoulos, Prediction of the distillation profile and cold properties of diesel fuels using mid-IR spectroscopy and neural networks, Fuel 85 (2006) 1131−1137.

[5] L.B. Lira, M.S. Albuquerque, J.A. Pacheco, T.M. Fonseca, E.S. Cavalcanti, L. Stragevitch, M.F. Pimentel, Infrared spectroscopy and multivariate calibration to monitor stability quality parameters of biodiesel, Microchem. J. 96 (2010) 126−131.

[6] W. Zhang, W. Yuan, Z. Zhang, M. Coronado, Predicting the dynamic and kinematic viscosities of biodiesel–diesel blends using mid-and near-infrared spectroscopy, Appl. Energ. 98 (2012) 122−127.

[7] L.B. Lira, F.C. Vasconcelos, C.F. Pereira, A.S. Paim, L. Stragevitch, M.F. Pimentel, Prediction of properties of diesel/biodiesel blends by infrared spectroscopy and multivariate calibration, Fuel 89 (2010) 405−409.

[8] B. Pavoni, N. Rado, R. Piazza, S. Frignani, FT-IR spectroscopy and chemometrics as a useful approach for determining chemical-physical properties of gasoline, by minimizing analytical times and sample handling, Ann. Chim. 94 (2004) 521−532.

[9] M. Sastry, A. Chopra, A. Sarpal, S. Jain, S. Srivastava, A. Bhatnagar, Determination of physicochemical properties and carbon-type analysis of base oils using mid-IR spectroscopy and partial least-squares regression analysis, Energy Fuels 12 (1998) 304−311.

[10] J.B. Braga, A.S. Junior, I.S. Martins, Determination of viscosity index in lubricant oils by infrared spectroscopy and PLSR, Fuel 120 (2014) 171−178.

[11] F.R. Van de Voort, J. Sedman, V. Yaylayan, C.S. Laurent, Determination of acid number and base number in lubricants by Fourier transform infrared spectroscopy, Appl. Spectrosc. 57 (2003), 1425−1431.

[12] Y. Felkel, N. Dörr, F. Glatz, K. Varmuza, Determination of the total acid number (TAN) of used gas engine oils by IR and chemometrics applying a combined strategy for variable selection. Chemom. Intell. Lab. Syst. 101 (2010) 14−22.

[13] J. Dong, F.R. Van de Voort, A.A. Ismail, E. Akochi-Koble, D. Pinchuk, Rapid determination of the carboxylic acid contribution to the total acid number of lubricants by Fourier transform infrared spectroscopy, Lubr. Eng. 56 (2000) 12−20.

[14] F.R. Van de Voort, J. Sedman, V. Yaylayan, C.S. Laurent, C. Mucciardi, Quantitative determination of moisture in lubricants by Fourier transform infrared spectroscopy, Appl. Spectrosc. 58 (2004) 193−198.

[15] A. Borin, R.J. Poppi, Application of mid infrared spectroscopy and iPLS for the quantification of contaminants in lubricating oil, Vib. Spectrosc. 37 (2005) 27−32.

[16] C.M. Andersen, R. Bro, Variable selection in regression - a tutorial, J. Chemom. 24 (2010), 728−737.

[17] T. Hesterberg, N.H. Choi, L. Meier, C. Fraley, Least angle and ℓ1 penalized regression: A review, Stat. Surv. 2 (2008) 61−93.

[18] T. Hastie, R. Tibshirani, J. Friedman, The Elements of Statistical Learning: Data Mining, Inference, and Prediction, Springer, Berlin, 2001.

[19] S. Canu, Y. Grandvalet, V. Guigue, A. Rakotomamonjy, SVM and Kernel Methods Matlab Toolbox. Perception Systemes et Information, INSA de Rouen, Rouen, France. 2005.

[20] A.J. Smola, B. Schölkopf, A tutorial on support vector regression, Stat. Comput. 14 (2004), 199−222.

[21] A.J. Burnham, J.F. MacGregor, R. Viveros, Latent variable multivariate regression modeling, Chemom. Intell. Lab. Syst. 48 (1999) 167−180.

[22] I. Jolliffe, Principal Component Analysis, second ed., Springer-Verlag, New York, 2002.

[23] S. Wold, K. Esbensen, P. Geladi, Principal component analysis, Chemom. Intell. Lab. Syst. 2 (1987) 37−52.

[24] S. Wold, M. Sjöström, L. Eriksson, PLS-regression: a basic tool of chemometrics, Chemom. Intell. Lab. Syst. 58 (2001) 109−130.

[25] P. Geladi, B.R. Kowalski, Partial least-squares regression: a tutorial, Anal. Chim. Acta 185 (1986) 1−17.

[26] L. Nørgaard, A. Saudland, J. Wagner, J.P. Nielsen, L. Munck, S.B. Engelsen, Interval partial least-squares regression (iPLS): a comparative chemometric study with an example from near-infrared spectroscopy, Appl. Spectrosc. 54 (2000) 413-419.

[27] C. Strobl, J. Malley, G. Tutz, An introduction to recursive partitioning: rationale, application, and characteristics of classification and regression trees, bagging, and random forests, Psychol. Methods 14 (2009) 323−348.

[28] L. Breiman, Random forests, Mach. Learn. 45 (2001) 5−32.

[29] L. Breiman, J. Friedman, C.J. Stone, R.A. Olshen, Classification and Regression Trees, CRC press, New York, 1984.

[30] J. Elith, J.R. Leathwick, T. Hastie, A working guide to boosted regression trees, J. Anim. Ecol. 77 (2008) 802−813.

[31] Y. Freund, R. Schapire, N. Abe. A short introduction to boosting. J. Jap. Soc. Artif. Intell. 14 (1999) 771−780.

[32] D-S. Cao, Q-S. Xu, Y-Z. Liang, L-X. Zhang; H-D. Li, The boosting: A new idea of building models, Chemom. Intell. Lab. Syst. 100 (2010) 1−11.

PART C – CHARACTERIZATION OF WASTE LUBRICANT OIL

The Part C of the thesis focuses on the extensive characterization of waste lubricant oils, which data were further used for different purposes along three chapters.

In Chapter 4, correlations were applied for the prediction of thermophysical properties.

Chapter 5 addresses in detail the integrated management system of WLO adopted in Portugal and evaluates the properties of WLO by type of producer (garage, industry and others) as a possible approach for segregation at the source.

In Chapter 6, the coagulation phenomena that occurs after alkaline treatment is studied in detail by assessing the properties of WLO. Advanced statistical methods were applied for the classification and discrimination of WLO by coagulation class to unravel the compounds responsible for the phenomena.

4. MEASUREMENT AND CORRELATION OF THERMOPHYSICAL PROPERTIES OF WASTE LUBRICANT OIL

Measurements of viscosity, density and surface tension of waste lubricant oil (WLO) were conducted at different temperatures. The dataset was constituted by nine WLO samples from different producers. The main purpose of the work is the investigation of the temperature dependence of viscosity, including the glass transition, T_g, and dynamic crossover, T_x. In addition, different correlations were evaluated to predict viscosity and surface tension starting from a property easily obtained such as density. WLO show rapid decrease of viscosity with shear rate, followed by an extensive and well defined Newtonian plateau. The temperature dependence of viscosity at the Newtonian plateau of WLO deviated from the Arrhenius behavior, and was accurately described by four different models: Williams–Landel–Ferry (WLF), MYEGA, power law and Ghatee. The minimum and maximum absolute average relative deviation (AARD) were 0.08% and 0.9%, respectively. T_g predicted by WLF equation varied between T = 170.5 K and T = 198.7 K, while MYEGA tends to predict lower T_g (about T = 20 K). The power law and Ghatee models estimate T_x nearly with the same accuracy. A ratio T_x/T_g of about 1.28±0.03 K was obtained for WLO, which agrees with the literature. Waste oil is a moderately fragile glass forming fluid with a fragility parameter, m, ranging from 47.8 and 64.5. New correlations were developed for the prediction of viscosity and surface tension from density at different temperatures. AARD of 7% was observed for viscosity and 2% for surface tension.

KEYWORDS

Waste lubrication oil; viscosity; density; surface tension; glass transition; dynamic crossover.

This chapter is based upon the publication:

C.T. Pinheiro, R.F. Pais, A.G.M. Ferreira, M.J. Quina, L.M. Gando-Ferreira, Measurement and correlation of thermophysical properties of waste lubricant oil, J. Chem. Thermodyn. 116 (2018) 137–146. doi: 10.1016/j.jct.2017.08.039.

4.1. INTRODUCTION

Lubricants are products designed to form a protective film that reduces friction and wear of machinery moving parts, cool surfaces, protect against corrosion and reduce energy consumption. During operation, lubricant oil undergoes chemical changes due to oxidation and contamination, decreasing its effectiveness up to a point that no longer meets quality specifications and needs replacement. The resulting waste lubricant oil (WLO) is a hazardous waste that requires proper disposal and treatment to reduce the risk of water, soil and air contamination [1,2]. Among the existing treatments, regeneration has become the preferred route, whereby base oil is produced by removing contaminants, oxidation products, and additives from the waste oil. Regeneration of WLO can prevent negative environmental impact, besides the inherent economic advantages [3,4]. The amount of crude oil required to produce a certain volume of lubricant is nearly nine times higher to produce the same volume from waste oil [2]. Various methods have been employed to carry out the waste oil regeneration, involving the removal of contaminants by distillation, acid treatment [5,6] solvent extraction [7], clay treatment, hydrogenation [8], or a combination of these processes.

The determination of thermophysical properties for quality control is essential throughout all stages of the lubricant supply chain, including the selection of the proper treatment route. According to national legislation, the decision of sending WLO to one of the recycling destinations is made after checking the conformity of certain technical specifications [9].

Properties of lubricant oil such as density, viscosity index, among others, are typically determined to assess its market value compared with the standards provided by the Society of Automotive Engineers. Udonne [10] evaluated different methods of recycling WLO (acid/clay treatment, distillation/clay, acid treatment and activated charcoal/clay treatment methods) by comparing density and viscosity of WLO with the final base oil. Isah et al. [10] performed a similar study using viscosity and density as probe properties. Kannan et al. [11] recycled WLO collected from automobile service stations which was subjected to dehydration, vacuum distillation followed by solvent extraction and finally the addition of additives to the re-refined oil. All these studies involved determinations of viscosity at 40 and 100 ºC and density at 15 ºC. However, it would be convenient to have determinations in wider ranges of temperature for engineering and efficient application of regeneration techniques. Few studies have been performed on the temperature dependence of WLO properties such as viscosity and density. Low-temperature fluidity is also an important property in lubricant rheology that is rarely addressed in the literature.

The surface tension is another property seldom mentioned in the literature although it can play an important role in the efficiency of regeneration [12]. After the work of Winchester and Reber in 1929 [13] on the temperature dependence of surface tension of fresh oil, this topic has been little investigated. The surface tension of mineral and aeronautical lubricant oil was assessed by Ross [14]. Jones and Wedeven [15] reported surface tension measurements for synthetic paraffinic, naphthenic and paraffinic mineral oil. To the best of our knowledge, only recently Kaldonsky and co-workers [16] evaluated the lubricity and surface properties of synthetic perfluoropolyether (PFPE) oil, comparing them with standard automotive oil. Studies have reported that changes in the surface tension of the oil can be the earliest sign of contamination, sludge potential and oxidation [17]. It is important to note that surface tension is intimately connected with the foaming tendency of lubricant oil [18]. It affects not only bubble formation and size but also the rate of liquid return to the void by bubble collapse or detachment [15]. Moreover, surface tension also influences oil cooling capacity by affecting spreadability. Poor wettability may reduce heat-transfer due to vapor phase formation [19].

In general, density measurement involves simple, fast and low-cost equipment. On the contrary, measurement of viscosity and surface tension is more complex and time-consuming, requiring more sophisticated and expensive instruments. Thus, if relationships between density, viscosity and surface tension are known, by measuring the former property the other two may be easily obtained.

Within this context, this work aims to investigate the temperature dependence of viscosity of waste lubricant oil, including low-temperature dynamics, from a glass transition and dynamic crossover standpoints. In addition, correlations between viscosity and density, and between density and surface tension at different temperatures are explored.

4.2. MATERIALS AND METHODS

4.2.1. WASTE OIL SAMPLES

A set of nine waste lubricant oil samples were collected in Portugal from different producers (garages, industry, and others) across the country. The samples were taken during the pumping of WLO to tank trucks. These trucks transport WLO to specific plants that are part of the integrated waste oil management system implemented in the country. About 0.5 L of sample were collected in each case in airtight plastic bottles and then stored at room temperature in the dark to maintain their integrity until analysis. Physicochemical characterization of the dataset was performed in our previous work presented elsewhere [9]. Nevertheless, some key properties for the present study were determined, namely the aromatic, naphthenic and paraffinic carbon content by FTIR based on the Indian Standard Method 13155:1991. This test method accounts for the carbon-hydrogen vibrations at different wavenumbers. The sum of aromatic, naphthenic and paraffinic percentages is 100%. The water content was determined by Karl Fischer titration following ASTM D6304. The results are listed in Table 4.1. Variation intervals of dynamic viscosity, η, density, ρ, and surface tension, σ, which were measured at different temperatures, are also listed in Table 4.1. The individual values at each temperature of these thermophysical properties are given in Table A.3 in the Annex A2, and the experimental procedures are described in Section 4.2.2.

Table 4.1. Aromatic, naphthenic, paraffinic and water contents, and viscosity, density and surface tension range of the analyzed waste oil samples for the liquid at temperature T and pressure P = 101.86 kPa.[a]

Sample	Arom. / wt%	Napht. / wt%	Paraf. / wt%	Water / wt%	η [b] / mPa.s	ρ [b] / kg.m^{-3}	σ [c] / mN.m^{-1}
S1	0.64	50.08	49.27	9.1	151.7–26.9	882.9–846.2	25.28–21.16
S2	4.94	43.57	51.49	3.3	151.3–24.8	896.6–860.1	28.90–23.18
S3	3.61	50.77	45.62	0.7	136.3–23.3	879.7–844.6	25.79–21.90
S4	3.26	51.87	44.87	4.0	112.7–21.6	881.9–845.3	25.83–22.24
S5	3.03	53.04	43.93	2.1	129.0–22.9	887.6–844.5	27.01–21.46
S6	4.07	46.47	49.46	2.7	102.3–22.3	885.0–852.4	26.98–22.66
S7	2.46	54.56	42.99	4.0	154.3–24.4	886.8–850.3	29.08–23.43
S8	2.61	51.95	45.44	0.6	97.8–19.1	868.6–830.7	26.41–20.99
S9	3.48	55.43	41.09	3.7	145.3–25.5	887.6–844.5	26.28–21.02

[a] Standard uncertainties u are $u_c(\eta)$ = 2%, $u_c(\rho)$ = 0.45 kg·m^{-3}, $u_c(\sigma)$ = 0.3 mN.m^{-1}, $u(P)$ = 0.23 kPa, u(Water) = 0.05 wt%, u(Arom.) = 0.9 wt%, u(Napht.) = 0.9 wt%, u(Paraf.) = 0.02 wt%. For η measurements, $u(T)$ = 0.2 K, for ρ measurements, $u(T)$ = 0.01 K and for σ, $u(T)$ = 0.1 K.

[b] Measured from T = 298.15 K to T = 343.15 K

[c] Measured from T = 303.15 to T = 343.15 K.

4.2.2. EXPERIMENTAL METHODS

4.2.2.1. TEMPERATURE DEPENDENCE OF VISCOSITY

Dynamic viscosity was measured using a HAAKE RheoStress 1 rheometer within a temperature range from 298.15 K to 343.15 K. The stirring action of the rotating spindle, plus the small sample volume helps to keep the temperature gradient across the sample to a minimum. A Julabo F12-ED thermostatic bath with water as circulating fluid was used in the circuit of the sample chamber which was held constant to ±0.2 K. A cylinder rotor Z34 DIN 53019 series 1 was used and shear rates, $\dot{\gamma}$, varying from 0 to 1000 s^{-1} collecting 100 points in 300 s for each measurement. Prior to viscosity measurements, the rheometer was calibrated with a Brookfield viscosity standard at 298.15 K with given viscosity 49.9 mPa.s. This standard is a silicon oil with Newtonian behavior, certified by methods traceable to the U.S. National Institute of Standards and Technology (NIST). We have measured η = (49.9 ± 0.8) mPa.s. Therefore, the uncertainty of the measurement relative to viscosity standard is about 1.6%. Taking into account the uncertainty of temperature, the relative combined uncertainty is estimated to be $u_c(\eta)$ 2%.

4.2.2.2. TEMPERATURE DEPENDENCE OF DENSITY

Experimental densities were measured using a densimeter Anton Paar DMA 60 digital vibrating-tube, with a DMA 512P measuring cell in a temperature range from 298.15 to 343.15 K. The temperature in the vibrating-tube cell was measured with a platinum resistance probe with uncertainty ± 0.01 K. The probe was previously calibrated over the range 273.15–373.15 K against a platinum resistance thermometer ERTCO-Eutechnics High Precision Digital Thermometer certified in the ITS90. A Julabo P-5 thermostatic bath with silicone oil as circulating fluid was used in the thermostat circuit of the measuring cell, which was held constant to ± 0.01 K. An NI PCI-6220 data acquisition board (DAQ) from National Instruments (NI) was used for the real-time registration period, temperature, and pressure values. For this task, a Labview application was developed. Modules of temperature (NI SCC-FT01) and pressure (NI SCC-CI20) were installed in an NI SC-2345 carrier and connected to a DAQ board. Water and toluene were used as reference fluids to fit the calibration equation proposed by Lampreia and Nieto de Castro [20]. The combined standard uncertainty of the density measurements estimated taking into account the influence of uncertainties associated with calibration equation, temperature, period of oscillations (six-digit frequency counter), viscosity, and density data of calibrating fluids was about $u_c(\rho) = 0.45$ kg·m^{-3}. The expanded uncertainty with confidence level 95% (coverage factor k = 2) was estimated to be $U(\rho) = 0.90$ kg·m^{-3}.

4.2.2.3. TEMPERATURE DEPENDENCE OF SURFACE TENSION

Surface tension measurements of WLO within 303.15 K to 343.15 K were performed by PC controlled KSV Sigma 70 tension balance using the Wilhelmy plate. The platinum plate was thoroughly cleaned by immersion in a concentrated solution of nitric acid during several hours. Then it was rinsed with acetone, carefully flamed, washed again with acetone and dried. The temperature inside the vessel was maintained and controlled within ±0.1 K using UltraTherm P Selecta bath. Temperature was measured with a platinum resistance thermometer ERTCO-Eutechnics High Precision Digital Thermometer certified in the ITS90.

Each experimental point results from a set of 10 measurements with an uncertainty of ±0.1 mN m^{-1}.

Prior to measurements, the balance was calibrated with n-butanol (Carlo Erba, 99.5 wt.%). This liquid was selected as calibration standard due to the availability of high accuracy surface tension data, which indicated 24.18 mN.m^{-1} at 298.15 K [21], and since it is within the range of surface tension measured for waste oils. A mean value of $\sigma = 23.90 \pm 0.03$ mN.m^{-1} was obtained. Therefore, the uncertainty of the measurement relative to surface tension standards is 1.2%. Taking into account the uncertainty of temperature, which is very low, the relative combined uncertainty is estimated to be $u_c(\sigma)$ =0.3 mN.m^{-1}.

The density and surface tension measurements were made with measuring cells open to the atmosphere. The measurement of the atmospheric pressure was made using a calibrated pressure transducer (AFRISO Euro-Index, DMU03). Taking the observed values covering January to March 2017 the mean value was $P = 101.86 \pm 0.23$ kPa.

4.2.3. THEORETICAL BACKGROUND

Viscosity is a transport property related to the motions of molecules under shear with a highly non-linear dependence on temperature. In general, viscosity models assume the existence of physical barriers opposing to the movement of molecular planes. One of the most popular models is the Arrhenius equation:

$$\eta = \mathrm{A} \exp\left(\frac{\mathrm{E_a}}{\mathrm{RT}}\right) \tag{4.1}$$

where η is the dynamic viscosity, A is a constant, E_a is the activation energy, R is the gas constant and T is the temperature. However, Eq. (4.1) cannot account for the experimental viscous rise of oil at low temperatures, unless by increasing of activation energy due to the more closely packed structure of liquid [22]. Several studies suggest that the rheological behavior of lubricating oils can be compared with glass forming liquids (GFL) [23,24] which can display marked departures from the Arrhenius behavior at low temperature when approaching glass transition temperature, T_g. GFL are classified as strong and fragile fluids, and in an Arrhenius plot ($\ln \eta$ vs $1 / T$) a strong liquid shows linear behavior, whereas a fragile liquid exhibits an upward curvature (non-Arrhenius behavior). The glass transition temperature is characterized by a viscosity typically near 10^{12} Pa.s. Numerous studies show evidence for the existence of two different regimes in the GFL temperature dependence of viscosity related to different dynamical processes [25]. As the temperature of a fragile liquid decreases, its temperature dependence of viscosity smoothly crosses over to a strong liquid (Arrhenius regime). This fragile-to-strong (FS) transition takes place at crossover temperature, T_x, located in the interval between T_g and the melting temperature, T_m. In a study of the temperature dependence of viscosity involving 84 liquids (organic, inorganic and polymers), Mallamace et al. confirmed the existence of a FS dynamical crossover at $\eta_x \approx 10^2$ Pa.s [25].

The Arrhenius equation has been reported to apply at $T > 1.3T_g$. At lower temperatures in the range from T_g to T_g + (100 to 150) ºC, the Williams–Landel–Ferry (WLF) equation is used instead [26,27]. WLF equation has been used to correlate and predict the behavior of viscoelastic properties of polymers [4], oil [15] and in food industry [27], all of these systems having a glass transition temperature. The WLF equation is defined by Eq. (4.2) [4],

$$\ln \alpha_T = \frac{-C1(T - T_r)\ln(10)}{C2 + (T - T_r)} \tag{4.2}$$

where $C1$ and $C2$ are parameters that describe the temperature dependence of the viscous process in the subcooled liquid at temperatures above the reference temperature T_r, α_T is the shift factor defined as $\eta T_r \rho_r / \eta_r T \rho$, where ρ is the density and the subscript r refers to properties of a reference state [26].

Since in the lubrication industry the viscosity is usually expressed as kinematic viscosity, the shift factor can be re-written as $\nu(T)T_r/\nu_r(T_r)T$, where $\nu = \eta/\rho$ is the kinematic viscosity. In general, $T_r = T_g$ is considered and the so-called "universal" parameters become $C_1 = 17.44$ and $C_2 = 51.6$ K [26]. However, it must be highlighted that for some substances one cannot assign a single temperature at the glass transition. As shown by differential scanning calorimetry (DCS) measurements, the glass transition takes place over a temperature range that varies with the system [23,24].

The viscosity deviation from an Arrhenius temperature dependence of GFL is usually described by the 'fragility' parameter m, introduced by Angell [28].

$$m = \left.\frac{d \ln \tau}{d\,(T_g/T)}\right|_{T=T_g} \tag{4.3}$$

Fragility is a measure of the decrease rate of the structural relaxation time, τ (or related properties, such as η) with increasing temperature near T_g when plotted on a normalized T_g/T plot. Small values of m are assigned to GFL with high polymerized networks such as SiO_2 (m=20) corresponding to strong materials. On the other hand, the systems with non-directional interatomic or intermolecular bonds exhibit high values of m and are fragile.

Recently, Mauro et al. [29] proposed a physically grounded three-parameter model for viscosity correlation in wide ranges of temperatures from T_g and beyond T_m for a great variety of GFL, described in Eq. (4.4) and parameters A, B and C defined in Eqs. (4.5a-c), respectively.

$$\ln \eta = A + \left(\frac{B}{T}\right) e^{(C/T)} \tag{4.4}$$

$$A = \ln \eta_\infty \tag{4.5a}$$

$$B = T_g \ln\left({}^{\eta_g}/_{\eta_\infty}\right) e^{\left[1 - \frac{\ln(10)\, m}{\ln\left({}^{\eta_g}/_{\eta_\infty}\right)}\right]} \tag{4.5b}$$

$$C = T_g \left[\frac{\ln(10)\ m}{\ln\left({}^{\eta_g}/_{\eta_\infty}\right)} - 1\right] \tag{4.5c}$$

Eq. (4.4) can be rearranged in terms of physically meaningful quantities, namely the T_g, the fragility index, m, the high temperature asymptotic limiting viscosity, $\ln \eta_\infty$, and the viscosity at T_g, $\ln \eta_g$, as indicated in Eq. (4.6).

$$\ln \eta = \ln \eta_\infty + (T_g/T) \ln\left({}^{\eta_g}/_{\eta_\infty}\right) e^{\left[\left(\frac{2.3\, m}{\ln\left({}^{\eta_g}/_{\eta_\infty}\right)} - 1\right)(T_g/T - 1)\right]} \tag{4.6}$$

Another important correlation for the temperature dependence of viscosity is the power law described in Eq. (4.7), according to the theoretical results from the mode coupling theory (MCT) [30–32],

$$\eta = \eta_0 \times \left(\frac{T - T_x}{T_x}\right)^{-\gamma} \tag{4.7}$$

where γ, η_0 and T_x are parameters characteristic of the liquid.

Ghatee et al. [33] have shown that, on the contrary to the viscosity, the fluidity $\left(1/\eta\right)$ is a smooth function of temperature, and the temperature dependence of viscosity can be described by the simple linear equation defined in Eq. (4.8),

$$\left(\frac{1}{\eta}\right)^{\phi} = a + b \times T \tag{4.8}$$

where a and b are constants characteristic of the liquid and ϕ is the fluidity exponent that depends on the liquid. It have been shown [34] that the parameters of Eq. (4.8) are related to the ones identified in Eq. (4.7), as can be seen in Eq. (4.9).

$$\gamma = \frac{1}{\Phi}, \qquad \eta_0 = -(a)^{-\gamma}, \qquad T_x = -\frac{a}{b} \tag{4.9}$$

In the vicinity of T_x, the two viscosity paths related with different dynamical regimes can be determined by power law, Eq. (6.7), in the non-Arrhenius regime for $T > T_x$ and by Arrhenius equation, Eq. (4.1), for $T < T_x$.

Some models have been proposed that relate viscosity and surface tension with density for liquids. However, for waste oil these relationships are lacking in the literature. For vegetable oil a simple correlation between density and viscosity was suggested [35,36]:

$$\rho = A + \frac{B}{\eta^{0.5}} \tag{4.10}$$

where A and B are fitting parameters. Alomair et al. [37] proposed a slightly more complex model (Eq. 4.11) for crude oil, which is able to predict oil viscosity data with an average absolute error of 8% and R^2 of 0.97 over wide ranges of temperature from 193.15 to 433.15 K.

$$\ln \eta = A + \frac{B}{T} + C\rho^2 \ln \rho \tag{4.11}$$

Sanchez [38] proposed an equation relating surface tension, σ, to the liquids isothermal compressibility, κ_T, and mass density. The derivation of this equation is based on a generalized square-gradient approximation for the free energy density of a nonuniform fluid, Eq. (4.12),

$$\sigma(\kappa_T/\rho)^{1/2} = A_0^{1/2} = constant \tag{4.12}$$

Eq. (4.12) can be rearranged to calculate the surface tension according to Eq. (4.13),

$$\ln\sigma = c - \frac{1}{2}\ln\kappa_T + \frac{1}{2}\ln\rho \tag{4.13}$$

A simple linear regression can be derived from Eq. (4.13) to describe the dependence of surface tension and density as shown in Eq. (4.14),

$$\ln\sigma = C + \lambda\ln\rho \tag{4.14}$$

where C and λ are parameters of the regression.

In this work, the temperature dependence of viscosity will be assessed by fitting several models, namely the WLF (Eq. 4.2), MYEGA (Eq. 4.6), power law (Eq. 4.7) and Gathee (Eq. 4.8). Correlations between viscosity and density data of WLO will be performed using Eqs. (4.10) and (4.11). The relationship between density and surface tension will be studied applying Eq. (4.14).

4.3. RESULTS AND DISCUSSION

4.3.1. TEMPERATURE DEPENDENCE OF VISCOSITY

The most important property of lubricant oil is the viscosity, as well as its variation with temperature in the equipment under certain operational conditions. Figure 4.1 shows the viscosity behavior for sample S8 as a function of shear rate varying from 0 to 1000 s^{-1} conducted at temperatures from 298.15 to 343.1 K. The WLO show thinning behavior with rapid decrease of viscosity with shear rate, followed by an extensive and well defined Newtonian plateau. In addition, a rapid decrease of viscosity with the increase in the temperature is observed.

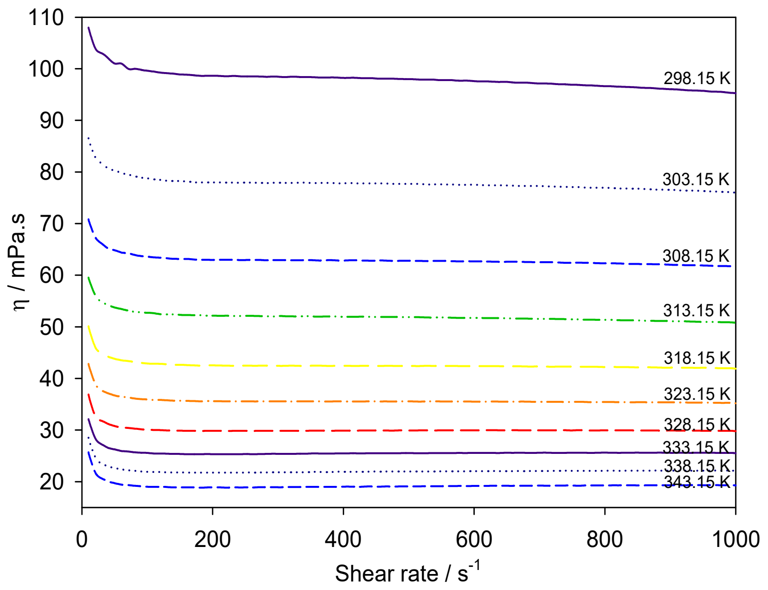


Figure 4.1. Viscosity behavior as a function of the shear rate at different temperatures for sample S8.

Since the Newtonian plateau is rapidly achieved with increasing shear rate for the nine samples studied, further studies will report the mean viscosity at $\dot{\gamma}$ = (200, 400 and 800) s^{-1} for all samples, as illustrated in Figure 4.2. The uncertainty on viscosity for the Newtonian regime has a maximum of 5 mPa.s at 298.15 K, and it is less than 1 mPa.s for higher temperatures.

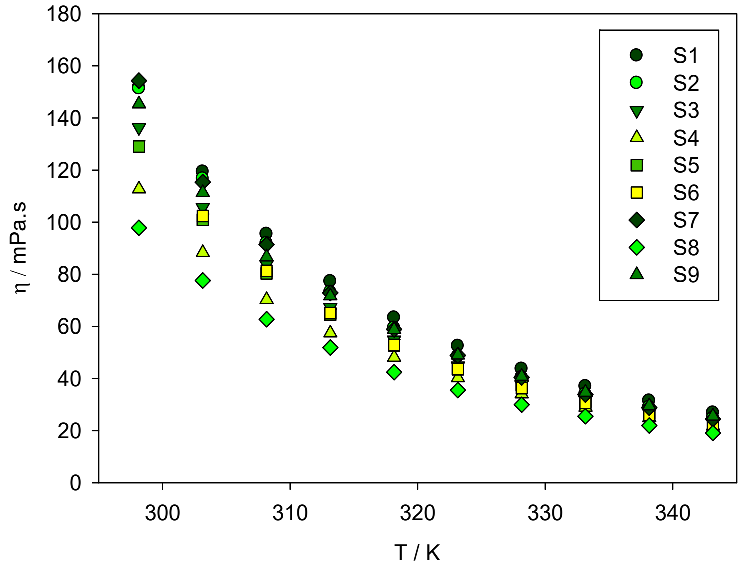


Figure 4.2. Dynamic viscosity as a function of the temperature for the analyzed waste oil samples.

A dramatic increase in viscosity with decreasing temperature causes a deviation from the Arrhenius behavior [31]. Thus, the use of the WLF model (Eq. 4.2) is usually of better accuracy on a wide range of temperatures compared to the Arrhenius model (Eq. 4.1). The parameters resulting from the WLF fitting, namely the predicted glass transition temperatures, T_g, coefficient of determination, R^2, and the absolute average relative deviation of calculated viscosities from experimental data, % AARD, are listed in Table 4.2. A total of 89 data points were evaluated (see Table S4.1 in the Supporting material – Chapter 4). The WLF equation shows a good fitting of the experimental data, with a minimum R^2 of 0.9997 and maximum AARD of 0.7099%. T_g varies from 170.5 to 198.7 K among WLO samples. T_g of lubricant oils have been reported in the literature [23,24,39]. Masson et al. [39] analyzed naphthenic and paraffinic oil by modulated differential scanning calorimetry (MDSC) and reported naphthenic samples with T_g in the range of 196 to 225 K and paraffinic between 180 K and 215 K. Moreover, their studies showed that aromatic content of oil can increase T_g, whereas saturated content may decrease this variable. In fact, the aromatic content has a noticeable effect on T_g since sample S1 has the lowest percentage of aromatics (0.64%, see Table 4.1) and displays the minimum predicted T_g among all WLO samples of 170.52 K. Additionally, the fact that this samples has high water content (9.1%), also influences T_g, which for pure water has been reported at 136 K [40,41]. The reasonable agreement between the T_g obtained from MDSC [24] and WLF fitting of viscosity measurements at temperatures greater than 100 K from the glass transition region should be highlighted . The constant C1 tends to a mean value of 16.0084±0.1602, which is in agreement with the values reported in the literature for GFL [42,43]. C2 is much less universal and is thus the carrier of the information about the fragility of the fluid [42,43].

Table 4.2. Fitting parameters of WLF equation (Eq. 4.2) for waste oil samples.

Sample	ΔT / K	Np[a]	ln (v_g / cSt)	T_g / K	$C1$	$C2$ / K	R^2	AARD[b] / %
S1	298.15-343.15	10	33.6650	170.52	16.3335	37.4429	0.999995	0.1137
S2	298.15-343.15	10	33.9425	192.43	15.9841	27.3029	0.999984	0.1771
S3	298.15-343.15	10	33.9303	190.27	15.9978	27.5845	0.999979	0.2211
S4	298.15-343.15	10	34.0661	190.21	15.8770	25.0529	0.999869	0.5074
S5	298.15-343.15	10	33.9372	187.95	15.9981	27.7954	0.999843	0.4232
S6	303.15-343.15	9	33.8152	185.91	16.1123	29.9469	0.999985	0.1551
S7	298.15-343.15	10	33.9834	195.23	15.9382	26.1688	0.999825	0.6062
S8	298.15-343.15	10	33.7871	177.09	16.1475	31.0871	0.999949	0.2659
S9	298.15-343.15	10	34.2019	198.70	15.7495	22.7225	0.999705	0.7099

[a] Np- number of viscosity data points

[b] Absolute average relative deviation, determined as %AARD = $\frac{1}{n}\sum^{n}\left|\frac{\eta_{experimental}-\eta_{calculated}}{\eta_{experimental}}\right| \times 100$

WLF model performance for describing the temperature dependence of the viscosity of waste oil can be checked when rewriting Eq. (4.2) as indicated by Eq. (4.15).

$$\frac{-C1}{\alpha_T} = 1 + \frac{C_2}{T - T_g} \tag{4.15}$$

Figure 4.3 shows that by plotting $C1/\alpha_T$ as a function of $C2/(T - T_g)$, the experimental data of all analysed samples scale onto a single line, indicating that Eq. (4.2) represents the temperature dependence of viscosity of all waste oil extremely well. The coefficient of determination of the fit of this whole set of data is $R^2 = 0.9999$.

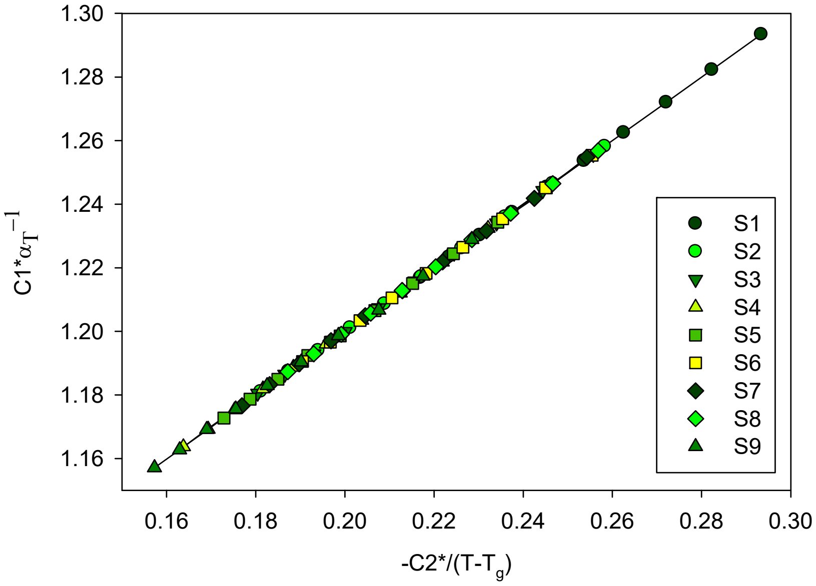


Figure 4.3. Fitting of Eq. (4.2) to the WLO experimental viscosity data. The straight line corresponds to Eq. (4.15) (R^2=0.9999) and different symbols correspond to experimental data-points for different WLO. Parameters *C1*, *C2* and T_g are given in Table 4.2.

The fitting of WLO experimental data using the MYEGA model (Eq. 4.5) allows the prediction of the fragility parameter, m, and results are shown in Table 4.3. At the glass transition it is widely admitted that the relaxation time is τ ~100 s or viscosity $\eta \sim 10^{15}$ mPa.s [41,22]. Thus, $\ln \eta_g$ was fixed at 34.5388 mPa.s and MYEGA becomes a three-parameter equation. From Table 4.3 one can conclude that the fittings are very good, with a minimum R^2 of 0.9997 and a maximum AARD of 0.7%. For the studied WLO, Eq. (4.5) predicts the fragility parameter ranging from 47.8 to 64.5, indicating WLO as moderate fragile liquids.

Table 4.3. Fitting parameters of experimental data using the MYEGA equation (Eq. 4.6).

Sample	ln (η_∞ / mPa.s)	T_g / K	m	R^2	AARD / %
S1	-2.1584	153.56	47.7512	0.999993	0.1361
S2	-0.8500	173.22	61.3440	0.999986	0.1757
S3	-0.9491	170.76	60.2479	0.999985	0.1821
S4	-0.6188	169.25	61.8564	0.999872	0.5193
S5	-0.9971	168.07	58.9337	0.999843	0.4367
S6	-1.3553	166.83	56.9789	0.999988	0.1407
S7	-0.7510	175.13	62.7809	0.999811	0.6662
S8	-1.6671	157.18	52.8552	0.999952	0.2726
S9	-0.3558	174.90	64.5301	0.999691	0.7417

Comparing MYEGA with WLF model, the former tends to predict lower T_g (about 20 K lower), varying from 153.6 to 175.1 K.

The power law (Eq. 4.7) was fitted to the WLO viscosities and the parameters are listed in Table 4.4. R^2 and %AARD indicate that this model describes the temperature dependence of viscosity of WLO quite accurately. As mentioned in Section 4.2.3, the crossover temperature, T_x, is an important reference marking the dynamical changes of fragile supercooled liquids below T_m. Table 4.4 shows that the dynamic crossover temperature varied from 226 K and 254 K, which, as expected, are higher than the T_g predicted by Eqs. (4.2) and (4.6). T_x of WLO can be related with T_g obtained from Eq. (4.2) as $T_x/T_g = 1.279 \pm 0.027$. This result is comparable with the ones obtained by Angell [44], suggesting $T_x/T_g \approx 1.3$ for various GFL. The power law exponents γ are in the range reported in the literature that claims to be between 2 and 4 for most liquids [45].

Table 4.4. Results of the fitting using the power law equation (Eq. 4.7).

Sample	γ	η_0 / mPa.s	T_x / K	R^2	AARD / %
S1	3.5729	2.5734	225.95	0.999998	0.0786
S2	3.1868	1.6995	239.59	0.999983	0.2730
S3	3.1733	1.7169	238.15	0.999984	0.2886
S4	2.5677	1.8664	247.93	0.999929	0.4928
S5	3.0580	1.8029	239.02	0.999928	0.4304
S6	3.2909	1.6798	235.59	0.999974	0.2181
S7	2.6582	1.6473	252.35	0.999792	0.7456
S8	3.2582	1.9221	229.45	0.999949	0.3262
S9	2.4406	2.0018	254.19	0.999721	0.8834

In Section 4.2.3 it was shown the equivalence between power law equation and the Ghatee model (Eq. 4.8) since the set of parameters of one equation could be obtained from the set of the other. Thus, Eq. (4.8) was also fitted to viscosities and the resulting parameters are presented in Table 4.5. According to R^2 and %AARD, it is possible to conclude that the temperature dependence of viscosity of the waste oil is accurately described as for the power law model. The value of ϕ range between 0.280 and 0.364 with an average value of 0.330±0.024. Table 4.5 also presents the results of the calculated T_x and η_0 using the relations described in Eq. (4.9) ($T_x = -(a/b)$ and $\eta_0 = -(a)^{-\gamma}$ with $\gamma = 1/\phi$). Comparing to the values obtained by the power law equation (Table 4.4), there is a strong agreement in the values of γ, T_x and η_0, using the two alternative methods. The maximum deviation between crossover temperature found by two methods is 7 K for samples S7 and S8. Comparing values of scaling law exponents, γ, very good agreement is obtained with maximum deviation of 0.3 for the same oil samples. For the high temperature limiting viscosity, η_0, maximum deviations of 0.07 mPa.s are found for S6 and S9 samples.

Table 4.5. Fitting parameters (ϕ, a and b) of Eq. (4.8) and the values of γ, η_0 and T_x calculated using Eq. (4.9).

Sample	ϕ	a	b×10^3	R^2	AARD / %	$\gamma = \frac{1}{\phi}$	$\eta_0 = -(a)^{-\gamma}$ / mPa.s	$T_x = -\frac{a}{b}$ / K
S1	0.280	-0.7677	3.3964	0.999994	0.1291	3.5689	2.5688	226.04
S2	0.328	-0.8448	3.4806	0.999973	0.2467	3.0525	1.6733	242.72
S3	0.329	-0.8428	3.4932	0.999966	0.2922	3.0423	1.6825	241.27
S4	0.364	-0.7962	3.2719	0.999918	0.3998	2.7465	1.8700	243.35
S5	0.332	-0.8239	3.4313	0.999855	0.4341	3.0120	1.7922	240.12
S6	0.330	-0.8588	3.5839	0.999977	0.2106	3.1299	1.6103	239.63
S7	0.336	-0.8525	3.4790	0.999873	0.4973	2.9780	1.6084	245.04
S8	0.316	-0.8224	3.5470	0.999937	0.2978	3.1666	1.8574	231.86
S9	0.364	-0.7870	3.1897	0.999764	0.6404	2.7495	1.9321	246.73

The fluidity data of WLO can be overlapped into a single curve by rearranging Eq. (4.8) and plotting ($\eta^{-\phi}/-a$) versus (T/T_x), as showed in Figure 4.4.

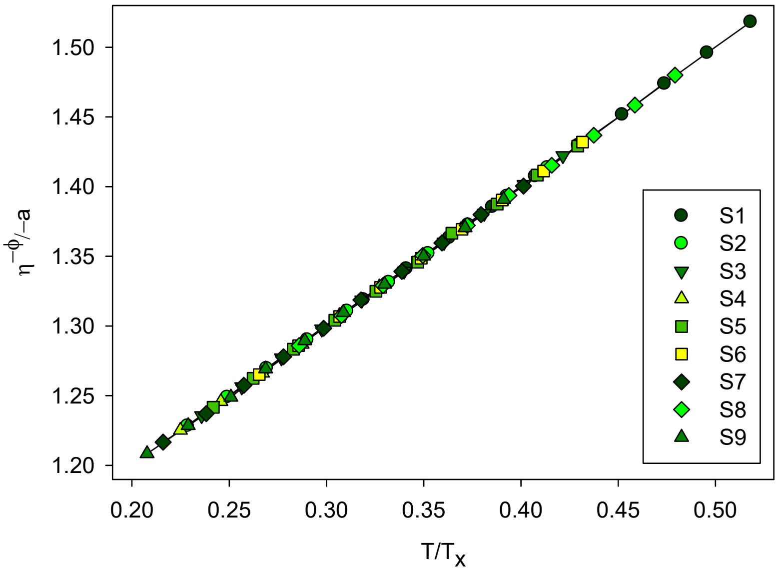


Figure 4.4. Scaling of viscosity data ($\eta^{-\phi/-a}$) as a function of the scaled temperature (T/T_x) for waste lubricant oil. The straight line corresponds to a linear fit (with R^2=0.9999) and different symbols correspond to experimental data-points for different WLO.

The exponent ϕ could be assumed as a universal constant for WLO, transforming Eq. (4.8) in a two-parameter equation, as shown in Figure 4.5. Ghatee et al. found universal exponents ϕ applied in ionic liquids (ϕ = 0.300) [32] and alcohols (ϕ = 0.312) [46] very close to ϕ = 0.330 found here for WLO.

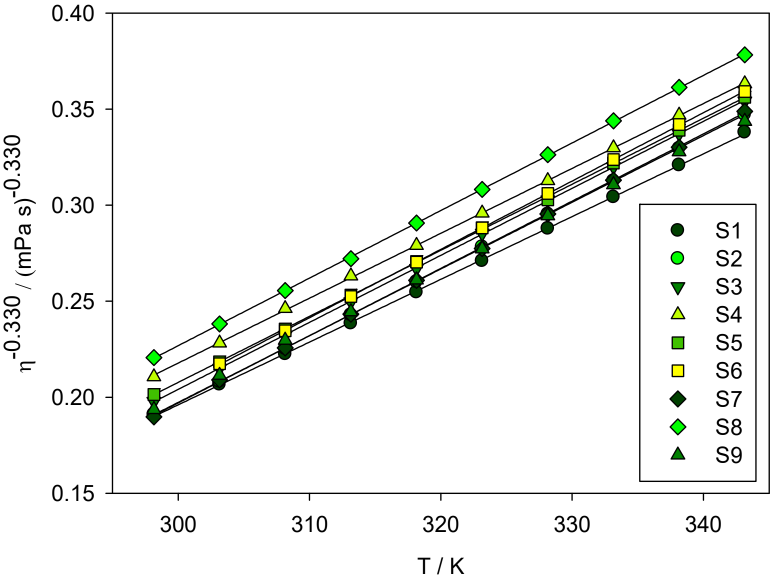


Figure 4.5. Dependence on temperature of $\eta^{-0.330}$.

The viscosity change with temperature can be accurately described by the four models tested in this work. WLF and MYEGA equations allow the prediction of T_g, but the former estimates values between 170.5 K and 198.7 K, while the latter predicts lower T_g (about 20 K) than WLF model. MYEGA equation has the advantage of providing information about the fragility parameter of waste oil. The power law and Ghatee equation estimate the dynamic crossover temperature nearly with the same accuracy.

4.3.2. RELATION BETWEEN DENSITY AND VISCOSITY

The dependence between viscosity and density have been successfully described by Eqs. (4.10) and (4.11) for vegetable oil [35,36] and crude oil [37], respectively. Both equations were applied to the viscosity and density data of waste oil. Eq. (4.10) resulted in an R^2 of 0.8343 and AARD of 21.7%. Establishing as main objective the prediction of viscosity of a WLO from the knowledge of density, it is clear that Eq. (4.10) will be unreliable for this purpose. Eq. (4.11) was also fitted to the data points after a slight analytical rearrangement into Eq. (4.16):

$$\ln \eta = A + \frac{B}{T} + CT + D\rho^2 \ln \rho \tag{4.16}$$

The least squares fitted coefficients are A = -42.7697, B = 9270.9285 K, C = 0.0616 K^{-1}, and D = 18.7989 $(g.cm^{-3})^{-2}$ with R^2 = 0.9773 and AARD = 7.2%. Figure 4.6 displays the *ln (η)* as a function of *ρ^2.ln(ρ)* at several isotherms for all the WLO samples. A reasonable quality of representation is obtained and this conclusion is reinforced from the obtained coefficient of determination, R^2, and the AARD.

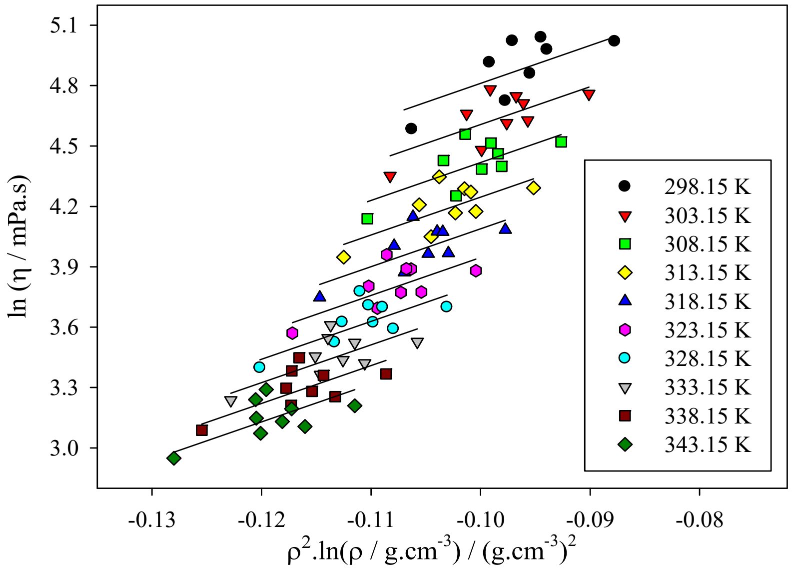


Figure 4.6. Dependence on ρ^2.ln(ρ) of ln (η) of waste lubricant oil. The symbols are data points off all the analyzed samples and the lines represent the fitting using Eq. (4.16).

The parity plot and the relative deviation between calculated viscosities from Eq. (4.16) and experimental data are given in Figures 4.7(a) and (b), respectively. It can be concluded that 32% of data show relative deviations within ± 5% and 78% within ± 10%. Sample S1 shows the higher deviations. In the lubricant industry, it is common to measure kinematic viscosity at T = 313.15 K. At this temperature, Eq. (4.16) can give an estimation of kinematic viscosities within ± 7%.

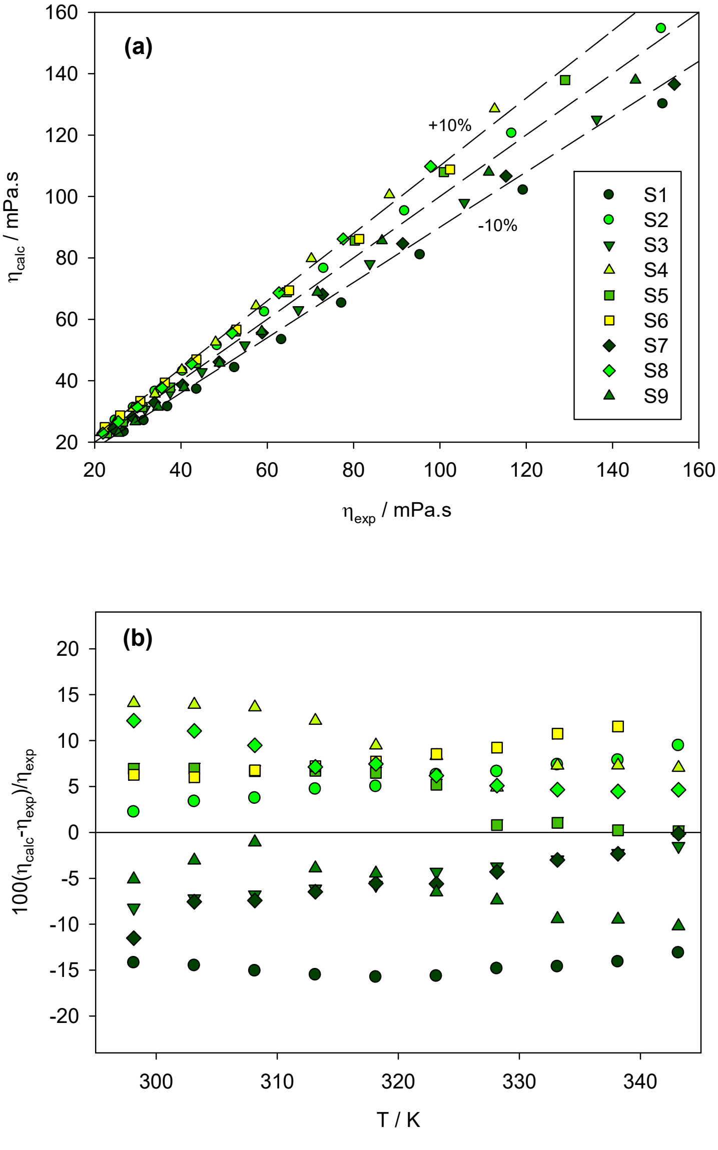


Figure 4.7. (a) Parity plot and (b) relative percentage deviation for calculated viscosity, η_{calc}, compared with experimental values, η_{exp}, of WLO samples.

4.3.3. RELATION BETWEEN SURFACE TENSION AND DENSITY

The correlation derived from the work of Sanchez described by Eq. (4.14) was used in the attempt to find a linear dependence between the natural logarithm of surface tension (ln σ) and the natural logarithm of density (ln *ρ*) for all WLO samples. A total of 45 data points were evaluated (see Table S4.1 in the Supporting material). The obtained results are shown in Figure 4.8.

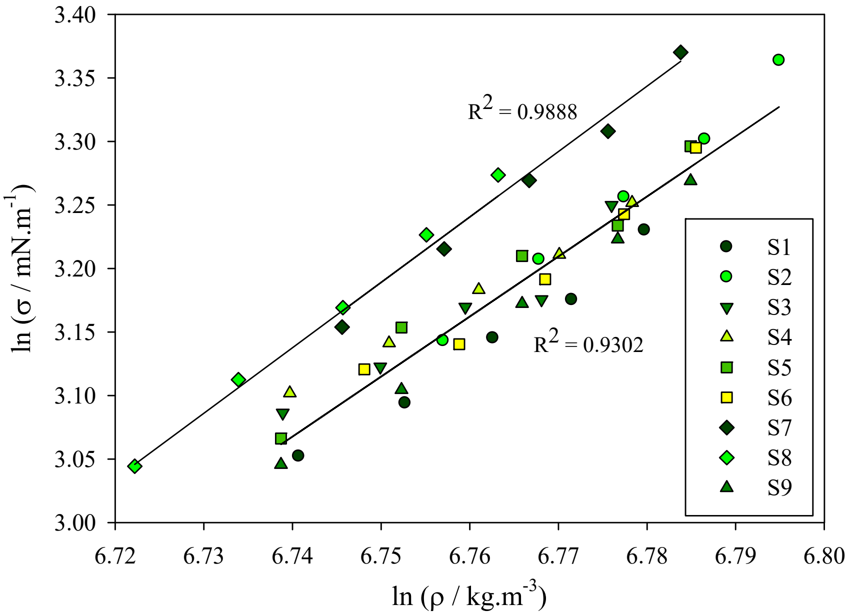


Figure 4.8. Correlation between density and surface tension of different waste lubricant oil.

It can be observed that samples S7 and S8 tend to have significantly higher surface tension than the rest of the samples and thus were treated separately. This may be explained by the fact that these samples might be originated from different applications than the others, showing a different chemical composition and physical behavior. The fitting of Eq. (4.14) applied to the data of samples S7 and S8 give C = -31.5853, λ = 5.1518 with a coefficient of determination, R^2 = 0.9888, and AARD = 0.9%. Fitting the set formed by the values of the other samples, C = -29.6675, λ = 4.8563, R^2 = 0.9302, and AARD = 1.7 %. The parity plot and the relative deviation between calculated viscosities from Eq. (4.14) and experimental data are given in Figures 4.9(a) and (b). It can be observed that low relative deviations of the calculated surface tension from the experimental values almost within ± 2% are obtained for the set including all WLO, except samples S7 and S8. Indeed, for S7 and S8 samples, the calculated values show relative deviations within ± 1% usually ± 0.5%. These results allow concluding that the linear correlation Eq. (4.14) provides a good representation of data and could be an interesting tool for surface tension prediction from lubricant oil density.

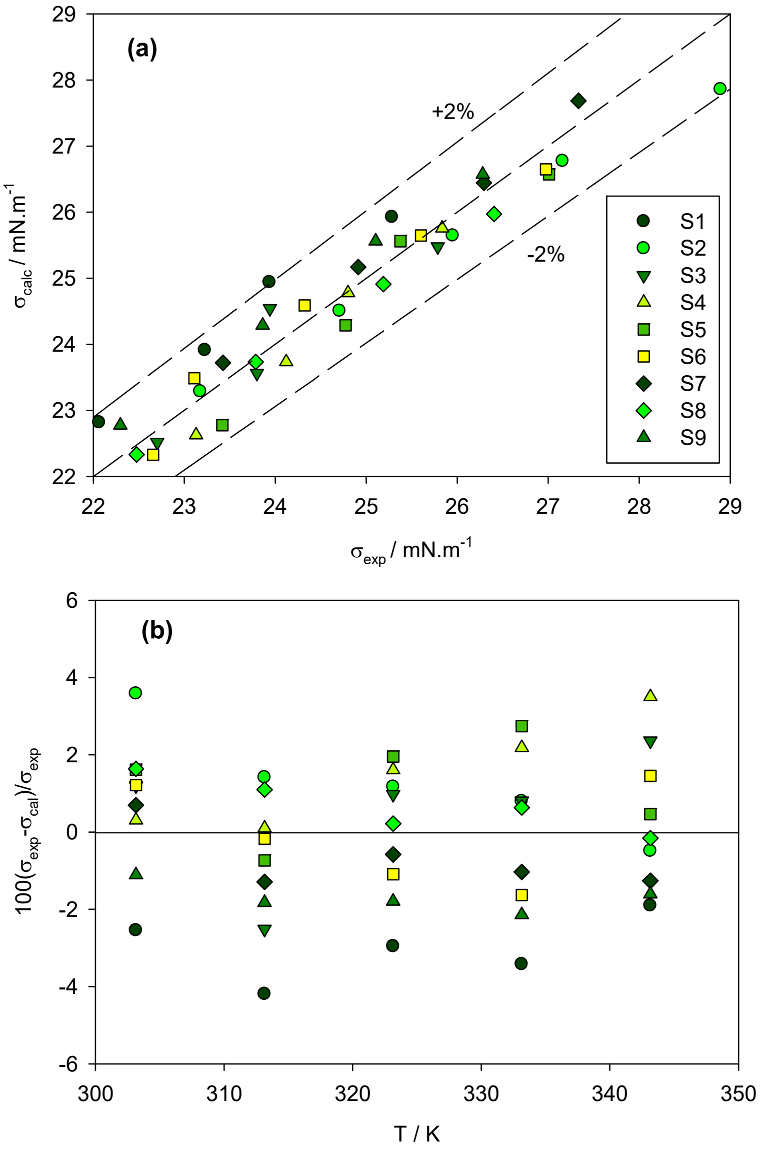


Figure 4.9. (a) Parity plot comparing the experimental and calculated surface tension of waste lubricant oil using Eq. (4.14) and (b) relative percentage deviations between calculated and experimental values.

The experimental surface tensions measured in this work for WLO are compared to values from literature corresponding to several fresh oils in Figure 4.10. It can be observed that with exceptions of samples S2 and S7, all other waste oils show significantly lower surface tension at a given temperature, especially at higher ones. Taking into account that the surface tension is the surface Gibbs energy, then the relationship with the surface enthalpy, H_s, and entropy, S_s, is $\sigma = H_S - TS_S$. This means that an increase of dσ/dT observed for waste oils corresponds to the increase of surface entropy comparing with fresh oils. Accordingly, the surface enthalpy is also increased with usage. This is in agreement with the studies reporting that changes in the oil surface tension will be the earliest sign of contamination, sludge potential and oxidation between other issues [17]. Quoting Forbes, "The interfacial tension test is the most valuable single test that can be used to evaluate a turbine oil. It is generally agreed that when the interfacial tension is between 15 and 20 dynes.cm^{-1} (= mN.m^{-1}), deposits may or may not be forming in the system. Safe practice would call for an oil change in this range" [47].

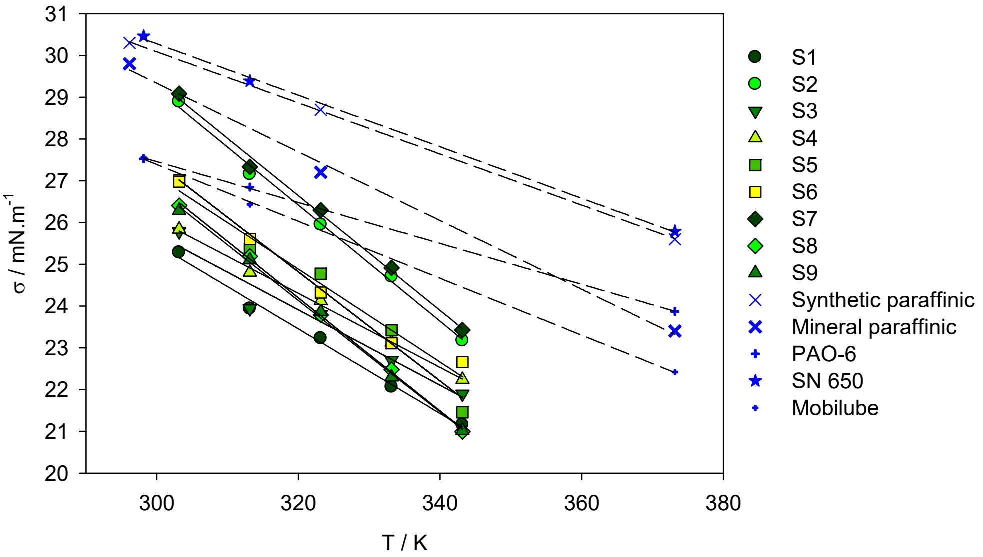


Figure 4.10. Surface tension of waste oil (samples S1 to S9) and of fresh lubricant oil from literature [15,16].

4.4. CONCLUSIONS

Rheological investigation on nine waste lubrication oil samples (WLO) was conducted at temperatures from 298.15 K to 343.15 K and shear rates from 0 to 1000 s^{-1}. The WLO show thinning behavior with rapid decrease of viscosity with shear rate, followed by an extensive and well defined Newtonian plateau. For each sample, viscosities corresponding to the plateau were correlated with Williams–Landel–Ferry (WLF), MYEGA, power law and Ghatee models. The viscosity of all WLO samples is very well correlated with these models with minimum and maximum AARD values of 0.08% and 0.9%, respectively. The glass transition temperature, T_g, predicted with WLF equation is in good agreement with calorimetric data selected from the literature. Combining the T_g results with the crossover temperatures, T_x, fitted with power law equation it was obtained that T_x/T_g= 1.28±0.03 K. Densities of the nine WLO samples were measured at temperatures in the range 298.15 K and 343.15 K and surface tension was measured in the same range. A new correlation between viscosity and density was found for WLO which enables the calculation of viscosity with AARD of 7%. The surface tension of WLO can be calculated from the linear correlation between logarithm of surface tension and logarithm of density with relative deviations within ±2%. The experimental surface tensions measured of most part of WLO samples show significantly lower surface tension than different clean oils which leads to the conclusion that the use of lubricant significantly increase surface entropy and enthalpy. The surface tension measurements can be a good route for developing new testing methodologies and standards of lubricating oil.

4.5. REFERENCES

[1] M.A. Reis, M.S. Jeronimo, Waste lubricating oil rerefining by extraction-flocculation. 1. A scientific basis to design efficient solvents, Ind. Eng. Chem. Res. 27 (1988) 1222–1228.

[2] S.O. Ogbeide, An investigation to the recycling of spent engine oil, J. Eng. Sci. Technol. Rev. 3 (2010) 32–35.

[3] C. Kajdas, Major pathways for used oil disposal and recycling. Part 1, Tribotest 7 (2000) 61-74.

[4] B. Boughton, A. Horvath, Environmental assessment of used oil management methods., Environ. Sci. Technol. 38 (2004) 353–358.

[5] A. Kamal, F. Khan, Effect of extraction and adsorption on re-refining of used lubricating oil, Oil Gas Sci. Technol. - Rev. l'IFP. 64 (2009) 191–197.

[6] N. Abdel-Jabbar, E. Al Zubaidy, M. Mehrvar, waste lubricating oil treatment by adsorption process using different adsorbents, Int. J. Chem. Bio. Eng. 3 (2010) 70–73.

[7] H.A. Durrani, M.I. Panhwar, R.A. Kazi, re-refining of waste lubricating oil by solvent extraction, MUR J. Eng. Tech. 30 (2010) 237–246.

[8] S. Jhanani, K. Joseph, Used oil generation and management in the automotive industries, Int. J. Environ. Sci. 2 (2011) 638–648.

[9] C.T. Pinheiro, V.R. Ascensão, C.M. Cardoso, M.J. Quina, L.M. Gando-Ferreira, An overview of waste lubricant oil management system: Physicochemical characterization contribution for its improvement, J. Clean. Prod. 150 (2017) 301–308.

[10] A.G. Isah, M. Abdulkadir, K.R. Onifade, U. Musa, M.U. Garba, A.A. Bawa, Y. Sani, Regeneration of used engine oil, in: Proceedings of the World Congress on Engineering (WCE) Vol I, July 3 - 5, London, UK, 2013, pp. 565–568.

[11] C.S. Kannan, K.M. Kumar, M.S. Hussain, N. DeepaPriya, K. Saravanan, Studies on reuse of re-refined used automotive lubricating oil, Res. J. Eng. Sci. 3 (2014) 8–14.

[12] A.M.A. Omar, R.A. El Adly, S.T. Keera, M.S. Mohamed, Recovery of residual lubricating oil from waste clay by flotation, Monatshefte Für Chemie / Chem. Mon. 129 (1998) 387–392.

[13] G. Winchester, R.K. Reber, Variation of surface tensions of lubricating oils with temperature, Ind. Eng. Chem. 21 (1929) 1093–1096.

[14] S. Ross, Variation with the temperature of surface tension of lubricating oils, National Advisory Committee for Aeronautics, Technical note 2030, 1950.

[15] W.R. Jones, L.D. Wedeven, Surface tension measurements in air of liquid lubricants to 200 °C by the differential maximum bubble pressure technique, NASA Technical Note D-6450, 1971.

[16] T.J. Kaádoński, L. Gryglewicz, M. Stańczyk, T. Kaádoński, Investigations on lubricity and surface properties of selected perfluoropolyether oils, J. KONES Powertrain Transp. 18 (2011) 199-212.

[17] J. Fitch, The surface tension test - Is it worth resurrecting? (2002). www.machinerylubrication.com/Read/376/surface-tension-test (accessed 7 April 2017)

[18] T.Ć. Prolić, A. Lepušić, Effect of foaming on the antiwear properties of lubricating oils, Goriva I Maz. 51 (2012) 29–46.

[19] V. Štěpina, V. Veselý, Lubricants and Special Fluids, Elsevier, Amsterdam, 1992.

[20] I.M.S. Lampreia, C.A. Nieto de Castro, A new and reliable calibration method for vibrating tube densimeters over wide ranges of temperature and pressure, J. Chem. Thermodyn. 43 (2011) 537–545.

[21] G. Benson, V. Lam, Surface tensions of binary liquid systems. II. Mixtures of alcohols, J. Colloid Interface Sci. 38 (1972) 294–301.

[22] N. Alves, J. Mano, J. Gómez Ribelles, J. Gómez Tejedor, Departure from the Vogel behaviour in the glass transition—thermally stimulated recovery, creep and dynamic mechanical analysis studies, Polymer (Guildf) 45 (2004) 1007–1017.

[23] M. Alsaad, S. Bair, D.M. Sanborn, W.O. Winer, Glass transitions in lubricants: Its relation to elastohydrodynamic lubrication (EHD), J. Lubr. Technol. 100 (1978) 404–416.

[24] R.S. Stearns, I.N. Duling, R.H. Johnson, Relationship of glass transition temperature to viscosity-temperature characteristics of lubricants, Ind. Eng. Chem. Prod. Res. Dev. 5 (1966) 306–313.

[25] F. Mallamace, C. Branca, C. Corsaro, N. Leone, J. Spooren, S.-H. Chen, H.E. Stanley, Transport properties of glass-forming liquids suggest that dynamic crossover temperature is as important as the glass transition temperature, Proc. Natl. Acad. Sci. U. S. A. 107 (2010) 22457–62.

[26] C.-Y. Liu, J. He, K. Roland, C. Bailly, New linearized relation for the universal viscosity−temperature behavior of polymer melts, Macromolecules 39 (2006) 8867–8869.

[27] P. Sopade, P. Halley, B. Bhandari, B. D'Arcy, C. Doebler, N. Caffin, Application of the Williams–Landel–Ferry model to the viscosity–temperature relationship of Australian honeys, J. Food Eng. 56 (2003) 67–75.

[28] C. Angell, Relaxation in liquids, polymers and plastic crystals — strong/fragile patterns and problems, J. Non. Cryst. Solids. 131–133 (1991) 13–31.

[29] J.C. Mauro, Y. Yue, A.J. Ellison, P.K. Gupta, D.C. Allan, Viscosity of glass-forming liquids., Proc. Natl. Acad. Sci. U. S. A. 106 (2009) 19780–19784.

[30] P. Taborek, R.N. Kleiman, D.J. Bishop, Power-law behavior in the viscosity of supercooled liquids, Phys. Rev. B. 34 (1986) 1835–1840.

[31] W. Götze, L. Sjögren, Relaxation processes in supercooled liquids, Reports Prog. Phys. 55 (1992) 241–376.

[32] H. Sillescu, Heterogeneity at the glass transition: A review, J. Non. Cryst. Solids. 243 (1999) 81–108.

[33] M.H. Ghatee, M. Zare, A.R. Zolghadr, F. Moosavi, Temperature dependence of viscosity and relation with the surface tension of ionic liquids, Fluid Phase Equilib. 291 (2010) 188–194.

[34] M.H. Ghatee, M. Zare, Power-law behavior in the viscosity of ionic liquids: Existing a similarity in the power law and a new proposed viscosity equation, Fluid Phase Equilib. 311 (2011) 76–82.

[35] C.M. Rodenbush, F.H. Hsieh, D.S. Viswanath, Density and viscosity of vegetable oils, J. Am. Oil Chem. Soc. 76 (1999) 1415–1419.

[36] B. Esteban, J.-R. Riba, G. Baquero, A. Rius, R. Puig, Temperature dependence of density and viscosity of vegetable oils, Biomass Bioenergy 42 (2012) 164–171.

[37] O. Alomair, M. Jumaa, A. Alkoriem, M. Hamed, Heavy oil viscosity and density prediction at normal and elevated temperatures, J. Pet. Explor. Prod. Technol. 6 (2016) 253–263.

[38] I.C. Sanchez, Liquids: Surface tension, compressibility, and invariants, J. Chem. Phys. 79 (1983) 405–415.

[39] J.-F. Masson, G.M. Polomark, S. Bundalo-Perc, P. Collins, Melting and glass transitions in paraffinic and naphthenic oils, Thermochim. Acta. 440 (2006) 132–140.

[40] Y. Yue, C.A. Angell, Clarifying the glass-transition behaviour of water by comparison with hyperquenched inorganic glasses, Nature 427 (2004) 717–720.

[41] I.I. Katkov, F. Levine, Prediction of the glass transition temperature of water solutions: comparison of different models, Cryobiology 49 (2004) 62–82.

[42] C.A. Angell, Entropy and fragility in supercooling liquids, J. Res. Natl. Inst. Stand. Technol. 102 (1997) 171–185.

[43] P. Abivin, K. Indo, Y. Cheng, D. Freed, S.D. Taylor, Glass transition and heavy oil dynamics at low temperature, in: World Heavy Oil Congress, Edmonton, Alberta, 2011, pp. 1–5.

[44] C.A. Angell, Perspective on the glass transition, J. Phys. Chem. Solids. 49 (1988) 863–871.

[45] O.E. Kalinovskaya, J.K. Vij, G.P. Johari, Mechanism of the major orientation polarization in alcohols, and the effects of steric hindrance-, and dilution-induced decrease on H-bonding, J. Phys. Chem. 105 (2001) 5061–5070.

[46] M.H. Ghatee, M. Zare, L. Pakdel, An insight into the dynamic crossover phenomenon in alcohols from the fluidity equation, Fluid Phase Equilib. 336 (2012) 98–103.

[47] W.G. Forbes, Lubrication of Industrial and Marine Machinery, John Wiley, New York, 1943.

5. AN OVERVIEW OF WASTE LUBRICANT OIL MANAGEMENT SYSTEM: PHYSICOCHEMICAL CHARACTERIZATION CONTRIBUTION FOR ITS IMPROVEMENT

Waste lubricant oil (WLO) management systems across Europe can be very heterogeneous, with significant discrepancies in its performance. The objectives towards a circular economy represent a challenge to continuously maximize the collection and regeneration of this hazardous waste. The quality of WLO is a limiting factor towards its potential for regeneration, in which producers have a great responsibility on the handling phase. In this context, the main objectives of this work are the evaluation and improvement of a national management system, based on the physicochemical characteristics of WLO collected by different producers (garage, industry and others). Data of critical parameters (sediments, water, chlorine and PCB) of 30,242 samples collected from 2008 to 2015 were analyzed. About 4.8% of those samples exceeded the Portuguese regulatory limit for WLO collection regarding sediments (3 wt. %) and 22.3% for water plus sediments (8 wt. %). On the contrary, 0.73% of the samples did not comply with the limit of chlorine (2000 ppm) and only 0.08% for PCB (50 ppm). Chlorine nonconformities were mostly registered in industrial producers. In addition, 60 samples collected in 2015 were characterized regarding other important properties, namely density, kinematic viscosity at 40 °C, total acid number, saponification number, elemental analysis and functional groups. These results gave important clues about the performance of the different producers. In particular, FTIR analysis revealed that about 60% of the samples may be contaminated with glycol compounds regardless the type of producer. The overall management system can be improved by preventing contamination with chlorine from industry WLO or glycol-containing compounds (such as brake fluid and antifreeze) for all producers.

KEYWORDS
Waste lubricant oil; management system; producers; characterization; selective collection.

This chapter is based upon the publication:
C.T. Pinheiro, V.R. Ascensão, C.M. Cardoso, M.J. Quina, L.M. Gando-Ferreira, An overview of waste lubricant oil management system: Physicochemical characterization contribution for its improvement, J. Clean. Prod. 150 (2017) 301–308. doi: 10.1016/j.jclepro.2017.03.024.

5.1. INTRODUCTION

Waste lubricant oil (WLO) is the most significant liquid hazardous waste stream in Europe. The main harmful contaminants present in WLO are heavy metals, poly-chlorinated hydrocarbons (PCB), poly-aromatic compounds (PAH), which are highly toxic to human health and can cause damage to the environment if not disposed and treated properly [1,2]. Europe represents 19% of total worldwide market volume of lubricants, consuming around 6.8 million tons in 2015 [3]. The purchased oil generates about 50% of WLO, and the remaining is partly lost during use by combustion processes, evaporation, leakages, residues remaining in the containers, etc. [4]. European Union (EU) manages approximately 3 million tons of WLO every year [5].

Waste oils are ruled by Waste Framework Directive 2008/98/EC, which repealed the Directive 74/439/EEC. In particular, the Article 21 requires that Member States take measures to ensure that: i) waste oils are collected separately, where this is technically feasible; ii) waste oils are treated in accordance with waste hierarchy, which gives priority to the regeneration process; iii) waste oils of different characteristics are not mixed and are not mixed with other kinds of waste or substances, whenever this is technically feasible and economically viable.

Management systems and legislative frameworks implemented in Member States can be very heterogeneous [4,6]. Free market basis management systems were implemented in countries such as the Netherlands and the United Kingdom, where the market value of waste oils plays an important role and operators in the recovery chain contract under free market conditions to ensure the appropriate collection and destination of WLO [7,8]. Finland applies a government-led system, where producers pay a fee to the State, which is responsible for the overall organization and remunerates the operators in the recovery chain [9,10]. France applies a management system similar to Finland. However, due to the drop in oil prices, since August 2016 the fee payed by producers is not used to finance the collection of WLO. Thus, an additional fee is charged by the authorized collection operators (according to the *Arrêté du 8 août 2016* amending the *arrêté du 28 janvier 1999* on the conditions for the collection of waste oils). Most of the EU countries apply Extended Producer Responsibility (EPR) programs, including Austria, Belgium, Bulgaria, Germany, Latvia, Poland, Portugal, Spain, Slovenia and Croatia [11,7]. EPR policy gives producers significant responsibility providing incentives to reduce waste at the source and support the achievement of collection and recycling management goals [12]. EPR schemes are usually managed by means of a consortium, the Producer Responsibility Organization (PRO) which supports the collection, transportation and management of WLO. Depending on the EPR scheme and national legislation, PRO acts on behalf of all the adhering companies to meet recycling targets [11].

In this study, difficulties were faced during collection and analysis of data from EU Member States to compare the efficiency of management systems, namely due to the lack of transparency and availability of reliable data. Thus comparison across European countries was very difficult. Though, Figure 5.1 depicts management data of some Member States reported in 2011 [11]. In this scope, it is important to note that according to the Directive 2008/98/EC, recycling refers to "any recovery operation by which waste materials are reprocessed into products, materials or substances whether for the original or other purposes". It includes the reprocessing of organic material, but excludes energy recovery and the reprocessing into materials that are to be used as fuels or for backfilling operations; regeneration refers to the "recycling operation whereby base oils can be produced by refining waste oils, in particular by removing the contaminants, the oxidation products and the additives contained in such oils".

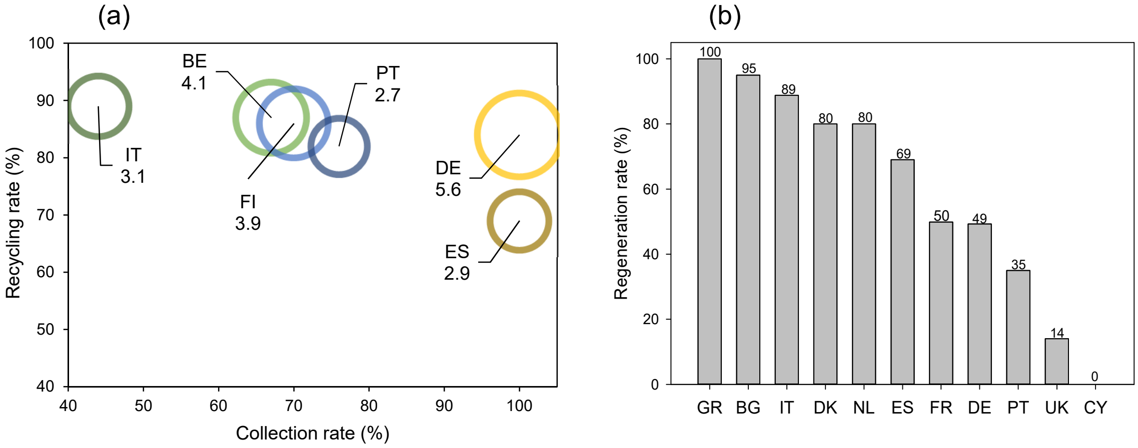


Figure 5.1. Waste lubricant oil management in some Member States in 2011 [11]. a) Recycling versus collection rates (circles size represents the performance in terms of kg/cap./year); b) Regeneration rate.

Figure 5.1(a) shows that WLO collected in 2011 range from 2.7 in Portugal to 5.6 kg/cap./year in Germany. Recycling rates were between 69% in Spain and 91% in Belgium. Energetic recovery (burning) continues to hinder regeneration of WLO across Europe [13]. Indeed, in some countries, the implementation of sound management systems is still in the early stages, and thus the regeneration rate may vary from 0% in Cyprus to 100% in Greece (Figure 5.1(b)).

EU seeks to accelerate the transition to a circular economy, where resources are re-used or re-introduced in production processes, instead of being discarded after use [14–16]. The introduction of collection and recycling targets for WLO would better support the objectives towards a circular economy, enabling the consistent implementation of the waste hierarchy, which prioritizes regeneration and would encourage the separate collection [17]. This goal represents a challenge for most Member States, including countries who have already well implemented management systems. The continuous maximization of regeneration targets requires a thorough understanding of the properties of WLO generated. Collection is a critical part of the management system. Producers play an important role in the collection system since they are responsible for handling, segregating and storage of different types of WLO before delivery it to authorized collectors that ensure adequate treatment [18].

At national level, WLO are frequently handled incorrectly by mixing them with liquids of different properties and containing contaminants such as brake fluids, antifreeze and other solvents, hampering further regeneration. In this context, this work emerges as a new approach to improve the WLO management system in an EU country. To this end, a detailed characterization of the most relevant physicochemical properties was performed on a significant number of samples collected in Portugal, covering the whole territory. This effort provided indications on how WLO have been handled by producers. To the best of our knowledge, the selective collection of WLO according to their producer has never been addressed in the literature. The influence of specific WLO characteristics on the regeneration potential was analyzed to optimize the selective collection operation and improve the management system in Portugal. The main conclusions may potentially be extended to the WLO management systems of other countries.

5.2. MATERIALS AND METHODS

5.2.1. SAMPLES DESCRIPTION

About 219,178 tons of WLO were collected by SOGILUB (the national organization responsible for the global WLO management system) from 2008 to 2015, of which 52.3% are from garages, 17.3% from industry and 30.4% from other producers (do-it-yourselfers, transportation, construction, agriculture or public sectors, etc.). During the collection period, samples were taken for quality control. In this study, 30,242 samples were analyzed regarding PCB, chlorine, sediments and water content. To complement the physicochemical characterization at lab scale, a set of 60 samples were selected according to the volume of WLO generated by the different producers: 38 samples from garages, 12 from industry and 10 from other producers.

5.2.2. PHYSICOCHEMICAL CHARACTERIZATION

The subset of 60 samples was characterized regarding the density, kinematic viscosity at 40 °C, total acid number (TAN), saponification number (SN), elemental analysis (P, Ca, Zn, Fe, S and Cl) and functional groups by Fourier transform infrared spectroscopy (FTIR). Most of these properties were determined using reference ASTM methods. Kinematic viscosity was obtained at 40 °C according to ASTM D7042, using an Anton Parr-SVM 3000 Stabinger Viscosimeter. The density was determined according to ASTM D4052, using a digital densimeter, Mettler Toledo DM40. Total acid number (TAN) was determined by potentiometric titration according to ASTM D664. Titrations were carried out using a solution of alcoholic potassium hydroxide (0.1 M) to neutralize the lubricant acidic components. A mixture of toluene, isopropanol and water (50, 49.5 and 0.5% v/v, respectively) was used as titration solvent. TAN was expressed in milligrams of KOH required to neutralize the acidic constituents per gram of oil. Saponification number (SN) was determined by potentiometric titration following ASTM D94. Oil samples are dissolved in a mixture of a KOH alcoholic solution (0.5 M) and butanone (50 mL each). Considering the difficulty to dissolve organic samples such as lubricant oil and some additives in these solvents, it was necessary to add 25 ml of White Spirit solution. The mixture is heated in total reflux for 30 min, and the condenser washed with 50 mL of naphtha to remove any remaining sample. Finally, the titration was performed with HCl (0.5M). The saponification number (SN) corresponds to the milligrams of KOH required to saponify fatty material present in one gram of oil.

The elemental content of P, Zn, Ca, S, Fe, and Si was determined by Energy Dispersive X-Ray Fluorescence (EDXRF) using a Nex CG Rigaku spectrometer. About 4 g of lubricant was weighed to a sample cell Chemplex 1330 with a Polypropilene TF-240 film. Since no sample preparation was required, the cell is placed on the equipment and the analysis is immediately performed.

FTIR spectra were recorded in transmittance mode using potassium bromide (KBr) pellets, prepared with a pneumatic press. One drop of lubricant was placed on the top of one pellet, creating a thin film, which was placed into an appropriate sample holder and immediately analyzed in a Jasco FT/IR – 4200. Each spectrum was obtained by 64 scans/sample with a resolution of 4 cm-1 in the 4000-500 cm-1 range. Every analysis was performed using a different pellet and before each measurement a background spectrum was obtained using one clean pellet without sample.

5.2.3. STATISTICAL ANALYSIS

Box and whiskers plot was used to summarize data and outliers identification, by means of SigmaPlot 11.0 software. The minimum (5th percentile), 25th percentile, median (solid line), mean (dashed line), 75th percentile, maximum (95th percentile) and outliers were the parameters indicated in these plots. Interquartile range (IQR) corresponds to data between the 25th and 75th percentiles, is represented by the box. A statistical t-student test was performed and the p-value (significance level) was determined to compare means using JMP software. A significance level of 5% was used. In addition, statistically different means (p-value <0.05) are marked with different lower case letters (a, b) in the box and whiskers plots.

5.3. RESULTS AND DISCUSSION

5.3.1. PORTUGUESE WASTE LUBRICANT OIL MANAGEMENT SYSTEM

In Portugal, *Decreto-Lei n.º153/2003* established the legal framework for the management of waste lubricant oil, amended by *Decreto-Lei n.º 178/2006* and then by *Decreto-Lei n.º 73/2011*, which transpose the European Directive 2008/98/EC on waste. This regulation orders that who places lubricating oils on the national market must submit the respective WLO generated to an individual or collective/integrated management system. At national level, WLO is managed via an integrated management system (SIGOU), which is the EPR instrument implemented by SOGILUB, the producer responsibility organization (PRO). SOGILUB is a non-profit organization that aims to provide integrated management of WLO, including organizing the collection, transport, storage, treatment and recovery, as well as the development and maintenance of information database. Thus, the system SIGOU is financed by fee payments (Ecovalor) from manufacturers and/or importers per litter of new oil placed on the national market (transferring the management responsibility) and by sales to final destination of treated WLO. The waste oil generated after use is stored by the producers (industry, garage and others) in tanks or containers, which in general are not segregated according to the waste oil type. As summarized in Figure 5.2, the operational management system includes a network of collection operators established throughout the national territory, providing the collection from producers, and transport to intermediate storage or pre-treatment units. In the pre-treatment units, WLO are subjected to water/solvent and sediment removal. This pre-treatment aims to increase WLO properties to meet technical requirements for the several destinations recognized in the legislation [8]. In Portugal, there are several solutions in terms of recycling operations, such as: regeneration (or re-refining) throug vacuum distillation to produce base oils; reprocessing of WLO into fuel oil by thermal cracking (then used to produce electricity in co-generation engines); use of the pre-treated WLO in the production of light expanded clay aggregate (LECA) where WLO is used as expansion agent.

A carbon footprint analysis of the waste lubricant oil management system in Portugal was performed in 2011 [19]. The analysis compared the real scenario, where 26,946 tons of WLO were recycled (51% through thermal cracking, 40% by regeneration and 9% as expansion agent in LECA production) with three hypothetical scenarios (100% recycled by thermal cracking or 100% by regeneration or 100% as expansion agent). The results reported that the worst scenario would be the use of 100% of pre-treated WLO to produce electricity through thermal cracking. Assuming that 100% of WLO is employed for LECA production, about 1.8 times lesser net greenhouse gas (GHG) emissions are produced than the real situation in terms of CO2 equivalent per total amount of treated WLO. Maximizing the regeneration option does not exhibited advantages in terms of carbon footprint compared to LECA production, although it is preferred based on the waste hierarchy principle.

The environmental performance (recycling and collection rates) and financial aspects of SIGOU are reported by SOGILUB to the Environmental Portuguese Agency (APA) and to the General Directorate of Economic Activities (DGAE).

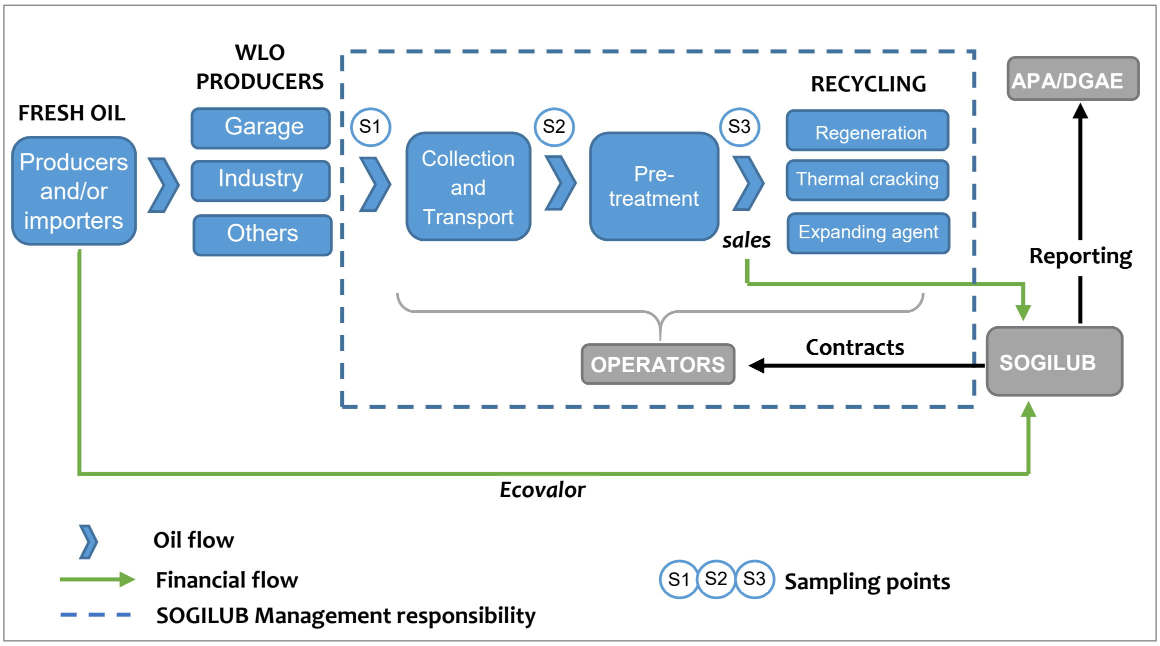


Figure 5.2. WLO management system in Portugal (SIGOU).

The recent license granted to SOGILUB (*Despacho n.º 4383/2015*) specifies that its activity must be developed to fulfill the management goals for collection, regeneration and recycling of WLO. As indicated in Table 5.1, from 2015 to 2019, increasing targets for collection, regeneration and recycling were specified in the license.

Table 5.1. Technical performance achieved in 2015 and targets for 2015 to 2019 (*Despacho n. º 4383/2015*).

Technical performance	Achieved	Target				
	2015	2015	2016	2017	2018	2019
Collection (%) [(a)]	91	85	90	95	100	100
Regeneration (%) [(b)]	69	65	70	75	80	80
Recycling (%) [(c)]	100	90	90	95	100	100

[(a)] over WLO generated; [(b)] over WLO after pre-treatment; [(c)] over WLO after pre-treatment and including regeneration.

In 2015, 61,350 tons of fresh lubricant oil were placed on the market, which potentially generated 26,994 tons of WLO. SIGOU achieved 91% of collection over WLO generated that was then sent to pre-treatment. After water and sediment removal, 69% of the WLO was regenerated (14,991 tons), while the rest (9,517 tons) was recovered by other forms of recycling. A recycling rate of 100% (including regeneration) was achieved, which demonstrate the fulfillment of the management objectives established in the legislation for 2015, as shown in Table 5.1. It should be highlighted that since 2007, Portugal has not sent WLO directly for energy recovery. Despite the very good results of SIGOU in 2015, challenging performance targets are imposed until 2019, reaching 100% of WLO collection and 80% for regeneration. This requires a continuous improvement of the WLO management system.

Namely, regeneration goals can only be achieved with the utmost care in handling and blending of oils, which highly influence the quantity and quality of WLO that can be regenerated.

Waste Framework Directive prohibits the mixture of different types of WLO and other wastes such as other fluids from vehicles or substances, whenever such mixing hinders their treatment. However, different types of waste oils are often mixed and contaminated by all kinds of materials. To ensure that oils with detrimental characteristics are not mixed in a given storage tank (e.g. oil contaminated with chlorine) and avoid mixing of regenerable with non-regenerable oils, a brief characterization of the collected and pre-treated oils is performed (S1 and S2 characterization points in Figure 5.2) by the operators. Decision of sending WLO to one of the recycling destinations is made after checking the conformity of the load (of a truck) with technical specifications (S3 characterization point). These technical specifications can be different across Member States, according to national legislation. In Portugal, contamination with organochlorides, such as PCB (which may be present in certain transformer oils) is of special concern. However, a limit of 50 ppm of PCB is fairly well established by the legislative arrangements in the individual countries [20].

Table 5.2 shows the technical specifications of WLO in Portugal, defined by the *Decreto-Lei n.º* 153/2003. All steps of the management system are limited by the physicochemical characteristics of the WLO, which are strongly affected by the incorrect handling in the producers.

Table 5.2. Technical specifications of WLO defined by Portuguese legislation into force from 2015 [21].

Parameter	Test Method	Waste Lubricant Oil			
		Collection	Pre-treatment	Regeneration	Recycling
Density at 15°C (kg/m^3)	ASTM D1298	-	800-980	800-1000	800-1000
Viscosity at 40°C (cSt)	ASTM D445	-	-	10-100	10-100
Water (wt %)	ASTM D6304	≤ 8 [(a)]	< 1	< 1	< 1
Sediments (wt %)	ASTM D893	≤ 3	< 1	< 1	< 1
Chlorine (ppm)	ISO 15597	≤ 2000	-	≤ 2000	≤ 2000
PCB (ppm)	EN 12766	< 50	< 50	< 50	< 50
Flash point (°C)	ASTM D92	> 65	> 120	> 120	> 120
Glycol content (wt %)	ASTM D4291	-	-	< 1	-
Saponification	ASTM D94	-	-	Negative	-

[(a)] water plus sediments.

The compliance of 30,272 samples collected over 2008 to 2015 with respect to sediments, water plus sediments and chlorine was analyzed in Figure 5.3. The results show that the percentage of samples exceeding the limit required for WLO collection regarding sediments (≤3 wt. %) varied between 3.2 and 7.7%, from 14.8 and 27.7% for water plus sediments (≤ 8 wt. %), and from 0.3 and 1.2% for chlorine (≤ 2000 ppm). On the basis of these results, there remains great room for improvement of the WLO management system. Concerning to polychlorinated biphenyls (PCB), which are also regulated (limit <

50 ppm), the nonconformities of collected samples have already been rare in Portugal, with just 25 cases (0.08% of the total samples) in the last 7 years. This is a result of the fact of the use of PCB was banned in many countries and in Portugal as well, due to toxic and persistent properties.

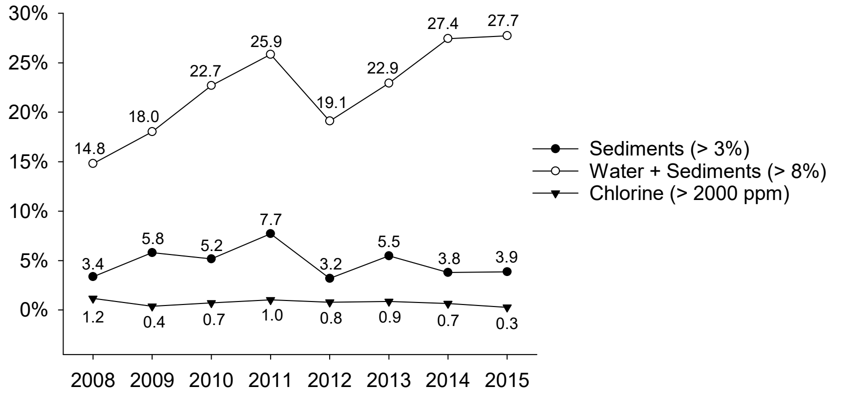


Figure 5.3. Percentages of non-conforming samples collected from 2008 to 2015 with respect to sediments, water plus sediments and chlorine considering the legal thresholds.

As previously mentioned, producers of WLO may play an important role in the management performance. The careful handling of different types of WLO increases the quality and enhances its inherent value for regeneration, in accordance with the waste hierarchy for treatment. The analysis of noncompliance with technical specifications by producer is presented in Figure 5.4. About 30,242 samples of WLO were collected by SOGILUB from 2008 to 2015, of which 12.6% from industry, 60.8% from garage, and 26.6% from other producers.

The analysis of noncompliance with legal threshold for sediments, Figure 5.4(a), and water plus sediments, Figure 5.4(b), suggests a distribution correlated to the number of samples analyzed by each producer. Raising awareness of producers for the segregation of oils from water and solvents and other wastes is highly recommended. In fact, producers are crucial players to minimize the occurrence of these contaminants in WLO and to support the improvement of the management system.

Figure 5.4(c) shows that the noncompliance with chlorine regulatory limit has a higher frequency within industrial producers (range from 44.4 to 81.0% over the nonconforming analysis). Despite the effort to reduce the use of chlorine in lubricants due to environment concerns, it still occurs in some industrial metalworking, hydraulic, insulating or heat transfer fluids as chlorinated hydrocarbons, esters or other additives with special characteristics such as chemical stability and fire-resistance. In addition, chlorinated hydrocarbons are more difficult to re-process, hindering the technical performance of regeneration processes and its ability to produce lubricant products of high quality [22]. Chlorine could also arise as contaminant due to accidental or deliberate mixing with chlorinated solvents widely used as cleaning agents [23].

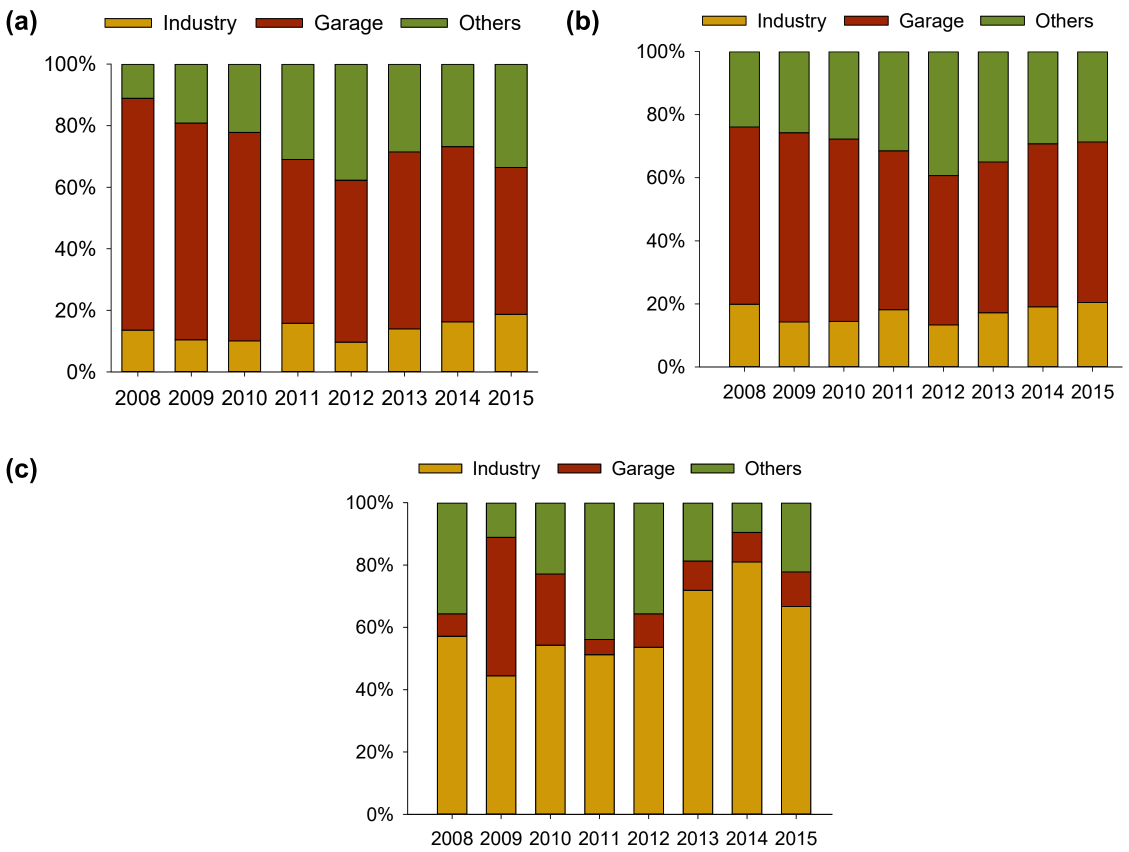


Figure 5.4. Distribution of noncompliance with legal thresholds for collection from 2008 to 2015 by WLO producer: a) sediments (> 3 wt.%), b) water plus sediments (> 8 wt. %) and c) chlorine (> 2000 ppm).

5.3.2. PHYSICOCHEMICAL CHARACTERIZATION

Figure 5.5 summarizes the results obtained for the 60 samples of WLO collected in industry, garage and others, regarding density, viscosity at 40ºC, SN and TAN. Producers where different lowercase letters (a or b) were assigned indicate that differences in mean values are statistically significant according to the t-student test with p-value <0.05.

The Student's t-test showed that differences in mean values of the density, viscosity, SN and TAN are not statistically significant for WLO produced both in industry and garages. For density and viscosity, the class "others" shows a higher data dispersion. The maximum density observed (971 kg/m^3) almost reaches the limit acceptable by Portuguese technical specifications for pre-treated oils (980 kg/m^3, Table 5.2). In the particular case of viscosity in the garage category (Figure 5.5(b)), outliers reveal samples with high contamination levels, namely with fluids less viscous than the oil (samples with viscosity of 0.8, 7.1 and 14.5 cSt). Broader ranges revealed by "others" producers are expected since this category can aggregate samples from very diverse applications with different chemical composition.

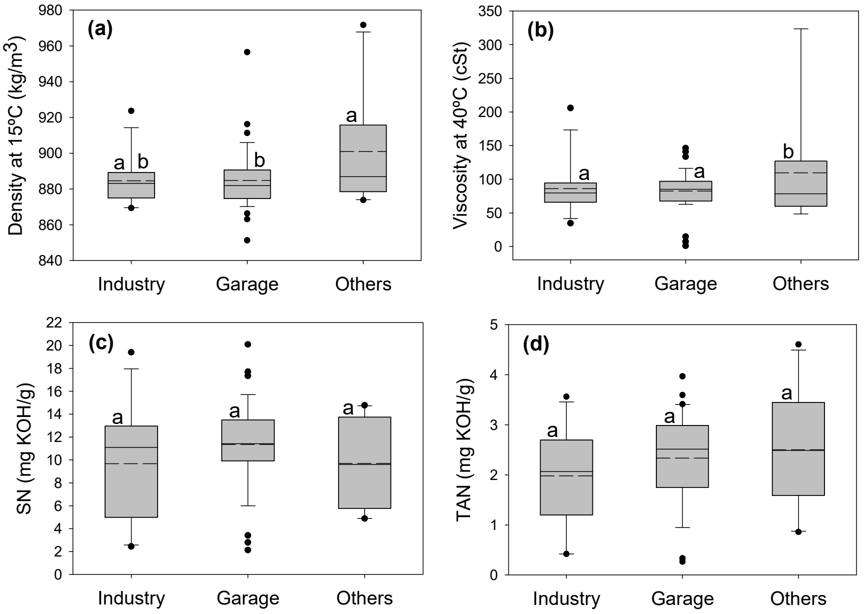


Figure 5.5. Physicochemical characterization of WLO regarding a) Density at 15 °C, b) Viscosity at 40 °C, c) SN and d) TAN.

TAN is intrinsically related to the type of the fresh oil, additives, application and usage period and can vary significantly [24]. Figure 5.5(d) shows high variability within each WLO producer, but no statistical differences in the mean values were observed. TAN maximum and minimum values ranged between 0.43 to 3.22 mg KOH/g in industry, from 0.95 to 3.41 mg KOH/g for garages and from 1.02 to 4.48 mg KOH/g for "others" producers.

SN is a particular important parameter in case WLO is intended for regeneration with technologies applying alkaline pretreatment for demetallization [18,25]. The use of aqueous solutions containing specific anions (e.g. hydroxide) allows the formation of low solubility metal salts present in the lubricant, causing their precipitation. The alkali-hydroxide (NaOH or KOH) is also an effective agent for neutralizing acids and free or bounded chlorine [22]. On the other hand, organic acids, esters or fatty acids in the WLO may react with metal hydroxides and forming a soap that decreases the fluidity of the oil and consequently may cause blocking problems in regeneration plant pipes and equipment [22]. The SN is a measure of the saponifiable matter that will react with potassium hydroxide. In Figure 5.5(c), it can be noticed that SN also exhibits great variability, regardless the type of producer. In the industry category, the IQR varies between 5.0 and 13.0 mg KOH/g. For garages maximum and minimum SN values range between 4.9 and 13.5 mg KOH/g and for other types of producers ranges between 5.8 and 13.7 mg KOH/g. The highest SN outliers, were 19.4, 20.1 and 14.8 mg KOH/g for industry, garage and other producers, respectively. The higher the SN, the greater will be the instability caused by the addition of KOH during regeneration phase. However, the relationship between the SN value of the WLO and its tendency to form soap with alkali addition requires more investigation.

The elemental analysis may be helpful to compare the WLO composition from different producers, specifically for detecting additives and external contaminants such as wear metals [26]. Figure 5.6 summarizes the determined content of P, Zn, Ca, S, Fe, and Si of WLO by producer.

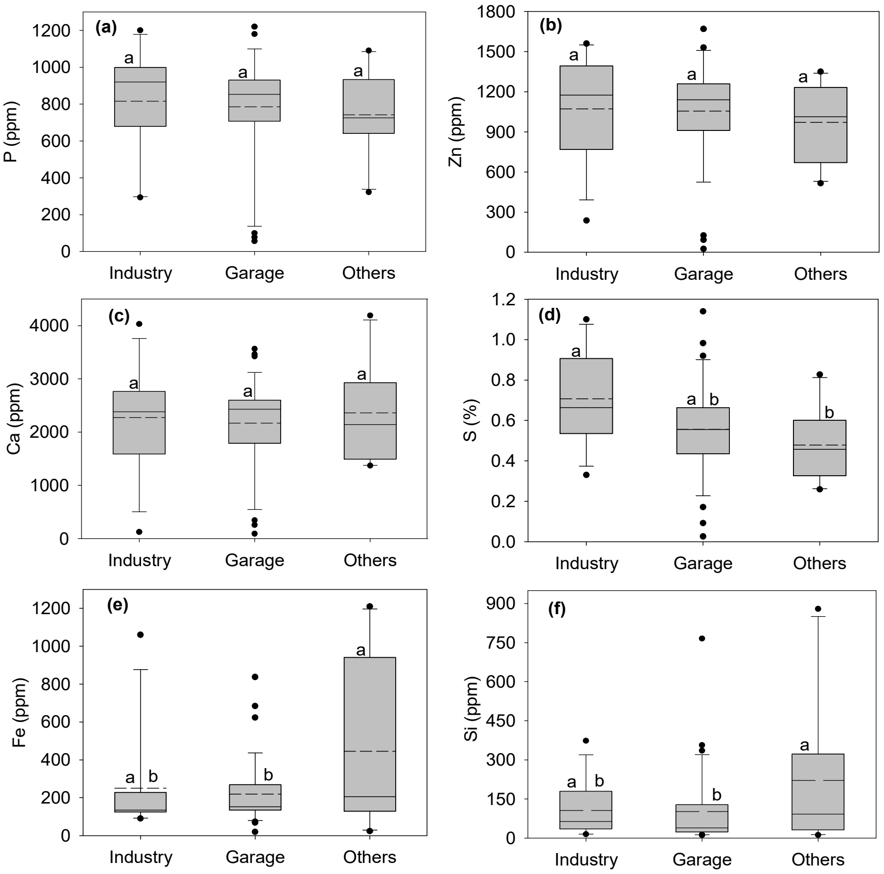


Figure 5.6. Content of P, Zn, Ca, S, Fe, and Si in waste oils according to the type of producer.

Phosphorous and zinc are elements typically found in antiwear additives, antioxidants and corrosion inhibition, used to protect metallic segments in demanding operating conditions. Characteristic concentrations of these elements in WLO are in the range of 800-1200 ppm and 1000-1200 ppm, respectively [23]. Figures 5.6(a) and 4.6(b) show that WLO from different producers have not significant different mean variability regarding these elements. The same has been observed for calcium (Figure 5.6(c)), which is mainly associated with detergents, providing cleaning action by suspending polar materials and acid neutralization in engine lubricants [27].

Besides being part of additives, sulfur can also arise from wear and corrosion of engine and segments [28]. Mean concentrations of sulfur for industry, garage and others producers were 0.71, 0.56 and 0.48%, respectively (Figure 5.6(d)), which is in accordance with the values found in the literature that lie around 0.7 – 0.9% in WLO [23]. Industry and "others" producers show significant statistically differences in mean values.

Contamination with wear metals, such as iron, from wear and corrosion of steel is common in lubricants. The concentrations and relative distribution patterns of the wear metals considerably vary among application and conditions of use. Iron concentration in WLO is generally in the range of 50-100 ppm [23]. Figure 5.6(e) shows that iron IQR range is narrow for industry and garage producers, varying from 124 to 227 ppm and from 131 to 264 ppm, respectively. On the other hand, “others” is characterized by large dispersion, ranging from 124 to 942 ppm, with a maximum concentration of 1195 ppm. Statistically one may refer that garage waste oils are characterized by a mean content of iron less than others producers. The same result is observed for silicon, which commonly is present in WLO in a range from 30 – 120 ppm, due to sediment contamination or some brake fluids.

Besides functional groups from mineral base oil and additives, FTIR spectra allow the detection of contaminants from oil usage or poor handling by WLO producers. Figure 5.7 shows typical examples of IR spectra of WLO samples from different producers. It is observed that samples from all producers display strong peaks in the region 3050 – 3650 cm^{-1}, characteristic of O-H vibrations. These vibrations can be related to the O-H stretching and the H-O-H bending bands of water and also by glycol or other alcohols [29]. In-plane H-O-H bending vibration are also detected at 1640 cm^{-1}. Peaks in the region of 1040 and 1080 cm^{-1} observed for garage and others producers are attributed to antisymmetric vibrations of the C-O-C moiety, which indicates the presence of ethylene glycol or other ethers commonly used as antifreeze agents, partially miscible with oil. In addition, a broad band in the region 1060-1130 cm^{-1} characteristic for antisymmetric vibrations C-O-C in samples of brake fluid based on ethylene glycol ethers is also evident in the industry sample [30–32].

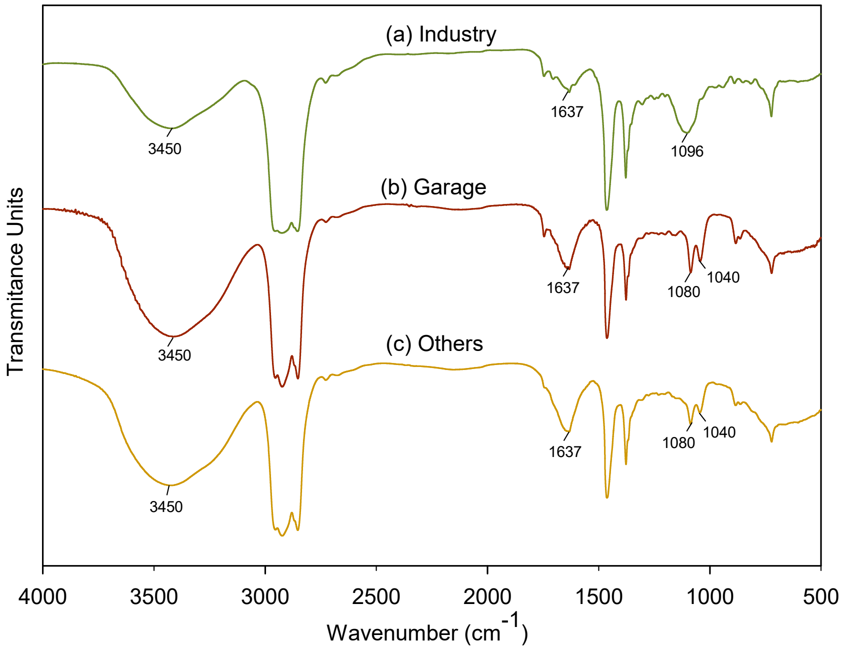


Figure 5.7. FTIR spectra of WLO collected from a) industry, b) garage and c) others.

It must be highlighted that the samples analyzed by FTIR in this study were collected according to the volume of oils locally produced. FTIR spectra analysis revealed that about 60% of all samples showed the presence of groups -OH at 3650 – 3050 cm^{-1}, H-O-H at 1640 cm^{-1} and C-O-C at 1040 and 1080 or 1060-1130 cm^{-1}, which in lubricant oils are typically due to ethylene glycol contamination from brake fluids or antifreeze. Glycol contaminations are critical for WLO regeneration, and a limit of 1 wt. % in WLO for regeneration are imposed by national legislation (Table 5.2). Brake fluids and antifreeze agents have very different chemical composition compared to mineral or synthetic type lubricants such as engine oil, gear, hydraulic, turbine, compressor, cutting fluid, metalworking, etc. From the recovery point of view, immiscibility of glycol with mineral oil is a positive factor enabling at least partial separation of these contaminants via simple centrifugation or decantation. Nevertheless, it is of great importance the segregated collection of used brake fluid and antifreeze regardless of the type of producer to prevent WLO contamination with glycol compounds.

5.4. CONCLUSIONS

The continuous maximization of regeneration targets requires a thorough understanding of WLO properties. One of the main limitations in WLO management systems that hinders the increase of regeneration rates are the wide variability in certain physicochemical characteristics of the collected oils, which are strongly affected by the incorrect handling by producers. Data obtained by the characterization of thousands of samples of WLO collected in Portugal from 2008 to 2015, have shown that 57.4% of the samples exceeding chlorine limits (> 2000 ppm) come from industrial producers. The possibility of segregation of industrial WLO to prevent contaminations of others oils with chlorine should be investigated. The nonconformity of PCB content has been a rare event in Portugal, with just 25 cases registered in the last 8 years. The characterization in the lab of 60 samples collected in 2015 by FTIR analysis suggested high contamination levels of WLO with glycol compounds. These molecules are mainly originated from brake fluids and antifreeze agents which are very different chemically from lubricant oils. Thus, these fluids must be segregated in the WLO producer to increase the efficiency of the management system. Future implementation of these improvements in the current collection system should take into account logistic and economic viability analysis.

5.5. REFERENCES

[1] R. Vazquez-Duhalt, Environmental impact of used motor oil, Sci. Total Environ. 79 (1989) 1-23.

[2] V. Kanokkantapong, W. Kiatkittipong, B. Panyapinyopol, P. Wongsuchoto, P. Pavasant, Used lubricating oil management options based on life cycle thinking, Resour. Conserv. Recycl. 53 (2009) 294–299.

[3] A. Kupareva, P. Mäki-Arvela, D.Y. Murzin, Technology for rerefining used lube oils applied in Europe: A review, J. Chem. Technol. Biotechnol. 88 (2013) 1780–1793.

[4] V. Monier, E. Labouze, Critical Review of Existing Studies and Life Cycle Analysis on the Regeneration and Incineration of Waste Oils.

http://ec.europa.eu/environment/waste/studies/oil/waste_oil.pdf, 2001 (accessed 20 September 2016).

[5] European Commission, Waste oils.

http://ec.europa.eu/environment/waste/oil_index.htm, 2016 (accessed 6 October 2016).

[6] M. Yu, H. Ma, Q. Wang, Research and recycling advancement of used oil in China and all over the world, in: Seventh International Conference on Waste Management and Technology (ICWMT 7), Beijing, 2012, pp. 239–243.

[7] A. Pires, G. Martinho, Waste lubricant oil management in Portugal: The experience of an extended producer responsability approach, in: 3rd International Conference on Industrial and Hazardous Waste Management, Crete, 2012, pp. 1–8.

[8] A. Pires, G. Martinho, Life cycle assessment of a waste lubricant oil management system, Int. J. Life Cycle Assess. 18 (2013) 102–112.

[9] V. Kapustina, J. Havukainen, T. Virkki-Hatakka, M. Horttanainen, System analysis of waste oil management in Finland, Waste Manag. Res. 32 (2014) 297–303.

[10] V. Kapustina, M. Horttanainen, A review of the existing waste oil management systems, J. Solid Waste Technol. Manag. 42 (2016) 948–961.

[11] European-Commission, Development of guidance on extended producer responsibility (EPR).

http://ec.europa.eu/environment/waste/pdf/target_review/Guidance%20on%20EPR%20-%20Final%20Report.pdf 2014 (accessed 10 October 2016)

[12] OECD, Working group on waste prevention and recycling. EPR policies and product design: economic theory and selected case studies.

http://www.oecd.org/officialdocuments/publicdisplaydocumentpdf/?doclanguage=en&cote=env/epoc/wgwpr(2005)9/final, 2006 (accessed 29 September 2016).

[13] GEIR, Waste Framework Directive revision: European waste oil re-refining industry position.http://www.geir-rerefining.org/documents/GEIRpositionpaperWFDrevision_2016_FINAL.pdf, 2016 (accessed 15 October 2016).

[14] N. Gregson, M. Crang, S. Fuller, H. Holmes, Interrogating the circular economy: the moral economy of resource recovery in the EU, Econ. Soc. 44 (2015) 218–243.

[15] P. Ghisellini, C. Cialani, S. Ulgiati, A review on circular economy: the expected transition to a balanced interplay of environmental and economic systems, J. Clean. Prod. 114 (2016) 11–32.

[16] X. Zeng, J. Li, A.L.N. Stevels, L. Liu, Perspective of electronic waste management in China based on a legislation comparison between China and the EU, J. Clean. Prod. 51 (2013) 80–87.

[17] GEIR, An environmental review of waste oils regeneration. http://www.geir-rerefining.org/documents/PositionpaperGEIR161104.pdf, 2004 (accessed September 15 2017).

[18] C. Kajdas, Major pathways for used oil disposal and recycling. Part 1, Tribotest 7 (2000) 61-74.

[19] A. Pires, G. Martinho, Carbon footprint analysis for the waste oil management system in Portugal, Br. J. Environ. Clim. Chang. 2 (2012) 278–287.

[20] BCTG, Technical guidelines on used oil re-refining or other re-uses of previously used oil. http://archive.basel.int/meetings/sbc/workdoc/old%20docs/tech-r9.pdf, 1995 (accessed 1 September 2016).

[21] APA, Especificações técnicas dos óleos usados.
https://www.apambiente.pt/_zdata/Politicas/Residuos/FluxosEspecificosResiduos/OU/Especificacoes_Tecnicas_Oleos_usados-Aprovado.pdf, 2015 (accessed 15 September 2016).

[22] J.G. Speight, D.I. Exall, Rerefining of Used Lubricating Oils, CRC Press, Boca Raton, 2014.

[23] F. Audibert, Waste Engine Oils. Rerefining and Energy Recovery, Elsevier Science & Technology Books, Amsterdam, 2006.

[24] Z. Pawlak, Tribochemistry of Lubricating Oils, Elsevier, Amsterdam, The Netherlands, 2003.

[25] C. Kajdas, Major pathways for used oil disposal and recycling. Part 2, Tribotest 7 (2000) 137-153.

[26] E.J. Ekanem, J.A. Lori, S.A. Thomas, The determination of wear metals in used lubricating oils by flame atomic absorption spectrometry using sulphanilic acid as ashing agent, Talanta. 44 (1997) 2103–8.

[27] T. Mang, W. Dresel, Lubricants and Lubrication, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2007.

[28] F. Audibert, Les Huiles Usagées: Reraffinage et Valorisation Énergétique, Edition Technip, Paris, 2003.

[29] E. Dominguez-Rosado, J. Pichtel, Chemical characterization of fresh, used and weathered motor oil via GC/MS, NMR and FTIR techniques, Proc. Indiana Acad. Sci. 112 (2003) 109–116.

[30] J. Lengyel, C. Ján, Non-lubricant related compounds in used mineral oils, Pet. Coal. 51 (2009) 237–243.

[31] F.R. Van De Voort, J. Sedman, R. a. Cocciardi, D. Pinchuk, FTIR condition monitoring of in-service lubricants: ongoing developments and future perspectives, Tribol. Trans. 49 (2006) 410–418.

[32] A. Borin, R.J. Poppi, Application of mid infrared spectroscopy and iPLS for the quantification of contaminants in lubricating oil, Vib. Spectrosc. 37 (2005) 27–32.

6. A DATA-DRIVEN APPROACH FOR THE STUDY OF COAGULATION PHENOMENA IN WASTE LUBRICANT OILS AND ITS RELEVANCE IN ALKALINE REGENERATION TREATMENTS

Coagulation phenomena can occur in certain types of waste lubricant oils (WLO) during regeneration processes involving alkaline treatments, causing plant shutdowns. In this context, this study addresses the nature of the compounds responsible for the coagulation phenomena after the alkaline treatment. For such, an empirical test was developed to assess the coagulation behavior of WLO, consisting in the addition of KOH to the WLO followed by heating under stirring conditions. This test was performed on 133 samples and four coagulation classes were identified: A; B1; B2 and C. Moreover, a physicochemical characterization of WLO was carried out regarding viscosity at 40°C, saponification number (SN), total acid number (TAN), surface tension, water content, elemental analysis and functional groups (FTIR). 56 samples of fresh lubricant oils for different applications were also characterized and their properties assessed and compared. Multivariate methods were applied to WLO to discriminate among coagulation classes based on FTIR spectra. It was found that coagulation classes A and B1 exhibit statistically similar patterns for all properties determined. Spectral discriminating analysis did not reveal discriminant peaks for class B1 samples, and the presence of specific additives was pointed as the possible factor underlying the increase in viscosity in this oils. Class B2 presents the absence of additives and oxidation products as differentiating features. In addition, B2 samples showed lower TAN and SN values, and lower concentration of some elements. Lubricants from gear or hydraulic applications can give rise to this class of WLO. Oils of Class C are mainly composed by synthetic ester type base oils, which hamper regeneration processes making use of alkaline pretreatments. In future studies, WLO type A and B1 can be classified as a single class. The coagulation phenomena classification becomes A – negative, B – precipitate formation and C – positive.

KEYWORDS

Waste lubricant oil; regeneration; coagulation phenomena; classification; characterization; FTIR spectroscopy.

This chapter is based upon the publication:

Pinheiro, C.T., Ascensão, V.R., Reis, M.S., Quina, M.J., Gando-Ferreira, L.M., 2017. A data-driven approach for the study of coagulation phenomena in waste lubricant oils and its relevance in alkaline regeneration treatments. Sci. Total Environ. 599–600, 2054–2064. doi:10.1016/j.scitotenv.2017.05.124.

6.1. INTRODUCTION

Waste lubricant oil (WLO) is one of the most significant hazardous waste streams across the world. Regeneration of WLO represents the best recovery option. Besides the direct environmental and public health benefits, regeneration mitigate the significant environmental burden of the primary production of lubricants, conserving energy and natural resources, and offering also economic advantages [1,2]. More specifically, the regeneration process aims at restoring the performance properties of WLO nearly to its original condition. Thus, it involves the removal of contaminants, oxidation products and additives, as well as recovering undamaged hydrocarbons molecules to yield base oil for the manufacture of lubricating products. Current regeneration technologies include physical or chemical pretreatment, atmospheric and vacuum distillation, solvent extraction, activated clay adsorption or hydrotreatment as finishing steps [3]. Modern regenerated products can fulfil high quality standards with equivalent quality to some base oil groups on the market [2,4].

The technical performance of regeneration processes is seriously affected by the feedstock's chemical composition, especially in technologies using chemical pretreatments [2]. The addition of a strong alkali agent, such as potassium hydroxide (KOH), is a common treatment adopted to increase the removal of contaminants and reduce plant fouling. Comparing to NaOH or LiOH, KOH was found to be the best degrading agent, because it ionizes quickly in water, forming stronger nucleophile OH^- ions to break polar bonds [5]. In fact, the addition of an aqueous solution containing hydroxides, allows for the formation of low solubility metal salts, causing their precipitation [6,7]. The alkali is also an effective agent in neutralizing acids and free or bound chlorine [4].

However, given the complexity of the WLO matrix, which comprises a wide variety of compounds, the alkali can interact with the oil in many different ways. WLO are considered colloidal multicomponent disperse systems comprising a dispersion medium (the base oil) and a dispersive phase (liquid or solid additives), which may accumulate contaminants such as oxidation products, metals, mechanical impurities and water [8,9]. The stability of the colloidal system is mainly related to electrostatic repulsive forces between the particles. Addition of a strong electrolyte, such as KOH, results in a compression of the electrical double layer surrounding each suspended particle by the interaction of oppositely charged ions (counter ions) on the surface of the colloids. The attractive forces become relevant and a destabilization of the particles occurs, i.e. the particles may interact, resulting in aggregate formation (coagulation) by Van der Waals forces [10,11]. In addition, under certain operating conditions (e.g. temperature, concentration of alkali solution, stirring, etc.), KOH promotes saponification reactions between long chain fatty acids or esters and the alkali, yielding a salt of the alkali, called soap [12]. Soaps impart a thickening effect on the oil, which in enough quantity can lead to the production of a gel-type oil [13]. In fact, a number of metallic soaps can be formed by a series of reactions. The production of metal salts of fatty acid can be a two-step process: production of potassium soap followed by its reaction with a metal salt that produce a metal soap, Eqs. (6.1) and (6.2). The reaction of fatty acids with metal oxides, hydroxides or carbonates can also form metal soaps, Eqs. (6.3-6.5) [14–16].

$$\underset{\text{Fatty acid}}{R-COOH} + \underset{\text{Potassium hydroxide}}{KOH} \rightarrow \underset{\text{Potassium soap}}{R-COOK} + H_2O \tag{6.1}$$

$$\underset{\text{Potassium soap}}{2R-COOK} + \underset{\text{Metal salt}}{MX} \rightarrow \underset{\text{Metallic soap}}{(R-COO)_2M} + \underset{\text{Potassium salt}}{K_2X} \tag{6.2}$$

$$\underset{\text{Fatty acid}}{2R-COOH} + \underset{\text{Metal oxide}}{MO} \rightarrow \underset{\text{Metallic soap}}{(R-COO)_2M} + H_2O \tag{6.3}$$

$$\underset{\text{Fatty acid}}{2R-COOH} + \underset{\text{Metal hydroxide}}{M(OH)_2} \rightarrow \underset{\text{Metallic soap}}{(R-COO)_2M} + 2H_2O \tag{6.4}$$

$$\underset{\text{Fatty acid}}{2R-COOH} + \underset{\text{Metal carbonate}}{MCO_3} \rightarrow \underset{\text{Metallic soap}}{(R-COO)_2M} + H_2O + CO \tag{6.5}$$

where M is a metal (Ca, Al, Zn, Pb, Cu, etc.) and X is an anion (Cl^-, SO_4^{2-}, etc.).

The occurrence of this phenomenon, hereinafter called “coagulation phenomena”, is highly detrimental for the regeneration process. The production of a gel during separation steps reduces the lubricant’s fluidity, possibly causing blocking problems in the plant [17]. Consequently, WLO with these characteristics cannot be subject to regeneration and must be managed by other alternative ways according to the waste treatment hierarchy, such as recycling or energy recovery.

To the best of our knowledge, the coagulation phenomena that occur in WLO subjected to alkali regeneration treatments have never been addressed in the literature and is not yet fully understood in the regeneration industry. The identification of compounds that cause these phenomena is of paramount importance since it could allow their segregation from waste oils generated by different producers and reduce the rejection of WLO loads to regeneration. In this article, we will explore the capabilities of Fourier transform infrared spectroscopy (FTIR) for this purpose.

FTIR is a powerful tool to detect functional groups that can help in the identification of compounds responsible for the coagulation phenomena. However, due to the bare nature of WLO, a direct and unambiguous discrimination among oils through the interpretation of isolated bands in the spectrum may be hampered by the complexity of the oil matrix and can be misleading. In this context, multivariate data analysis techniques applied to FTIR have demonstrated to provide very useful insights due to their ability to extract relevant information from high-dimensional spectral data. Researchers have reported the use of chemometric tools for performing classification and identification of compounds based on FTIR in a wide variety of applications. Examples include: monitoring wood biodegradation using multivariate analysis to correlate chemical composition in wood samples with the FTIR spectral data [18]; classification of blue pen ink according to types and brands [19]; classification and identification of bacteria [20,21]; evaluation of adulteration in olive oil [22–24]; identification of different apple varieties [25]; separation between defective and non-defective coffees [26]; among many other examples. In lubricant analysis, FTIR has been used to: predict properties [27]; characterize qualitatively different constituents in the scope of monitoring lubricant oil degradation [28,29]; evaluate the adulteration of high quality motor oils samples with lower quality oils [30]; distinguish between samples with varying degrees of use [31]; classify the lubricating oil type (mineral, synthetic or semi-synthetic) [32].

In this context, the main objective of this work is to identify the main compounds causing coagulation phenomena during the alkali pretreatment in regeneration processes and to devise a quick procedure to signal a potential harmful WLO for the regeneration process. Thus, a physicochemical characterization of WLO was performed and fresh lubricant oil samples were also characterized with the purpose of comparing their properties with those from WLO. In addition, multivariate statistical analysis combined with FTIR spectroscopy was used as a tool to classify waste oils according to their regeneration potential and to identify the compounds that restrain regeneration.

6.2. MATERIALS AND METHODS

6.2.1. SAMPLING

A set of 133 waste lubricant oil samples were collected in Portugal from different WLO producers (garages, industry and others) across the country. The samples were selected in order to have an equitable distribution of the coagulation test results (described in Section 6.2.2). The waste oil was taken from the producers during the pumping of WLO to tank trucks. These trucks transport WLO to specific plants that are part of the integrated waste oil management system implemented in the country. About 0.5 L of sample were collected in each case in airtight plastic bottles and then stored at room temperature in the dark to maintain their integrity until analysis.

Additionally, a set of 56 fresh oil samples were selected based on the most representative lubricants currently available in the Portuguese market. A variety of commercial brands designed for different applications was considered, including cutting fluids (N = 2 samples), hydraulics (N = 4), gear (N = 11), engine (N = 31), marine (N = 2) and others (N = 6), from a total of 11 different producers.

6.2.2. COAGULATION TEST

The coagulation test is an empirical method often used in the regeneration industry to evaluate potential adverse reaction of WLO during alkaline pretreatment phase. Potassium hydroxide (KOH) is added in excess to ensure the detection of these reactions and avoid blocking problems in the regeneration plant. The test involves the addition of 10 g of an aqueous solution of KOH (50 wt. %) to 100 g of WLO and then heated up to 180 °C under magnetic stirring. The mixture is then cooled down to room temperature. The outcome of the test is one of the classes presented in Table 6.1.

Table 6.1. Possible outcomes of the coagulation test.

Coagulation class	Observation
A	Oil matrix remains unaffected.
B1	Viscosity increase.
B2	Precipitate formation.
C	Gel-type oil formation.

6.2.3. PHYSICOCHEMICAL CHARACTERIZATION

All WLO samples were characterized according to the physicochemical properties described next. The data set of fresh lubricant oils was analyzed regarding, viscosity at 40 °C, total acid number (TAN), saponification number (SN) and elemental content.

Kinematic viscosity was obtained at 40 °C according to ASTM D7042, using an Anton Parr-SVM 3000 Stabinger Viscosimeter.

Water content in oil samples was determined by coulometric Karl Fischer titration using the Mettler Toledo C20 KF Coulometric Titrator. This determination was performed according to ASTM D6304 using HYDRANAL Coulomat Oil and HYDRANAL Coulomat CG as reagents. When water content is higher than 5% (w/w) the ASTM D95 distillation method was used, which allows for the quantification of water in the range from 0 to 25% (v/v) in petroleum products.

TAN was determined by potentiometric titration according to ASTM D664. Titrations were carried out using an alcoholic potassium hydroxide solution (0.1 M) to neutralize the lubricant acidic components. A mixture of toluene, isopropanol and water in a proportion of 50:49.5:0.5% (v/v) was used as titration solvent. TAN is expressed in milligrams of KOH required to neutralize the acidic constituents per g of oil.

SN was measured by potentiometric titration according to ASTM D94. Oil samples were dissolved in a mixture of a KOH alcoholic solution (0.5 M) and butanone (50 mL each). About 25 mL of white spirit solvent was added to dissolve organic samples (e.g. lube oil and some additives). The mixture was heated in total reflux for 30 min, and the condenser washed with 50 mL of naphtha. Lastly, the titration was accomplished with 0.5 M HCl. SN is defined as milligrams of KOH required to saponify fatty material present in one gram of oil.

The elemental content of P, Ca, Zn, S, Fe, Al, Cl and Si was determined by Energy Dispersive X-Ray Fluorescence (EDXRF) using a Nex CG Rigaku spectrometer according to ASTM D4927. About 4 g of lubricant was weighed to a sample cell Chemplex 1330 with a Polypropilene TF-240 film. Since no sample preparation was needed, the samples cell is placed on the equipment and the analysis was immediately performed.

Surface tension was determined using a KSV Sigma 70 tensiometer with a Wilhelmy plate, which procedure consists in raising a thin plate immersed into the liquid and measuring the force required to break the film formed between the liquid surface and the plate [33].

Fourier Transform Infrared (FTIR) spectroscopy spectra were recorded in transmittance mode using potassium bromide (KBr) pellets, prepared using a pneumatic press. One drop of lubricant was placed on the top of one pellet, creating a thin film, which was placed into an appropriate sample holder and immediately analyzed in a Jasco FT/IR – 4200. 64 scans/sample with a resolution of 4 cm-1 were carried out in the 4000-500 cm-1 range. Every analysis was performed using a different pellet and before each measurement a background spectrum was obtained using one clean pellet without lubricant.

Scanning electronic microscopy and energy dispersive X-ray spectroscopy (SEM-EDS) was performed on WLO solid residues after ignition at 550 °C to remove the organic matter and concentrate inorganic elements. SEM-EDS analyses were obtained in a ZEISS MERLIN Compact/VP Compact, field emission scanning electron microscope (FDSEM) coupled with an Oxford, X-MAXN Silicon Drift Detector. The chemical characterization of the residues was performed with a voltage of 10 KV.

6.2.4. CLASSICAL STATISTICAL ANALYSIS

Box-and-whiskers plots were used to summarize data and to identify univariate outliers. The software used for this purpose was Minitab® 17. The minimum (5th percentile), 25th percentile, median (solid line), 75th percentile, maximum (95th percentile), mean (⊕ symbol) and outliers (* symbol) were computed and analyzed, as well as the Interquartile range (IQR), which corresponds to the difference between the 75th and 25th percentiles. A statistical *t*-student test was performed and the *p*-value (significance level) was determined to compare means, using JMP® Pro 12 software [34]. A significance level of 5% was used for the statistical hypothesis tests. Coagulation classes with statistically different means (p-value <0.05) are indicated with different lowercase letters (a, b) in the box-and-whiskers plots.

6.2.5. CHEMOMETRIC METHODS

Chemometric methods were used to cope with the high-dimensionality and strong correlation of FTIR spectra. A procedure was devised to develop a classification model for predicting the coagulation class from FTIR data, following three fundamental steps: preprocessing, dimension reduction and classification. All spectra collected were preliminarily preprocessed in order to maximize the extraction of predictive information concerning the coagulation phenomena. The preprocessing used included the following operations: Binning, Median Centering and Multiplicative Scatter Correction). Given the high-dimensionality of the data set composed by the 133 spectra, and the redundancy among such variables (transmittance for each wavelength), a supervised multivariate projection methodology was adopted for dimension reduction, namely Partial Least Squares for Discriminant Analysis [35]. In this way, the original high-dimensional samples were projected onto a lower dimensional subspace that contains information for discriminating among the several coagulation classes under analysis. The dimensionality of this space was preliminarily determined by cross-validation. The classification step involved the implementation of a discriminant classifier in the low dimensional PLS-DA subspace, in order to attribute the coagulation class to each sample under analysis. Fisher discriminant analysis (FDA) was the classifier adopted for this task. More specifically, the linear Fisher classifier, given its parsimonious and optimal discriminating properties for Gaussian clusters with similar distributions.

The classification performance of the composite PLS-DA/FDA mapping was rigorously accessed through a conservative and robust Monte-Carlo Cross-Validation protocol. In brief terms, this protocol consists in dividing all the available samples in K groups (in our case, K=10), K-1 of them being used to develop the classifier (estimate the PLS-DA and FDA models) and the other one to assess its performance under testing conditions. This process is repeated for all the K groups, so that one is kept aside once and only once, and the associated predictions recorded. In order to stabilize the estimate of the prediction accuracy, this cycle was repeated again 10 times (after reshuffling all observations), and the prediction accuracy in the test sets recorded. In this work, we will report the mean of the true classification rates obtained in all the cross-validation cycles, i.e., the average accuracy rate.

Besides the development of classification models, a spectral discriminating analysis was also performed, in order to identify the chemical origin of what makes a given class unique and different from all the others. This analysis will be described in Section 6.3.5.

6.3. RESULTS AND DISCUSSION

6.3.1. COAGULATION

As mentioned above, the coagulation test is important to prevent that this phenomenon may occur in a regeneration plant during the alkaline pretreatment. However, it does take some time to perform and it would be very useful to have at our disposal a fast procedure that could signal, with high accuracy, potentially problematic WLO – this is the purpose of using FTIR as the basis for developing the classification procedure, whose results will be presented further ahead in this article. For developing this classifier, the coagulation classes for all the samples were previously determined. Therefore, the coagulation tests were conducted for the 133 samples, which revealed four different patterns that were classified as indicated in Table 6.1. A prototype of each class (A, B1, B2 and C) is shown in Figure 6.1.

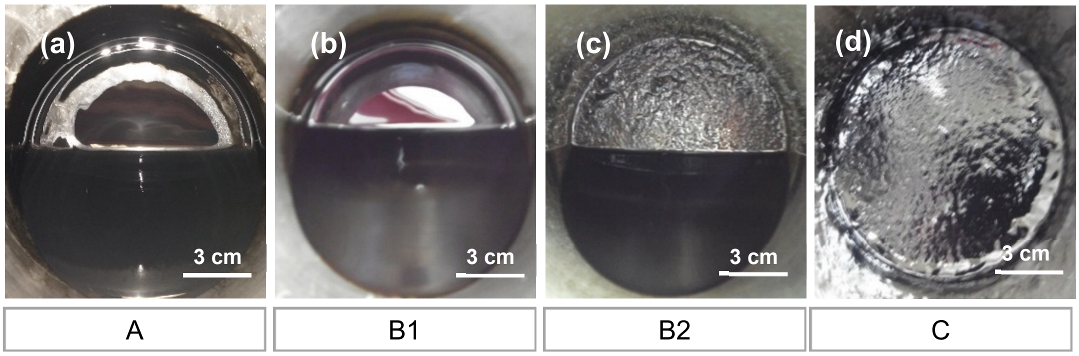


Figure 6.1. Outcome of the coagulation test. The Figure shows the vessel in which the coagulation test was performed and the different behavior of WLO after the addition of KOH under specific conditions, which were classified as: (a) class A - negative; (b) class B1 - viscosity increase; (c) class B2 - precipitate formation and (d) class C - positive.

In Figure 6.1(a) it can be observed that the oil matrix can remain unaffected with the addition of KOH to the WLO, a result that was categorized as a negative result (class A). In contrast, the test was classified as positive (class C) if the addition of KOH forms a gel-type oil that impedes further regeneration, as shown in Figure 6.1(d). Intermediate results observed are classified as a viscosity increase (class B1) if a significant change on viscosity (about 500% over the original value of each sample, which mainly varied from 65 – 91 cSt) is detected but the WLO can still be regenerated, depicted in Figure 6.1(b). Precipitate formation (class B2) is assigned if more than 10% of the mass of WLO precipitates, presenting high risk of plant fouling, as illustrated in Figure 6.1(c). Consequently, it is assumed that WLO which originate classes B2 and C after KOH addition are problematic for regeneration processes involving alkali treatment. Among the 133 samples analyzed, 24.1% were classified as coagulation class A, 26.3% as class B1, 17.3% as class B2 and 32.3% of class C.

6.3.2. PHYSICOCHEMICAL CHARACTERIZATION

Since it was considered that the coagulation behavior of WLO samples may be a crucial aspect, the physicochemical data was grouped as a function of classes A, B1, B2 and C. Figure 6.2 shows the characterization of WLO regarding total acid number (TAN), saponification number (SN), kinematic viscosity at 40°C, water content and surface tension. Figure 6.3 presents the elemental content of P, S, Ca, Zn, Fe, Al, Cl and Si in WLO.

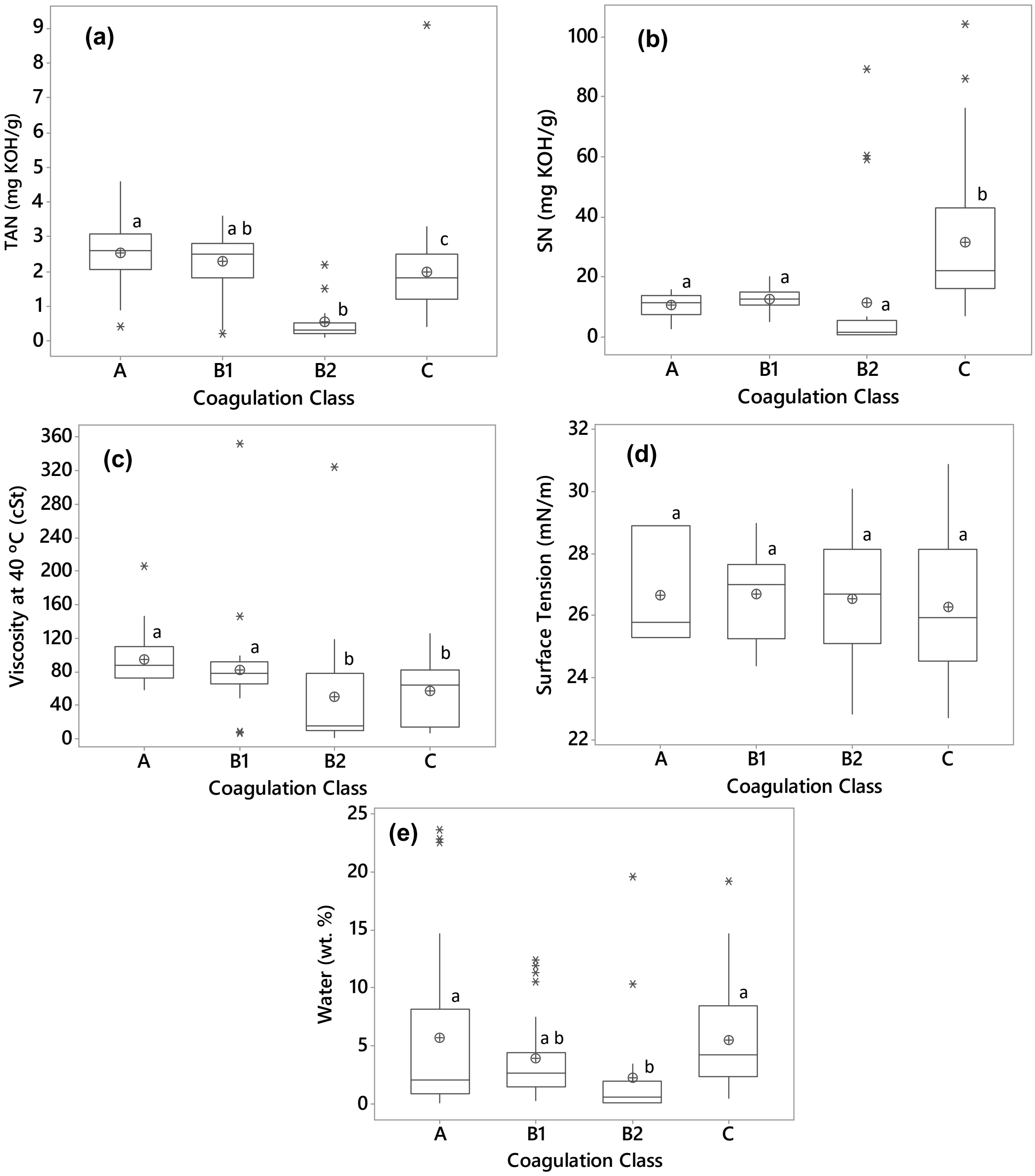


Figure 6.2. Physicochemical properties of waste oils by coagulation class: (a) TAN; (b) SN; (c) kinematic viscosity at 40°C; (d) water content; (e) surface tension.

In Figures 6.2 and 6.3 one can observe that according to the *t*-Student's test for the pairwise comparison of means, coagulation classes A and B1 exhibit statistically similar behavior (boxes marked with a) for all the determined properties. These results indicate that small differences in the chemistry of WLO may lead to similar physicochemical properties but with different coagulation results.

Class B2 reveals statistically differences and significantly lower distribution of TAN comparing to the other classes, Figure 6.2(a). 50% of the TAN values are in the range from 0.2 to 0.5 mg KOH/g, compared to about 1 to 3 mg KOH/g for the other classes. It should be noted that 9 out of the 23 samples in class B2 have TAN values below the equipment's quantitation limit (0.05 mg KOH/g).

Table 6.2 illustrates the physicochemical characteristics of the fresh lubricant oil samples studied in this work. The results show that lower TAN values are associated with cutting fluids, gear, hydraulic and other applications, when compared to the range of values found for engine and marine oils. This can be explained by attending to the fact that lubricants for automotive or marine combustion engines have a higher volume of additives to increase its service time, which in turn contributes to an increase of the TAN value of the fresh lubricant [4].

Table 6.2. Physicochemical characterization of 56 samples of fresh lubricant oils.

	Viscosity at 40 °C (cSt)	**TAN (mg OH/g)**	**SN (mg KOH/g)**	**P (ppm)**	**Ca (ppm)**	**Zn (ppm)**	**S (%)**
Cutting fluid (N = 2)							
Mean	13	0.66	10.80	10	4396	<QL	0.6
Max	22	1.30	20.80	20	8750	<QL	1.3
Min	4	0.03	0.80	<QL	42	<QL	0.0
Sd	9	0.64	10.00	10	4354	---	0.6
Gear (N = 11)							
Mean	174	1.10	6.69	605	531	557	0.8
Max	491	2.21	32.15	1500	3700	1370	2.2
Min	19	0.38	1.74	241	39	<QL	0.0
Sd	162	0.56	8.22	388	1081	575	0.7
Hydraulic (N = 4)							
Mean	38	0.88	0.89	365	559	540	0.5
Max	48	2.11	1.24	399	1690	1200	0.9
Min	22	0.31	0.64	329	107	48	0.3
Sd	10	0.72	0.24	25	659	416	0.2
Engine (N = 31)							
Mean	93	2.73	3.64	929	2564	1034	0.5
Max	149	5.35	13.66	1340	4240	1380	1.3
Min	51	0.93	0.11	492	113	585	0.1
Sd	20	0.73	2.37	205	845	183	0.3
Marine (N = 2)							
Mean	125	1.58	2.72	781	3400	746	0.8
Max	141	1.99	2.77	947	4290	946	0.8
Min	109	1.16	2.66	614	2510	546	0.8
Sd	16	0.41	0.06	166.5	890	200	0.0
Others (N = 6)							
Mean	41	0.13	15.81	20	44	<QL	0.2
Max	77	0.43	64.24	81	58	<QL	0.7
Min	10	0.00	1.27	<LQ	40	<QL	<LQ
Sd	26	0.15	23.07	30	6	---	0.3

QL – quantitation limit
Sd – standard deviation

In Figure 6.2(b) and (e) one can observe that for SN and water content, the distribution of values of the class B2 is clearly bellow the distributions for the other classes. Mean values are influenced by outliers, which for SN and water content increase considerably its value and bias the *t*-Student's test. Figure 6.3 shows that class B2 presents lower concentration of elements (P, S, Ca, Zn, Al and Cl) than the other classes. In general, hydraulic fluids display the lowest SN (Table 6.2), and thus class B2 waste oils might come from this application.

The lowest concentration of elements from the additives such as P, S, Ca and Zn is typically found in gear, hydraulic and lubricants for other applications, as demonstrated in Table 6.2. Therefore, one can conclude that class B2 has clearly distinct physicochemical properties in comparison with other classes and may be originated from lubricants applied in gears or hydraulic systems.

Class C displays SN values statistically different and higher than the other classes: in the range of 16 and 43 mg KOH/g. These results show that samples with high SN values have a strong tendency to originate a class C in the coagulation test.

Regarding viscosity results, Figure 6.2(c), class B2 and C show statistically similar mean values but lower than A and B1. Although both classes have an asymmetric distribution, class B2 viscosity values are more concentrated at the bottom of the IQR interval, about 50% of the class B2 values lie below 15 cSt and class C values more concentrated at the top range of the IQR interval, above 60 cSt. It should be noted that an outlier value of 324 cSt in class B2 has a pronounced influence in the mean calculation, increasing its value. Considering the median values, class B2 has significantly lower viscosity values compared to the other classes. Viscosity is one of the most important properties in lubricant oils, which can provide useful information about its formulation, including base oil type, additives and indicate the presence of contamination in waste oils [36]. The results indicate that, in general, the chemical composition of class B2 oils is different compared to other classes, that leads to lower viscosity oils. The comparison between the viscosity of WLO and fresh lubricants analyzed in this work (Table 6.2) is difficult since extensive degradation of molecules during service may occur, as well as external contamination with low molecular weight compounds such as fuel.

Regarding the surface tension results, in lubricant oils it can be strongly dependent on the presence of surfactants or other additives since they alter the balance of intermolecular forces in the liquid-gas interface [37]. The charges on polar head groups of surfactants are expected to have significant effects on the colloidal behaviour. However, the surface tension determinations did not show significant differences between coagulation classes, the IQR interval varying from 24 to 29 mN/m. The values obtained are in good agreement with those found in the literature for different types of lubricants, which report surface tensions between 26 and 30 mN/m [38].

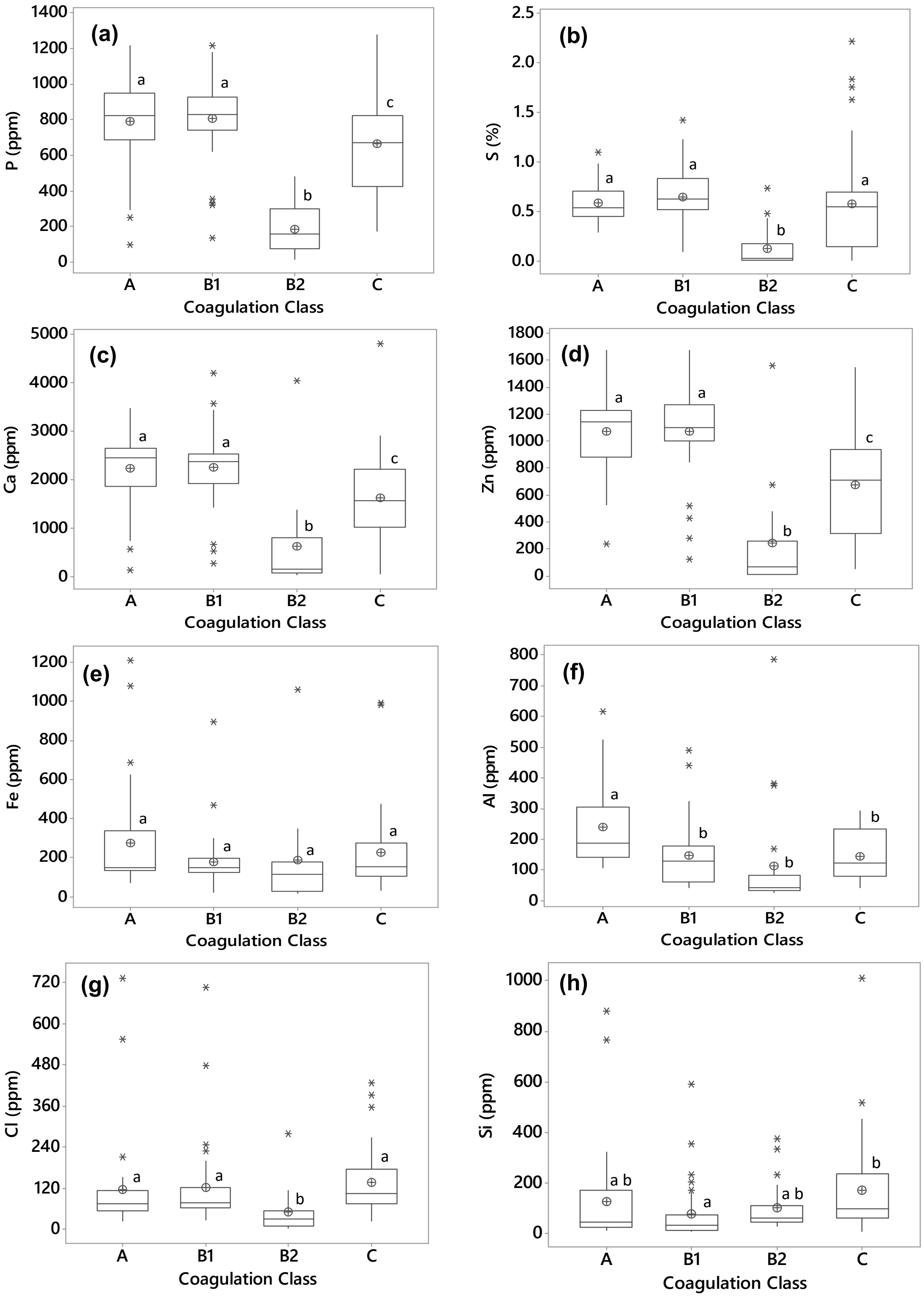


Figure 6.3. Content of P, S, Ca, Zn, Fe, Al, Cl and Si in waste oils by coagulation class.

6.3.3. FTIR ANALYSIS

In general, IR spectroscopy is a useful technique for the identification of organic compounds and functional groups, but for WLO the analysis is quite complex. Figure 6.4 shows the typical characteristic absorption bands in FTIR spectra of WLO for different coagulation classes.

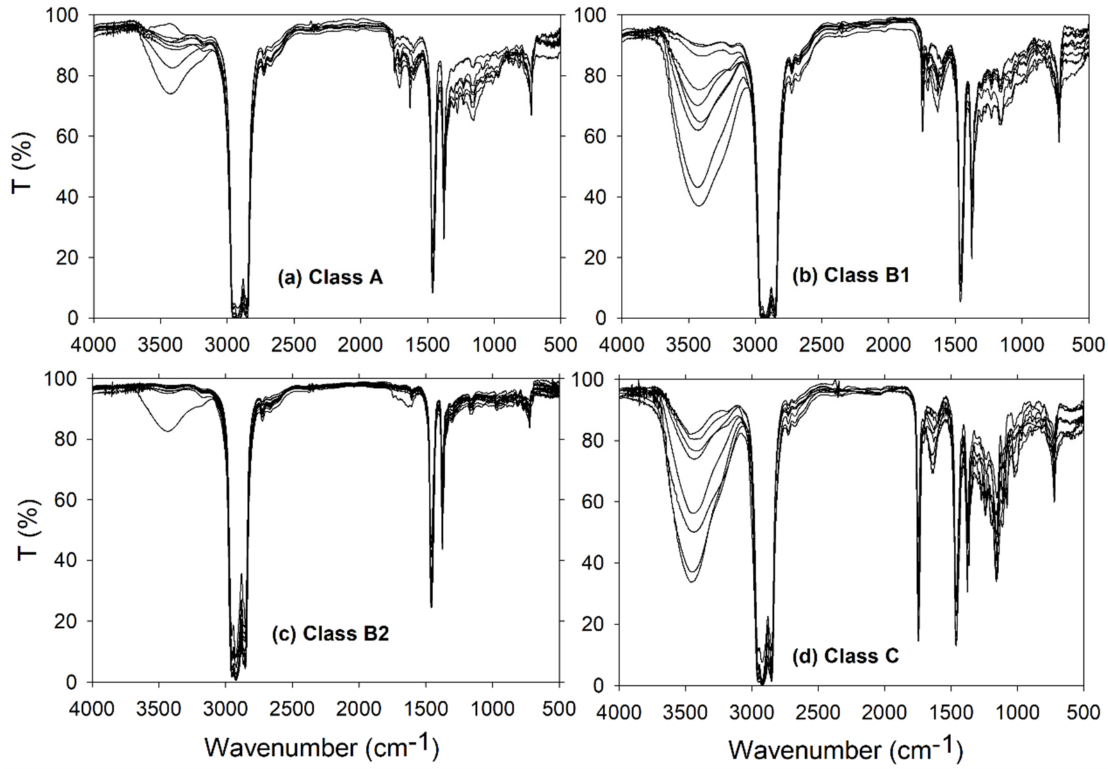


Figure 6.4. FTIR spectra of waste lubricant oils typically corresponding to classes A, B1, B2 and C.

Given the complexity of the WLO matrix, which comprises a large variety of compounds, the differentiation of coagulation classes by FTIR can be extremely difficult. In general, samples belonging to all coagulation classes show multiple bands in the 2980 – 2836 cm^{-1} region associated with –CH$_2$ e -CH$_3$ stretching vibrations and peaks at 722, 1376 and 1460 cm^{-1} corresponding to –CH and =CH groups. These bonds are characteristic of aliphatic components from the base oil, whose origin can be mineral, synthetic or semisynthetic. In fact, the infrared spectrum of synthetic type oils such as polyalphaolefins is often indistinguishable from mineral hydrocarbons. One distinct feature of the spectra of samples belonging to class C is the intensity of the peaks at 1750 cm^{-1} and of 1250 – 1100 cm^{-1}, which indicates the presence of synthetic ester type oils.

FTIR spectroscopy is also a powerful technique to identify many of the chemical properties of used lubricants, related to the presence of additives, which were found in general in all samples. P-O-C bands associated with zinc dithiophosphates (e.g. ZDDP) lie around 920-1050 cm^{-1}, depending on the organic nature of the compound. The vibrational frequency characteristic P = S bonds is between 800 – 600

cm^{-1} [31]. Sulfur-based S-O absorptions associated with the presence of sulfonates in engine lubricant oil additives exhibit characteristic peaks at 1376 and 1152 cm^{-1} [40]. Overbased calcium sulfonates absorb at 850 and between 1490-1410 cm^{-1}. Dispersants such as succinimides exhibit weak absorption bands that can be overlapped by other components, making their identification difficult from the infrared spectrum. However, N-H bands are found at 3220 cm^{-1}, C = O absorptions between 1750 – 1670 cm^{-1} and vibrational bands C-N and N-H at 1310 – 1210 cm^{-1} [40]. Peaks around 1800 – 1700 cm^{-1} suggest the presence of polymethacrylates, used as viscosity modifiers or pour point depressants, and may also be identified at 1152 cm^{-1}. Vibrational frequencies of the hydroxyl (O-H) group from alcohols and phenols present in antioxidants can be detected around 3615 cm^{-1} [31,41].

Besides these compounds, FTIR spectra also allow for the identification of compounds associated with oil contamination. In the range of 3500-3350 cm^{-1}, one can observe a band related to O-H and H-O-H vibration groups from water (visible in classes A, B1 and C). This band can also be associated with oil contamination with ethylene glycol from antifreeze. In some samples, the peaks identified in the region between 1130-1060 cm^{-1} can be assigned to C-O-C vibration from ethylene glycol ethers. The increase of oil degradation products such as carboxylic acids, ketones, aldehydes and other salts may contribute to the increase of carbonyl groups (C=O) that are detected between 1750-1700 cm^{-1}.

The use of single peaks or narrow wavenumber ranges to obtain useful information to distinguish between coagulation classes only by visual observation is very difficult. The differences among FTIR spectra of different coagulation classes revealed to be clearly small and occurred only in limited regions for specific samples. Therefore, FTIR data was processed with chemometric multivariate statistical analysis techniques, better suited to extract useful chemical information for high-dimensional data sets.

6.3.4. CLASSIFICATION OF THE COAGULATION CLASSES

Infrared spectroscopy combined with advanced multivariate analysis is a powerful alternative to the analytical coagulation test, given the fast implementation for assessing the WLO potential for regeneration. Figure 6.5 shows the project observations of all WLO samples, according to their coagulation classes, onto the reduced space of the first two discriminant functions of the PLS-DA/FDA composite mapping. The discriminant functions were calculated from the FTIR spectra by linear combination of the transmittances at different wavenumbers using a PLS-DA/FDA composed mapping. The spatial distribution of the samples indicates the possibility of a rapid discrimination among some of the coagulation classes. The smaller the overlap between classes, the greater discrimination capability of the method.

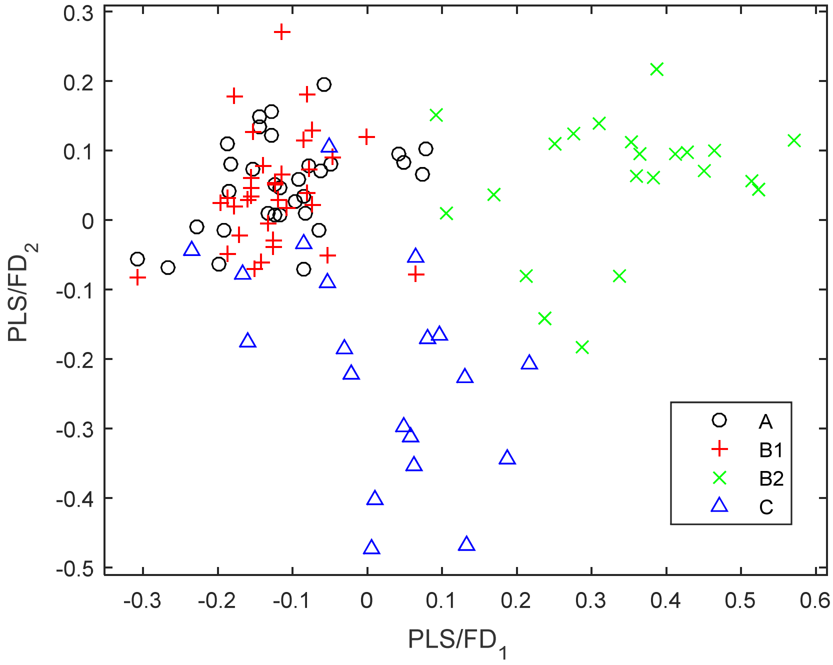


Figure 6.5. Projection of FTIR spectra for all the WLO samples onto the two-dimensional output subspace of the composite PLS-DA/FDA mapping.

On the basis of the distribution of projections obtained for the different classes, one can infer the existence of some clear patterns. Figure 6.5 shows that coagulation classes A (○ symbol) and B1 (+ symbol) present an extensive overlap and are virtually indistinguishable from the standpoint of the IR spectral bands analyzed. On the other hand, these classes (A and B1) are perfectly separated from class B2 (x symbol) and reasonably well separated from class C (Δ symbol). Classes B2 and C are also reasonably separated from each other. Thus, FTIR spectra confirm what was found in the aforementioned physicochemical characterization that WLO from classes A and B1 have similar chemical compositions. In contrast, the classes B2 and C exhibit particular characteristics that allow for their discrimination.

In this context, different arrangements of classes and classification models were considered to discriminate among them (i.e., several PLS-DA/FDA composite models, one for each scenario of class agglomeration). Table 6.3 presents the average classification accuracy (under cross-validation conditions) for each scenario.

Table 6.3. Coagulation accuracy rate for different clusters of coagulation classes.

Class combination	Average Accuracy Rate (under cross-validation)
{A} vs {B1} vs {B2} vs {C}	0.59
{A} vs {B1} vs {B2, C}	0.63
{A, B1} vs {B2, C}	0.83

The robust cross-validation scheme allows us to conclude that it is possible to differentiate, with good accuracy (83%), between the combination of classes {A, B1} on one hand, and classes {B2, C} on the other hand. This result is very interesting from the practical point of view, as it means that one is able to discriminate between samples that do not present any constraint for regeneration (classes A and B1) from those that do present it (classes B2 and C). This accuracy value is quite positive, and a clear discrimination of classes these two groups of classes is achieved, even though some samples from class C are classified as A or B1, and vice versa. The other class arrangements do not lead to similar performance metrics, due to the overlap between classes mentioned above. We would like to point out that, sometimes, even the operator experiments some difficulties to distinguish among the different coagulation classes in the analytical test, which means that there is also some uncertainty in the specification of the coagulation class, that ultimately is transferred to the observed classification accuracy reported in Table 6.2.

6.3.5. SPECTRAL DISCRIMINANT ANALYSIS

In order to complement the classification models developed above to find out discriminating regions that may be responsible for the separation among classes, the FTIR spectra were also inspected. A discriminant analysis was performed, where the contribution of individual wavenumbers for the discrimination of coagulation classes was evaluated. This information paves the ground to the subsequent identification of the associated functional groups, and finally to possible compounds responsible for the coagulation behavior of WLO. This analysis was conducted using the Jii statistic, which is essentially a univariate metric of the separation of sample groups. In our analysis, we have considered the case where one class is in one group and all the other classes are gathered in the other group, in order to identify what is unique in each class. More specifically, the statistic provides the ratio between the intergroup variance and the intragroup variance. Therefore, the higher the value of the Jii statistic, the higher the discriminating power of the associated wavenumber. Figure 6.6(a) shows the mean FTIR spectrum of the 133 samples. Figure 6.6(b)-(e) indicate the Jii statistic contribution of each wavenumber for the segregation of the coagulation classes A, B1, B2 and C. For example, Figure 6.6(b) represents the discriminant power of wavenumbers for samples in the class A against all the others (classes B1, B2 and C), and the sample applies for (c), (d) and (e), regarding the remaining classes.

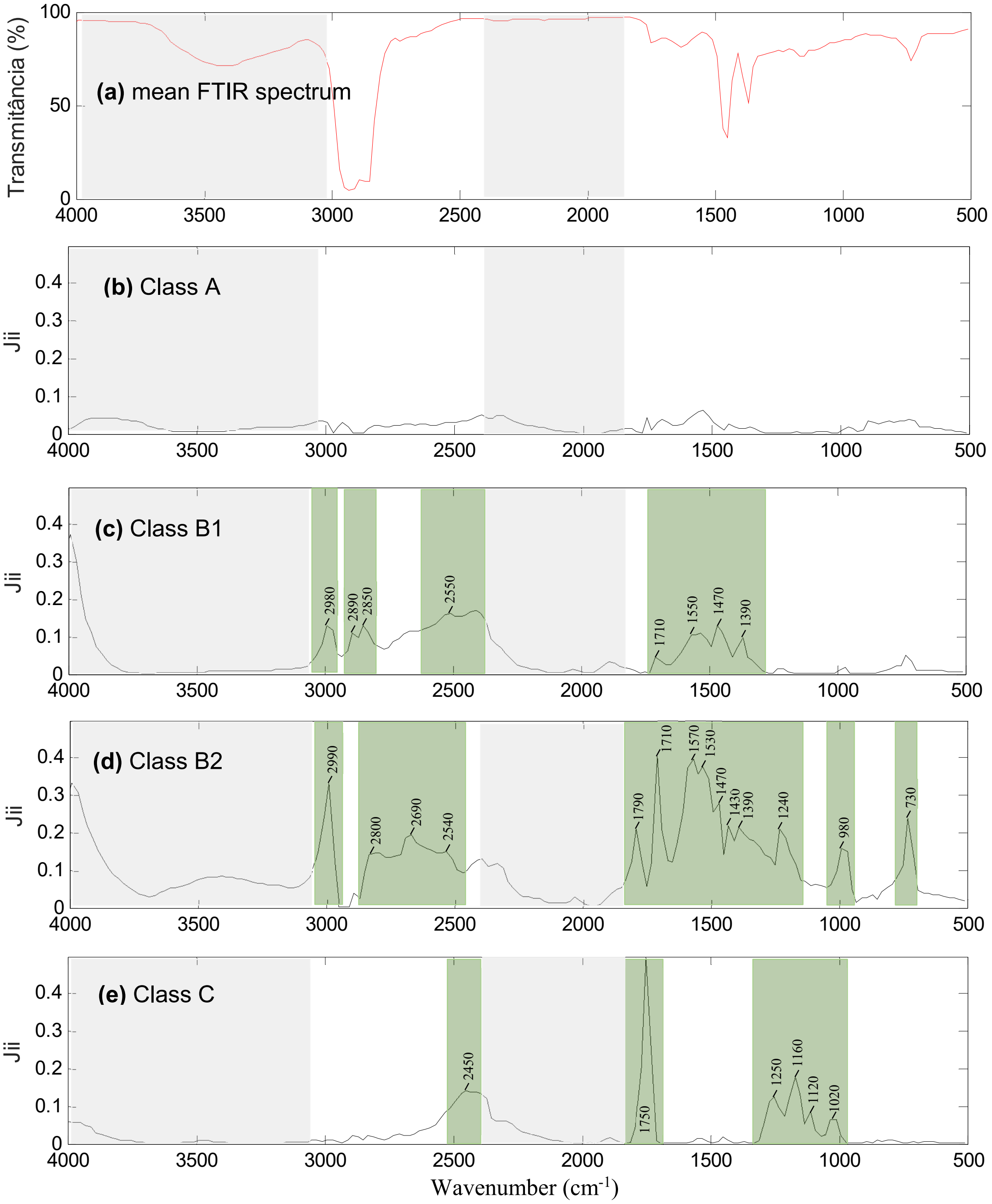


Figure 6.6. Wavenumbers selected for each coagulation class discrimination.

In Figure 6.6, the areas highlighted in light gray between 4000 and 3800 cm^{-1} will not be discussed because they contain no useful chemical information and consist mainly of instrumental noise [37]. The range with wavenumbers varying from 2420 to 2220 cm^{-1} will also not be examined since it corresponds to the band of CO_2 absorption. The spectral zones better discriminating the classes under analysis are highlighted in green.

It should be noted that peaks associated with CH, CH_2 and CH_3 vibrations present in mineral or synthetic oils (2980 – 2840, 1370, 1460 e 722 cm^{-1}), or -OH vibrations from water contamination (3600 – 3400 cm^{-1}) must not contribute to the discrimination of any coagulation classes, since they are generally present in all samples.

Despite the physicochemical characterization in Section 6.3.2 has shown that oils from classes A and B1 have similar properties, the discriminant analysis based on FTIR reveals compositional differences of such oils, as observed in Figure 6.6(b) and 6.6(c). Regarding the class A, there is a lack of discriminant peaks, i.e., there are no specific compounds significantly different that allow its discrimination from the other classes. This suggests that WLO samples classified as class A have a very low content of substances (additives and undesirable contaminants) with potential to promote the increase of viscosity, precipitate or gel formation during the alkaline treatment. For samples belonging to class B1, it is possible to recognize a set of bands typically found in lubricating oils corresponding to several additives (see Table A.5 in the Annex A4). These additives can form soaps after the interaction with KOH which impart a thickening effect in the oil. Thickening agents are generally a metallic soap formed by saponification of a fatty acid, but can also be a non-soap product such as a polymer [13]. Therefore, additives such as zinc dithiophosphates - ZDDP (970 cm^{-1}), nitrogen containing compounds, such as succinimides (1230 e 1530 cm^{-1}), calcium sulfonates (1470 cm^{-1}), amine antioxidants (1550 cm^{-1}) or polymethacrylates (970, 1710, 2980 cm^{-1}) might be responsible for coagulation class B1. Also, peaks corresponding to oxidation products (ketones, aldehydes, etc.) also might contribute to the thickening effect when interacting with KOH.

Figure 6.6(d) shows a great number of discriminant peaks for class B2, most of them can also be associated with additives and oxidation products (see Table S6.1). However, by taking a closer look to the FTIR spectra in Figure 6.4(c), those peaks are significantly less prominent in class B2, which typically presents smoother spectra compared to the other classes. Thus, the spectral discriminant analysis reveals a discrimination of coagulation class B2 spectra by the lack of presence of peaks that must correspond to additives or oxidation products.

In order to analyze the chemical nature of the precipitate formed in WLO samples of class B2, further FTIR analyses on the solid were performed (Figure S6.1). However, the spectra did not clarify its chemical composition, which suggests that the precipitate might have an inorganic origin. Thus, with the objective of characterizing the inorganic compounds present in the precipitate, two different samples were ignited at 550 °C to remove organic matter in the solid. The ignited residue was then analyzed by SEM-EDS. The results shown in Figure 6.7 indicate that the precipitate is composed by agglomerates mostly constituted by potassium (≈ 64 and 68 wt. %). In addition, besides some carbon and oxygen from the hydrocarbons and other organic compounds that must remain after ignition, traces of aluminum and silicon were detected. It must be emphasized that the physicochemical characterization revealed low TAN values for class B2 oils, which indicates that these waste oils do not have acid neutralization capacity to the KOH added. Saponification reactions between the fatty acids and KOH should not occur since SN values are rather low. In addition, due to fact of class B2 oils typically exhibit a lower concentration of elements such as Ca, Zn, Fe and Al, compared to other classes, the formation of low solubility of metal hydroxides should also not occur. Thus, the KOH added may not undergo any significant interaction with the oil matrix, which must have low solubility in the base oil, eventually precipitating. Therefore, the necessity of alkaline pretreatment for class B2 oils should be questioned, since most of the KOH added will form precipitates. Further studies should be carried out to evaluate the possibility of processing this type of WLO through regeneration technologies without alkaline treatment and reduce the number of rejected loads for regeneration.

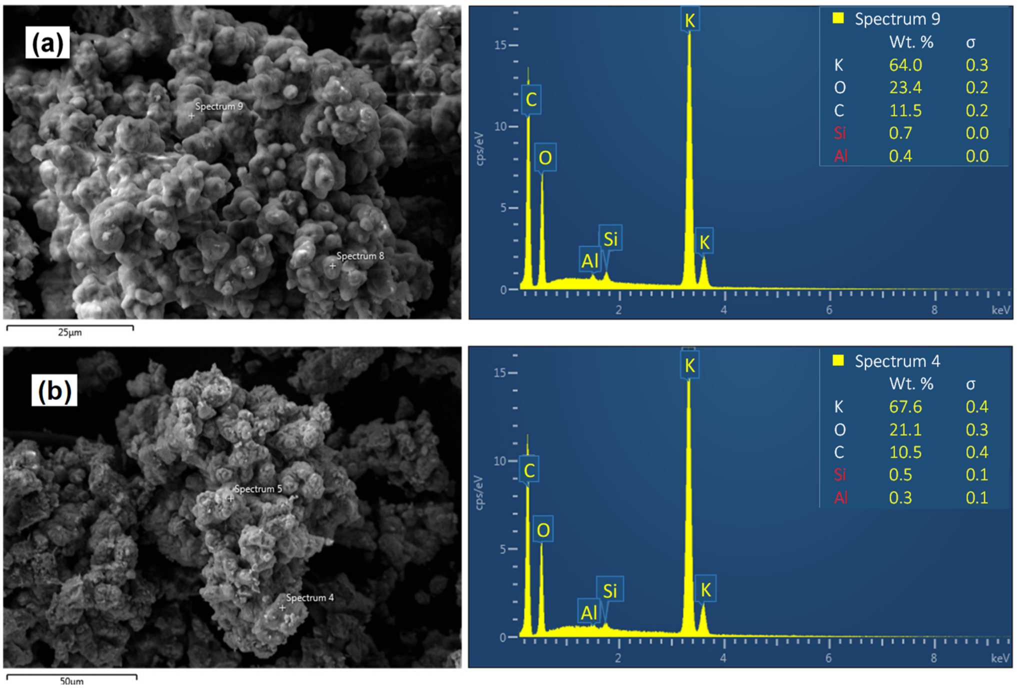


Figure 6.7. SEM-EDS results of the precipitate formed in two class B2 oil samples.

The discriminant analysis results obtained for class C (Figure 6.6(e)) revealed a higher discriminant value at 1750 cm^{-1}, which corresponds to the vibrational frequency of carbonyl groups (C = O), strongly present in esters. In addition to the latter, other discriminant peaks are also detected at 1110, 1160 and 1250 cm^{-1}. This result allows us to confirm that coagulation class C is in most of the observed cases due to the presence of synthetic ester type oils that react with KOH though saponification reactions, forming soaps that cause a gelling effect. Esters are a diverse family of high performance synthetic oil base used in applications in severe environments due to its excellent physical and chemical properties [42]. They may be used individually or combined with polyalphaolefin (PAO) to increase the solubility of additives. In 2014 the global demand for synthetic oils was 8-10% of the total lubricant. Of these, about 30% were ester type oils, with an upward trend expected for the forthcoming years [43]. This trend may be problematic for regeneration processes using technologies via alkaline treatments.

6.4. CONCLUSIONS

A systematic approach was developed in order to understand the fundamental nature of the coagulation phenomena of waste lubricant oils after its alkali pretreatment in regeneration processes. Thus, 133 WLO samples were submitted to a coagulation test and extensively characterized using analytical and multivariable statistical methods.

The application of the empirical analytical test to the samples in order to evaluate the regenerability of WLO prior to entering a regeneration plant revealed four different patterns: class A – the addition of KOH does not affect the oil matrix; class B1 – a significant change on viscosity is observed; B2 – precipitates are formed; class C – the oil forms a gel-type oil that impedes regeneration.

The physicochemical characterization revealed that coagulation classes A and B1 exhibit similar properties. Samples classified as class B2 showed significantly lower distribution of values in properties such as TAN, SN, water content, viscosity at 40°C and also lower concentration of major elements (P, S, Ca and Zn). Class C oil samples display SN values statistically different and in a higher range of values than the other classes, from 16 to 43 mg KOH/g. One distinct feature of class C samples spectra is the intense peaks at 1750 cm^{-1} and 1250 – 1100 cm^{-1}, which indicates synthetic the presence of ester type oils.

The classification analysis applied to FTIR spectra correctly classified 83% of the waste oils according to their coagulation class. The discriminant analysis based on the chemical identification of FTIR peaks showed that there are compositional differences between coagulation classes A and B1. Class A oil samples did not reveal specific discriminating compounds. Class B1, on the other hand, lead to the identification of a set of bands typically found in lubricating oils corresponding to several additives that may impart a thickening effect in the oil. However, classes A and B1 do not prevent regeneration to be done, and can be referred as a single class. The spectral discriminating analysis enabled a characterization of coagulation class B2 spectra by the lack peaks that must correspond to additives or oxidation products. SEM-EDS results revealed that the precipitate is mostly constituted by potassium (about 66 wt.%). Class C oils have the higher discriminant score at 1750 cm^{-1}, which corresponds to the vibrational frequency of carbonyl groups (C = O), strongly present in esters.

6.5. REFERENCES

[1] GEIR, An Environmental Review of Waste Oils Regeneration. hwww.geir-rerefining.org/documents/PositionpaperGEIR161104.pdf, 2004 (accessed September 15, 2017).

[2] A. Kupareva, P. Mäki-Arvela, D.Y. Murzin, Technology for rerefining used lube oils applied in Europe: A review, J. Chem. Technol. Biotechnol. 88 (2013) 1780–1793.

[3] V. Monier, E. Labouze, Critical Review of Existing Studies and Life Cycle Analysis on the Regeneration and Incineration of Waste Oils, 2001.

[4] J.G. Speight, D.I. Exall, Rerefining of Used Lubricating Oils, CRC Press, Boca Raton, 2014.

[5] M. Diphare, E. Muzenda, Influence of solvents on the extraction of oil from waste lubricating grease: a comparative study, in: 2nd International Conference on Agricultural, Environment and Bioliogical Sciences (ICAEBS 2013), December 17-18, Pattaya, Thailand, 2013, pp. 76–78.

[6] C. Kajdas, Major pathways for used oil disposal and recycling. Part 1, Tribotest. 7 (2000) 61-74.

[7] C. Kajdas, Major pathways for used oil disposal and recycling. Part 2, Tribotest. 7 (2000) 137-153.

[8] M.J. Alves dos Reis, Regeneração de óleos lubrificantes usados por extração/floculação, Ph.D. Thesis, University of Porto, Portugal, 1982.

[9] V.L. Lashkhi, I.G. Fuks, G.I. Shor, Colloid chemistry of lubricating oils (in the conditions of use), Plenum Publ. Corp. (1992) 311–319.

[10] T. Cosgrove, Colloid Science: Principles, Methods and Applications, second ed., Wiley, Bristol, 2010.

[11] J.J. McKetta, Unit Operations Handbook, Volume 2. Mechanical Separation and Materials Handling, Marcel Dekker, Inc., New York, 1993.

[12] M.M. Chakrabarty, Chemistry and Technology of Oils and Fats, Allied Publishers Pvt. Ltd., New Delhi, 2003.

[13] J.E. Martín-Alfonso, G. Moreno, C. Valencia, M.C. Sánchez, J.M. Franco, C. Gallegos, Influence of soap/polymer concentration ratio on the rheological properties of lithium lubricating greases modified with virgin LDPE, J. Ind. Eng. Chem. 15 (2009) 687–693.

[14] R.E. Wendt, E.F. Wagner, Applications of fatty acids in metallic soaps, J. Am. Oil Chem. Soc. 31 (1954) 590–593.

[15] R.G. Bossert, The metallic soaps, J. Chem. Educ. 27 (1950) 10–15.

[16] M.-C. Corbeil, L. Robinet, P., X-ray powder diffraction data for selected metal soaps, Powder Diffr. 17 (2002) 52–60.

[17] F. Audibert, Les Huiles Usagées: Reraffinage et Valorisation Énergétique, Edition Technip, Paris, 2003.

[18] A. Ferraz, J. Baeza, J. Rodriguez, J. Freer, Estimating the chemical composition of biodegraded pine and eucalyptus wood by DRIFT spectroscopy and multivariate analysis, Bioresour. Technol. 74 (2000) 201–212.

[19] C.S. Silva, F. de S.L. Borba, M.F. Pimentel, M.J.C. Pontes, R.S. Honorato, C. Pasquini, Classification of blue pen ink using infrared spectroscopy and linear discriminant analysis, Microchem. J. 109 (2013) 122–127.

[20] G. Kenne, D. van der Merwe, Classification of toxic cyanobacterial blooms by Fourier-transform infrared technology (FTIR), Adv. Microbiol. 3 (2013) 1–8.

[21] D. Helm, H. Labischinski, G. Schallehn, D. Naumann, Classification and identification of bacteria by Fourier-transform infrared spectroscopy., J. Gen. Microbiol. 137 (1991) 69–79.

[22] M.J. Lerma-García, G. Ramis-Ramos, J.M. Herrero-Martínez, E.F. Simó-Alfonso, Authentication of extra virgin olive oils by Fourier-transform infrared spectroscopy, Food Chem. 118 (2010) 78–83.

[23] P. de la Mata, A. Dominguez-Vidal, J.M. Bosque-Sendra, A. Ruiz-Medina, L. Cuadros-Rodríguez, M.J. Ayora-Cañada, Olive oil assessment in edible oil blends by means of ATR-FTIR and chemometrics, Food Control. 23 (2012) 449–455.

[24] R.M. Maggio, L. Cerretani, E. Chiavaro, T.S. Kaufman, A. Bendini, A novel chemometric strategy for the estimation of extra virgin olive oil adulteration with edible oils, Food Control. 21 (2010) 890–895.

[25] A. Fernández-González, J.M. Montejo-Bernardo, H. Rodríguez-Prieto, C. Castaño-Monllor, R. Badía-Laíño, M.E. Díaz-García, Easy-to-use analytical approach based on ATR–FTIR and chemometrics to identify apple varieties under Protected Designation of Origin (PDO), Comput. Electron. Agric. 108 (2014) 166–172.

[26] A.P. Craig, A.S. Franca, L.S. Oliveira, Evaluation of the potential of FTIR and chemometrics for separation between defective and non-defective coffees, Food Chem. 132 (2012) 1368–1374.

[27] C.T. Pinheiro, R. Rendall, M.J. Quina, M.S. Reis, L.M. Gando-Ferreira, Assessment and prediction of lubricant oil properties using infrared spectroscopy and advanced predictive analytics, Energy Fuels 31 (2017) 179–187.

[28] C. Besser, N. Dörr, F. Novotny-Farkas, K. Varmuza, G. Allmaier, Comparison of engine oil degradation observed in laboratory alteration and in the engine by chemometric data evaluation, Tribol. Int. 65 (2013) 37–47.

[29] R.F. Lara, S.M. Azcarate, M.Á. Cantarelli, I.M. Orozco, M.E. Caroprese, M. Savio, J.M. Camiña, Lubricant quality control: A chemometric approach to assess wear engine in heavy machines, Tribol. Int. 86 (2015) 36–41.

[30] M. Bassbasi, A. Hafid, S. Platikanov, R. Tauler, A. Oussama, Study of motor oil adulteration by infrared spectroscopy and chemometrics methods, Fuel 104 (2013) 798–804.

[31] J. Zięba-Palus, P. Kościelniak, M. Łącki, Differentiation of used motor oils on the basis of their IR spectra with application of cluster analysis, J. Mol. Struct. 596 (2001) 221–228.

[32] A. Borin, R.J. Poppi, Multivariate quality control of lubricating oils using Fourier transform infrared spectroscopy, J. Braz. Chem. Soc. 15 (2004) 570–576.

[33] H. Norgaard, L. Nygaard, Measurement and Calculation of Surface Tension of Oil, Gas and Glycol, Master Thesis, Norwegian University of Science and Technology, Trondheim, Norway, 2014.

[34] J. Sall, A. Lehman, M. Stephens, L. Creighton, JMP® Start Statistics: A Guide to Statistics and Data Analysis Using JMP®, fifth Ed., SAS Institute Inc., Cary, North Carolina, 2012.

[35] M. Barker, W. Rayens, Partial least squares for discrimination, J. Chemom. 17 (2003) 166–173.

[36] G.E. Totten, R.J. Shah, Fuels and Lubricants Handbook: Technology, Properties, Performance and Testing, ASTM International, West Conshohocken, PA, 2003.

[37] G. Biresaw, K.L. Mittal, Surfactants in Tribology, Volume 3, CRC Press, New York, 2013.

[38] K.S. Pedersen, A. Fedenslund, P. Thomassen, Properties of Oils and Natural Gases, Gulf Publishing Company, Houston, 1989.

[39] T.J. Kaádoński, L. Gryglewicz, M. Stańczyk, T. Kaádoński, Investigations on lubricity and surface properties of selected perfluoropolyether oils, J. KONES Powert. Transp. 18 (2011) 199–212.

[40] D.L. Wooton, Applications of spectroscopy in the fuels and lubrication industry, Appl. Spectrosc. Rev. 36 (2001) 315–332.

[41] M.A. Al-Ghouti, L. Al-Atoum, Virgin and recycled engine oil differentiation: a spectroscopic study., J. Environ. Manage. 90 (2009) 187–95.

[42] L. Rudnick, R. Shubkin, Synthetic Lubricants and High-Performance Functional Fluids, second ed., CRC Press, Boca Raton, Florida, 1999.

[43] IHS, Synthetic Lubricants. https://www.ihs.com/products/chemical-syntheticlubricants-scup.html, 2015 (accessed 16 Novemeber 2016).

PART D – TREATMENT BY SOLVENT EXTRACTION

The Part D of the thesis addresses the solvent extraction process for the regeneration of WLO.

In Chapter 7, a methodology is developed for the selection of sustainable solvents considering process constraints, greenness, performance and cost criteria.

In Chapter 8, the most sustainable solvents assessed in the previous chapter were applied to WLO segregated by coagulation class, and the best operation conditions were determined for each system.

7. A NEW METHODOLOGY OF SOLVENT SELECTION FOR THE REGENERATION OF WASTE LUBRICANT OIL USING GREENNESS CRITERIA

Waste lubricant oil (WLO) is an absolute hazardous entry in the European List of Waste that requires proper treatment. Solvent extraction is one of the most effective deasphalting processes for the regeneration of WLO, with a strong contribute to the circular economy. This study aims to propose a new methodology for the selection of solvents for WLO regeneration, which balances technical, economical and greenness criteria. The method involves two phases for screening a list of 154 solvents. In the first phase, five criteria were used: water and acidic properties; selectivity towards the base oil and flocculation capacity; number of carbon atoms between three and five; melting point lower than 10 ºC and a boiling point between 60 and 130 ºC; yield greater than 85%. In the second phase, three metrics of sustainability were employed: greenness, efficiency, and cost. Globally, a score was attributed to each solvent based on the assessment of the individual metric. From a list of 154 solvents, 1-butanol, isobutanol, and methylethyl ketone revealed to be the most sustainable solvents for the regeneration of WLO. The approach developed for WLO may be adapted to other fields requiring solvents.

KEYWORDS
Waste lubricant oil, regeneration, solvent selection, sustainability, greenness, efficiency, economics, process constraints.

This chapter is based upon the publication:

C.T. Pinheiro, M.J. Quina, L.M. Gando-Ferreira, New methodology of solvent selection for the regeneration of waste lubricant oil using greenness criteria, ACS Sustainable Chem. Eng. 6 (2018). 6820−6828. doi: 10.1021/acssuschemeng.8b00646.

7.1. INTRODUCTION

Solvent extraction has been widely used as one of the cheapest and efficient techniques for the regeneration of waste lubricating oil (WLO). The process allows the recovery of undamaged base oil for the manufacture of fresh lubricant oils, while unwanted components are segregated. Among the compounds to be removed at this stage are: (i) high -molecular -weight oxidation products; (ii) metallic particles produced by wear; (iii) carbonaceous particles formed by partial coking of fuels; and (iv) additives such as viscosity index improvers, pour point depressants, dispersants, detergents, antifoaming and extreme pressure agents, etc., comprising a great variety of chemical products such as succinimides, sulfonates, dialkyldithiophosphates of zinc, amines, phenols, silicones, carboxylic acid salts, and polymers, such as polyolefins and polymethacrylates [1]. The amount of components and accumulation of contaminants depends on the original base oil, additives package, application type, time of service, among others [2].

Regeneration is the most interesting treatment route, mitigating the significant negative environmental burden of this hazardous waste. Moreover, regeneration entirely supports the objectives towards a circular economy, where resources/by-products are re-used after an appropriate treatment phase [3].

Solvents are used in large volumes in many industrial processes as auxiliary substances and/or as part of product formulations [4]. Although solvents have a wide range of applications, most of them may pose serious environment, health, and safety (EHS) concerns, including human and eco-toxicity issues, process safety hazards and waste management problems [5]. In many industrial processes, the mass of solvents in product formulations may be greater than all the other compounds and because of the large amounts used, they can cause a significant environmental impact [6].

The application of solvents for the refining of WLO produces good quality base oils. Supercritical propane has been widely used as re-refining solvent in the industry [7]. This method is similar to that used in crude oil refining to separate asphaltenes for producing heavy neutral base oil. A major drawback of propane is the safety concerns due to high flammability, which increases the risk of fire and explosion. Moreover, the operation typically occurs at high pressure, making the construction and safe operation of plants expensive [8]. As an alternative, other solvents which operate at ambient temperature and pressure have been reported as extraction-flocculation components. The solvent dissolves the base oil and segregate the degraded additives, carbonaceous particles and polymeric compounds from the mixture by exerting an anti-solvent effect. The particles aggregate to sizes large enough that precipitate from the liquid phase by sedimentation [9]. Rincón and coworkers [10] reported that polar solvents such as 2-propanol, 2-butanol, 2-pentanol, methyl ethyl ketone, or methyl n-propyl ketone are possible alternatives for the segregation of undesirable components from the base oil. Martins [11] proposed the ternary organic solvent composed by n-hexane/2-propanol/1-butanol for the effective extraction-flocculation process.

In recent years, the growing environmental awareness of both scientific and industrial communities has led to the incorporation of green chemistry and green engineering principles into sustainable design of chemical processes. Decision-support methodologies have been developed, which can address entire processes, or focus on specific aspects such as solvent selection. In this field, attempts have been made to identify meaningful metrics for selection of greener alternatives to conventional solvents. Several solvent selection guides using environment, health and safety (EHS) metrics have been published by industry for pharmaceutical applications [12,13]. Indeed, organic solvents account for 75-80% of the waste from pharma processing [14]. Some of the solvent selection guides were published by AstraZeneca [15], Pfizer [16], Sanofi [12], and GlaxoSmithKline (GSK) [14]. In most of those guides, the overall greenness criteria are also based on EHS categories. However, a meaningful solvent selection must rely not only on greenness criteria but also on specific process constraints and cost [6]. In the literature a few studies are available describing solvent selection methodologies considering environmental and process constraints trade-offs. Guides for different applications such as leather processing [17], olefin metathesis [18], biomass processing [19], and for aldehyde-based direct reductive amination processes [20] have been developed. However, to the best of our knowledge, none studies are available for the selection of solvents in the regeneration process of WLO.

In this context, the main objective of this work is the development of a new methodology for the selection of extraction-flocculation solvents for the regeneration of WLO at ambient temperature and pressure, taking into consideration not only process constraints, efficiency, and economic issues but also greenness criteria. These criteria were based on the updated GSK guide [14], which was developed by taking into consideration waste, environment, human health, and process safety issues.

7.2. METHODOLOGY

7.2.1. SOLVENT DATASET AND METRICS

The set of solvents considered in this study were based on the updated GSK solvent selection guide, which are listed in Table A.6 in the Annex A.5. It includes 154 solvents grouped in the following categories: water and acids (WA1 to WA6), alcohols (A1 to A29), esters (Es1 to Es25), carbonates (C1 to C5), ketones (K1 to K7), aromatics (Ar1 to Ar11), hydrocarbons (HC1 to HC12), ethers (Et1 to Et20), dipolar aprotic (DA1 to DA14), halogenated (Hal1 to Hal17) and others (O1 to O8).

7.2.2. SOLVENT SELECTION METHODOLOGY

The methodology developed for the selection of solvents applied to the regeneration of WLO consists of two main phases, as illustrated in Figure 7.1. The first phase comprises a sequential screening based on process constraints aiming at identifying possible extraction-flocculation candidates. In a second phase, solvents are evaluated simultaneously regarding three major aspects of the process: greenness according to the GSK solvent selection guide, performance of extraction and cost. Since the metrics in the Phase 2 reflect distinct properties, units, and ranges, a score in the range between 1 to 10 was defined for comparison purposes. The method comprises the calculation of individual scores for the metrics. The scores are further combined to obtain a single overall score for each solvent, providing an indication of its sustainability. Further details about the criteria used in each phase will be given in the Section 7.3.

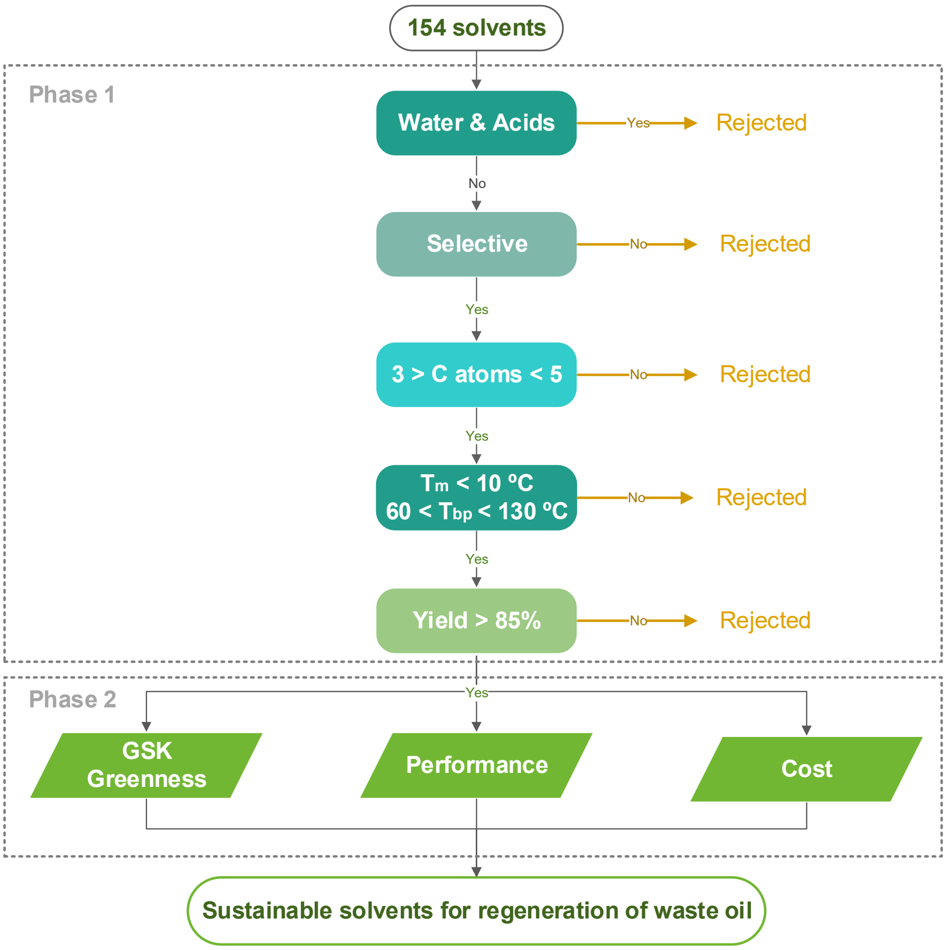


Figure 7.1. Solvent selection methodology.

7.2.3. EXPERIMENTAL EXTRACTION PROCEDURE

The extraction procedure was adapted from Reis and Jerónimo [1]. Previously weighed centrifugal tubes were filled with a mixture of 20 g of WLO sample ($W_{waste\ oil}$) and solvent at a specified ratio. The samples were stirred by magnetic stirring at 500 rpm, for 20 min. The tubes were centrifuged at 4000 rpm for 20 min. Then, the wet sludge phase (additives and impurities) was separated from the mixture solvent/oil. The solvent was recovered by vacuum distillation in a rotary evaporator. Distillation flasks were previously weighed, and the mass of the recovered oil ($W_{base\ oil}$), and solvent was calculated by difference. The yield was determined by Eq. (7.1).

$$Yield\ (\%) = \frac{W_{base\ oil}}{W_{waste\ oil}} \times 100 \tag{7.1}$$

The tubes were then placed in the oven for 1 h at 80 ºC to evaporate any remaining solvent. The wet sludge was redispersed by addition of 7 mL of n-hexane to separate the sludge, followed by 28 mL of isopropanol to produce again large flakes. The purpose of this washing phase is to reduce the interstitial oil content in the sludge that would not evaporate by simple drying. Finally, after centrifugation, the washing liquid was discarded, and the tubes were introduced into the oven and dried for 1 h at 80 ºC. After cooling, the tubes with the sludge but without any oil were weighed ($W_{dry\ sludge}$) and the percent of sludge removal (PSR) was calculated according to (7.2).

$$PSR\ (\%) = \frac{W_{dry\ sludge}}{W_{waste\ oil}} \times 100 \tag{7.2}$$

7.3. SOLUBILITY PARAMETER

The Hildebrand solubility parameter, δ (MPa$^{1/2}$), introduced by Hildebrand and Scott [21], is defined as the relative solvency behavior of a specific solvent, and may be derived from the square root of the cohesive energy density (Eq. 7.3),

$$\delta = \sqrt{\left(\frac{E}{V_m}\right)} = \sqrt{\left(\frac{\Delta H - RT}{V_m}\right)} \tag{7.3}$$

where V_m is the molar volume (cm^3/mol), E is the energy of vaporization (J/mol), ΔH is the enthalpy of vaporization in (J/mol), R is the gas constant (cm^3.MPa/mol.K) and T is the absolute temperature (K). Classical solubility parameters can be useful to predict interactions between the solvent, the base oil, and different impurities and will be explored in this work.

Free energy of mixing must be zero or negative for the solubilization process to occur spontaneously. The free energy change for the solubilization process is given by the relation:

$$\Delta G^M = \Delta H^M - T\Delta S^M \tag{7.4}$$

where ΔG^M is the free energy of mixing (J/mol), ΔH^M is the heat of mixing (J/mol), and ΔS^M is the entropy change in the mixing process (J/mol.K). Patterson, and coworkers [22] showed that the noncombinatorial free energy of solution, $\Delta G^M_{noncomb}$, which includes all free energy effects other than the combinatorial entropy of solution that results by simply mixing the components, is given by Eq. (7.5),

$$\Delta G_{noncomb}^{M} = V_{mix}\phi_1\phi_2(\delta_1 - \delta_2)^2 \tag{7.5}$$

where V_{mix} is the total molar volume of the mixture (cm^3/mol), ϕ is the volume fraction, and subscripts 1 and 2 refer to the solvent and base oil, respectively. Fluids with similar solubility parameters, $\delta_1 - \delta_2 \approx 0$, are likely to be miscible.

7.1. SENSITIVITY ANALYSIS

The sensitivity of the final sustainability scores (see Eq. (7.12) in Section 7.2) was performed by considering that the weights assigned to greenness (w_1), performance (w_2) and cost (w_3) scores are subject to uncertainty. A Monte Carlo method [23] was employed using the function RandomReal (Rule 30 CA) in the software Mathematica® [24] to randomly generate values for w_1 and w_2 within the interval 0.2 – 0.5, and the third weight calculated by difference [$w_3 = 1-(w_1 + w_2)$].

The sustainability score is then calculated for a large number of scenarios, here set to 10,000. Once the population of weights are generated, the mean and standard deviation can be inferred to measure the sensitivity of final sustainability scores toward w_1, w_2 and w_3. The results were analyzed based on a boxplot graph.

7.2. RESULTS AND DISCUSSION

7.2.1. PHASE 1

Important extraction process constraints for the regeneration of WLO were identified in this phase for the screening of 154 solvents. Namely, water and solvents with acidic properties, selectivity, number of carbon atoms, melting and boiling points, and yield were considered. The screening was performed sequentially, and in each step the solvents that do not comply with the criteria were rejected. In this section, the first phase of the global methodology for sustainable solvent selection will be discussed in detail.

7.2.1.1. WATER & ACIDS

The earliest and widely adopted technology in the past for regeneration of waste oils was the acid/clay process [25]. Good quality base stocks were produced by this simple technology. However, problems associated with secondary pollution as the disposal of spent clay and acid sludge and low yield (45–65%) discouraged the use of this process, which has been banned since the early 1970s [8]. Recently, Hamawand and coworkers addressed the recycling of waste oils treated using acetic acid [26]. Still, the same environmental concerns are encountered. Therefore, although removal of impurities from WLO may be achieved by using acids, these solvents (WA2 – WA6, Hal12 – Hal14 and O6) will not be considered as sustainable for regeneration. In addition, recovery of acids is not possible since they react with the impurities, remaining in the formed sludge. Water (WA1) is also not a suitable solvent for this system, since it is not miscible with base oil.

7.2.1.2. SELECTIVITY

Waste lubricant oil is a complex mixture of recoverable base oil molecules and impurities (additives, carbonaceous particles and other contaminants). These impurities are kept in dispersion by detergent and dispersant additives and electrostatic interactions between heteroatoms and asphaltic compounds [1]. To recover the base oil fraction, the solvent must completely dissolve the base oil and segregate undesirable impurities by destabilizing the dispersion and exerting an anti-solvent effect. The particles aggregate with each other and may be separated from the liquid phase by sedimentation. Nowadays, lubricants may be produced from petroleum fractions (mineral oils) or may be obtained by controlled synthesis (such as polyalphaolefin (PAO), organic esters, glycols and phosphate esters). In 2015, synthetic base stocks, only accounted for 10.5% of the total lubricant market, and thus mineral oils are still relevant [27]. In mineral oils, the heteroatoms and additives introduce some polarity to the nonpolar hydrocarbon structures characteristic of base oil molecules. However, since the base oil molecules are mostly nonpolar, highly polar solvents will not be soluble in the base oil. Thus, from GSK solvent guide listed in the Annex A5, dipolar aprotic (DA1 to DA14) solvents are not miscible with the base oil due to their high polarity [28]. Even so, N-methyl-2-pyrrolidone (DA8) is used in the largest waste oil regeneration industry in Germany, the Mineralöl –Raffinerie [29]. However, DA8 is used for removing aromatics and sulfur compounds [30]. Therefore, dipolar aprotic solvents were rejected due to lack of selectivity for the extraction process considered in this work.

In addition to the solvent ability to solubilize the base oil matrix, flocculation of impurities must occur to separate them out from the fluid. In previous studies, n-hexane [31]. petroleum ether [31], isoctane, cyclopentane, cyclohexane, benzene and toluene [1] did not revealed significant flocculation capacity. Hence, solvents classified as hydrocarbons (HC1 to HC12) and aromatics (Ar1 to Ar11) were rejected. Nevertheless, studies indicate that the use of hydrocarbons such as n-hexane [11,32] in a composite solvent approach may increase the removal of impurities. However, composite solvents are outside the scope of this study. Halogenated solvents (Hal 1 to Hal17) demonstrate similar behavior to hydrocarbons. Among the halogenated solvents, carbon tetrachloride was tested [31] but minimum flocculation action was observed, and thus it was rejected. In fact, according to Burrel's [33] classification of solvents, hydrocarbons, chlorinated hydrocarbons, and nitrohydrocarbons are weak hydrogen bonding solvents, which has been reported [10] to be closely related to the flocculation capacity of solvents.

To the best of our knowledge, esters, ethers, and carbonates have never been tested as solvents for the extraction-flocculation process of WLO. The main reason is their incapacity to destabilize the WLO impurities. Indeed, esters may be used both as synthetic lubricant base stocks or as additives [34]. The inherent polarity of esters improves their performance in lubrication by reducing volatility, increasing lubricity and solubility of additives. Examples of compounds widely used are complex/polyol esters, methyl esters, monoesters and dicarboxylic acid esters [35]. Ethers also have applicability as synthetic base stocks. Among oxygen-containing fluids, alkylated benzofuran, alkylated diphenyl ether, and alkylated anisole are reported to be excellent synthetic base stocks [36]. Similarly, carbonates were also rejected because they can be used both as lubricant base oils and performance fluid components due to their performance characteristics, low toxicity, and favorable economics. As an example, dimethyl carbonate (C4 in the solvent list) has been reported to provide benefits as a component in hydraulic fluids [37]. Table 7.1 summarizes the categories of solvents rejected, making a total of 104 solvents excluded because of lack of desired selectivity.

Table 7.1. Categories of solvents rejected due to lack of selectivity.

Solvent category		Comment
○ Not miscible with base oil		
DA1 – DA14	Dipolar aprotic	Highly polar compounds
○ Miscible with base oil but no flocculation capacity		
Es1 – Es25	Esters	Used as synthetic base oils
C1 – C5	Carbonates	Used as synthetic base oils or additives
Ar1 – Ar11	Aromatics	Solubilize all WLO matrix
HC1 – HC12	Hydrocarbons	Solubilize all WLO matrix
Et1 – Et20	Ethers	Used as synthetic base oil
Hal1 – Hal17	Halogenated	Solubilize all WLO matrix

At this screening phase, 43 compounds remain in the running for sustainable solvents: alcohols (A1 to A29), ketones (K1 to K7), and other (O1 to O5, O7, and O8) solvents. A number of methods to differentiate the solubilizing characteristics of solvents may be used. As aforementioned, the solubility parameters can be useful to predict interactions between the solvent and the base oil.

Voelkel and Fall [38] determined the solubility parameter of mineral, synthetic and semi-synthetic base oils. The values varied from 16.2 to 19.7 $MPa^{1/2}$. The hypothesis in which lower solubility difference between base oil and solvent leads to higher oil miscibility will be explored. Assuming an intermediate solubility parameter of the base oil of 18 $MPa^{1/2}$, Table 7.2 displays the difference of solubility parameters for the different solvents. For polymers, it has been reported that solubility in organic solvents is expected if $|\delta_1 - \delta_2|$ is less than 3.5-4.0 [39]. For base oils, according to the literature, 1-butanol [1] is still completely miscible with base oils, but nitromethane [40] is not. Indeed, this fact may also be explained by the difference of polarity, measured by the dipole moment between nitromethane (3.53 D) and a typical base oil (1.23 – 1.64 D) [41]. Thus, solvents where $|\delta_1 - \delta_2|$ is close or higher than 7 are expected to be immiscible with the base oil. The candidates marked in Table 2 with the superscript (b) were rejected. Indeed, Levin and Redelius [40] tested the miscibility of several solvents in the base oil observing that 1,3-propanediol (A1), ethylene glycol (A5), 1,2-propanediol (A8), ethanol (A20), methanol (A27), nitromethane (O7) were not soluble.

Table 7.2. Difference between the solubility parameter of solvents (δ_1) and base oil (δ_2=18 $MPa^{1/2}$).

Solvent		δ_1 (a) ($MPa^{1/2}$)	$\lvert\delta_1-\delta_2\rvert$	Solvent		δ_1 (a) ($MPa^{1/2}$)	$\lvert\delta_1-\delta_2\rvert$
K3	3-Pentanone	18.2	0.2	A14	Cyclohexanol	22.4	4.4
O8	Triethylamine	17.8	0.2	A15	Isobutanol	22.7	4.7
K5	2-Pentanone	18.3	0.3	O3	Dihydrolevoglucosenone	22.7	4.7
O4	*N,N*-Dimethyloctanamide	19.0	1.0	A18	1-Butanol	23.2	5.2
K4	Methylisobutyl ketone	17.0	1.0	A22	2-Propanol	23.6	5.6
K6	Methylethyl ketone	19.1	1.1	A9	Benzyl alcohol	23.8	5.8
K2	Cyclohexanone	19.6	1.6	O1	Furfural	24.4	6.4
K7	Acetone	19.9	1.9	A19	1-Propanol	24.6	6.6
A3	2-Ethyl hexanol	20.1	2.1	A29	2-Methoxyethanol	24.8	6.8 (b)
O2	*N,N*-Dimethyldecanamide	20.1	2.1	O7	Nitromethane	25.1	7.1 (b)
A4	1-Heptanol	20.5	2.5	A24	1,2-Isopropylidene glycerol	26.1	8.1 (b)
A11	1-Octanol	20.6	2.6	A20	Ethanol	26.5	8.5 (b)
A17	1-Hexanol	21.0	3.0	A26	IMS (ethanol, denatured)	26.5	8.5 (b)
A23	*t*-Amyl alcohol	21.2	3.2	A7	Tri(ethylene glycol)	27.5	9.5 (b)
A10	Isoamyl alcohol	21.3	3.3	A8	1,2-Propanediol	29.1	11.1 (b)
A16	2-Pentanol	21.5	3.5	A6	Di(ethylene glycol)	29.1	11.1 (b)
O5	*N,N*-Dimethylaniline	21.7	3.7	A27	Methanol	29.6	11.6 (b)
A25	*t*-Butanol	21.8	3.8	A13	1,4-butanediol	31.3	13.3 (b)
A2	1-Pentanol	21.9	3.9	A1	1,3-Propanediol	31.7	13.7 (b)
A28	Tetrahydrofurfuryl alcohol	22.1	4.1	A5	Ethylene glycol	33.0	15.0 (b)
K1	Cyclopentanone	22.1	4.1	A12	Glycerol	36.2	18.2 (b)
A21	2-Butanol	22.2	4.2				

(a) From reference [42].
(b) Solvents rejected.

Although the solubility parameter is a useful method to predict the miscibility behavior of solvents, use of the literature is advantageous for rejecting solvents that have already been tested and are not suitable for the regeneration of WLO. Indeed, furfural (O1) is a known solvent in the refining industry since it is selective for the removal of aromatic hydrocarbons [43]. However, it is not miscible with paraffinic and naphthenic base oils, which can be associated with its polarity. In fact, the dipole moment of furfural (3.57 D) [41] is significantly different to the dipole moment of a typical base oils (1.23-1.64 D) and thus is not selective toward the base oil.

Dihydrolevoglucosenone (O3) has been studied as a bio-based alternative for dipolar aprotic solvents, since it has comparable characteristics with NMP[44]. 2-Methoxyethanol (A29) might be soluble in the base oil, it is used as an additive and should not have any flocculation power in lubricants [45]. Therefore, these solvents were also rejected.

On the basis of the data collected about the selectivity, the number of solvents decreased from 145 to 28.

7.2.1.3. NUMBER OF CARBON ATOMS

Reis and Jerónimo [32] conducted a comprehensive study about WLO and pointed out that the capability of solvents to segregate sludge from WLO is closely related to their number of carbons atoms. They observed that alcohols and ketones having fewer than 3 carbon atoms are immiscible with the base oil. In addition, the flocculation action for alcohols decreases from 1-propanol (C_3H_8O) to 1-hexanol ($C_6H_{14}O$). For ketones, methyl ethyl ketone (C_4H_8O) exhibits a more active flocculating action than methyl n-propyl ketone ($C_5H_{10}O$), which in turn is more effective than methyl isobutyl ketone ($C_6H_{12}O$).

In crude refining, the solvent deasphalting process generally involves the use of alkane solvents with 3 to 6 carbon atoms. It has been observed that, upon increasing the number of carbons of the solvent, the yield of oil increases but the quality is lower, because solvents with longer carbon chains are able to dissolve heavier oil components [46].

Thus, possible process constraints require that the selected solvents have between 3 and 5 carbon atoms in their molecules because solvents with lower molecular weight cannot dissolve base oil and those with longer chain length may prevent aggregation of waste oil impurities [1,32].

Thus, 2-ethyl hexanol (A3), 1-heptanol (A4), benzyl alcohol (A9), 1-octanol (A11), cyclohexanol (A14), 1-hexanol (A17), cyclohexanone (K2), Methylisobutyl ketone (K4), N,N-Dimethyldecanamide (O2), N,N-Dimethyloctanamide (O4), N,N-Dimethylaniline (O5), and Triethylamine (O8) were rejected. The number of solvents was thus reduced from 28 to 16.

7.2.1.4. MELTING AND BOILING POINTS

One of the requirements for the extraction-flocculation process is that the solvent must be in liquid state at room temperature. Thus, their melting and boiling point temperatures are important properties to be considered and a maximum melting point of 10 ºC was defined as criteria. Therefore, *t*-butanol (A25) and cyclopentanone (K1), were rejected. In addition, a minimum boiling point of 60 ºC would be preferred. From the remaining solvents, acetone (K7) has a boiling point of 56 ºC and will be rejected.

Moreover, a cost-effective recovery of solvents by distillation is a central criterion for their selection. The heat of vaporization and solvent/oil ratio are important variables that affect the cost of solvent recovery [47] and will be explored in the Section 7.4.2.3. The main associated cost is related with the steam used in the reboiler to evaporate the solvent [46]. When the boiling point is higher, the steam pressure required to vaporize is higher. Thus, a maximum boiling point of 130 ºC was set as criteria because it influences the pressure and temperature of the steam to be generated. Applying this screening criterion, 1-pentanol (A2), isoamyl alcohol (10) and tetrahydrofurfuryl alcohol (A28) were rejected, remaining 10 solvents in the running.

7.2.1.5. YIELD

The ability of a solvent to effectively segregate impurities from the base oil can be evaluated by the yield of extraction. It is desirable that the solvent remove most impurities to improve the base oil quality, and simultaneously recover as much as possible base oil to make the process profitable. At industrial scale, the yield of extraction using propane is about 93%, but can reach 80% depending on the operating conditions [48,49]. Therefore, for the extraction-flocculation process, a minimum yield of 85% was considered a process constraint.

Validation of the remaining candidates was experimentally assessed at laboratory scale. For comparison purposes, the same operating conditions were applied to all solvents. As reported by Pinheiro and coworkers [50], for the same extraction conditions different waste oil samples may have different yield due to differences in base oil and/or in contamination level. Therefore, the extraction potential of the solvents was tested considering the same WLO sample.

The results illustrated in Figure 7.2 show that 1-propanol (A19) and 2-propanol (A22) have low yield compared to the other solvents. This is due to the fact that in both cases the sludge formed is not well separated from the oil matrix.

In fact, the solubility differences between base oil and these solvents (Table 7.2) are high (6.6 and 5.6 MPa$^{1/2}$, respectively), which could indicate problems with miscibility and high oil losses. Consequently, 1-propanol and 2-propanol were rejected, with 8 remaining solvents from the initial list.

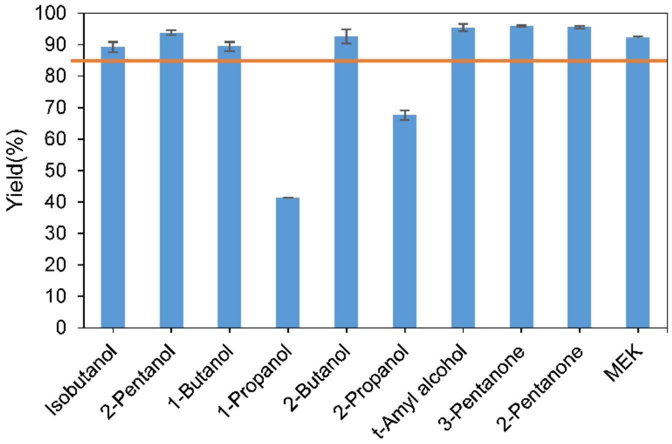


Figure 7.2. Yield of extraction for different solvents (operating conditions: solvent/oil ratio = 5/1; contact time = 20 min; T = 25 °C and mixing speed = 500 rpm).

7.2.2. PHASE 2

The objective of Phase 2 was to evaluate the 8 best solvents screened from Phase 1 considering simultaneously GSK greenness criteria, efficiency of extraction and cost.

7.2.2.1. GSK GREENNESS CRITERIA

The assessment of greenness was based on the GSK solvent selection guide [14]. Table A.7 in the Annex A.5 summarizes the four main green metrics, categories and areas of assessment considered in the guide, and includes the nomenclature used in this section. Each category considers multiple areas, which are individually assessed and combined in scores ranging from 1 to 10. Scores of 3 or less indicate solvents with major concerning issues in that category, scores between 3 and 8 indicate some issues and scores higher than or equal to 8 correspond to few issues. The detailed methodology for assignment of scores for each category and area of assessment can be found elsewhere [14].

Figure 7.3(a)-(b) illustrates the scores of each category of five alcohols and three ketones, respectively. In general, high scores (i.e. lower impact) on health hazard, reactivity, and aqueous environmental impact were observed for all of these solvents. The most problematic areas are recycling, biotreatment, and the air environmental impact.

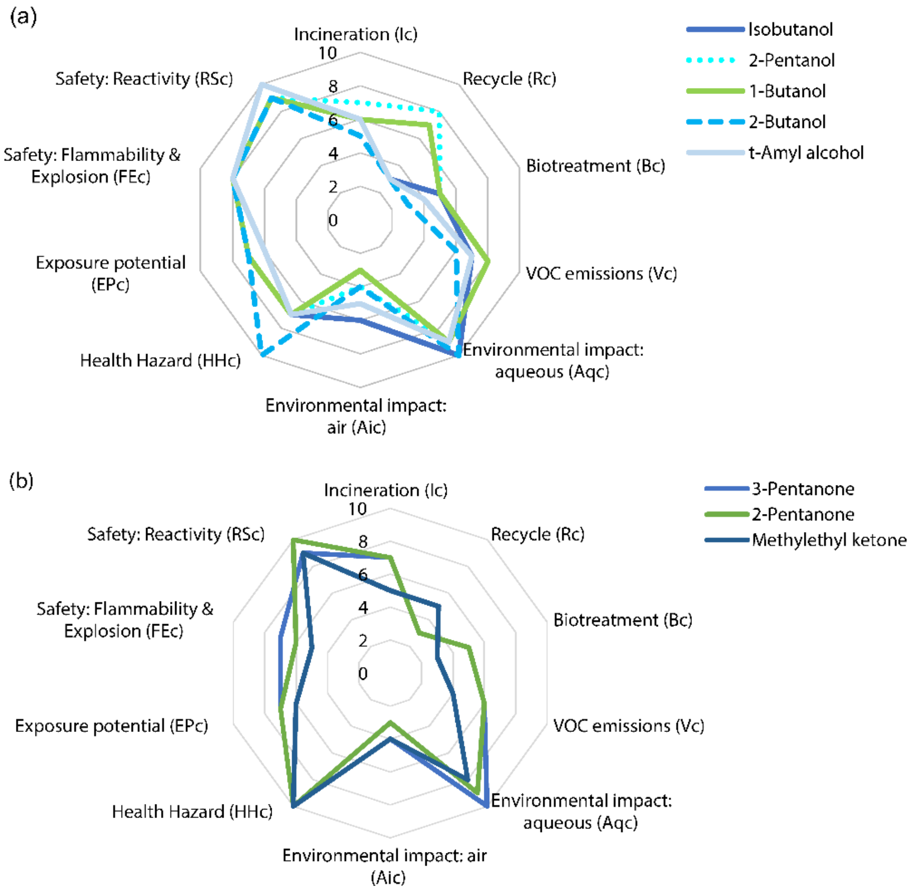


Figure 7.3. Green metric scores assigned by GSK for different (a) alcohols and (b) ketones.

While a major benefit of the solvent selection guide lies in highlighting individual categories associated with the greenness of certain solvents, there are also benefits of an overall classification. Therefore, the assessment of relevant summary metrics such as waste, environment, health, and safety issues was performed according to the GSK guide [14]. The summary score is defined as the geometric mean of each of the relevant categories, as described by Eqs. (7.6-7.9).

$$\text{Waste (Wm)} = \sqrt[4]{\text{Ic} \times \text{Rc} \times \text{Bc} \times \text{Vc}} \tag{7.6}$$

$$\text{Environment (Em)} = \sqrt{\text{Aqc} \times \text{Aic}} \tag{7.7}$$

$$\text{Human Health (HHm)} = \sqrt{\text{HHc} \times \text{EPc}} \tag{7.8}$$

$$\text{Process safety (PSm)} = \sqrt{\text{FEc} \times \text{RSc}} \tag{7.9}$$

The overall greenness score of a solvent, was obtained through the geometric mean according to Eq. (7.10) and the results are shown in Table 7.3.

$$\text{GSK greenness score} = \sqrt[4]{\text{Wm} \times \text{Em} \times \text{HHm} \times \text{PSm}} \tag{7.10}$$

The results show that the lowest scores are observed mainly for Waste (Wm) and Environment (Em) and the highest for Safety (PSm). None of these solvents have a GSK greenness score lower than 3. However, the highest global score is 7.0 for 2-Pentanol. The lowest value is 5.9 and was obtained for methylethyl ketone (MEK).

Table 7.3. GSK greenness, efficiency and cost scores.

	GSK greenness					**Efficiency score**	**Cost**		
Solvent	Wm	Em	HHm	PSm	**Combined score**		SA	Re	**Combined score**
Isobutanol	5.0	7.7	7.0	8.5	**6.9**	**8.8**	9.5	5.3	**7.1**
2-Pentanol	6.9	6.0	7.0	8.5	**7.0**	**5.5**	1.0	1.0	**1.0**
1-Butanol	6.4	5.2	7.0	8.5	**6.7**	**10.0**	10.0	4.6	**6.8**
2-Butanol	4.1	6.3	8.4	8.5	**6.5**	**7.5**	10.0	5.7	**7.6**
t-Amyl alcohol	4.7	6.7	6.5	8.9	**6.6**	**1.0**	7.9	6.5	**7.2**
3-Pentanone	5.0	6.3	8.4	7.9	**6.8**	**1.4**	9.0	9.0	**9.0**
2-Pentanone	5.0	5.2	8.4	7.7	**6.4**	**2.6**	6.3	9.1	**7.6**
Methylethyl ketone	4.2	5.7	7.7	6.7	**5.9**	**6.9**	10.0	10.0	**10.0**

7.2.2.2. PERFORMANCE OF EXTRACTION

One of the most critical steps in solvent selection is the efficiency of extraction in order to segregate out of WLO impurities, and obtain a good quality base oil. At this stage, performance was evaluated through the PSR defined by Eq. (7.2). The obtained results are illustrated in Figure 7.4, where little flocculation action (low PSR) can be observed for *t*-amyl alcohol, 3-pentanone and 2-pentanone. The best results are obtained by 1-butanol, followed by isobutanol, 2-butanol, and MEK. These results are consistent with several works reported in the literature [1,10,51,52].

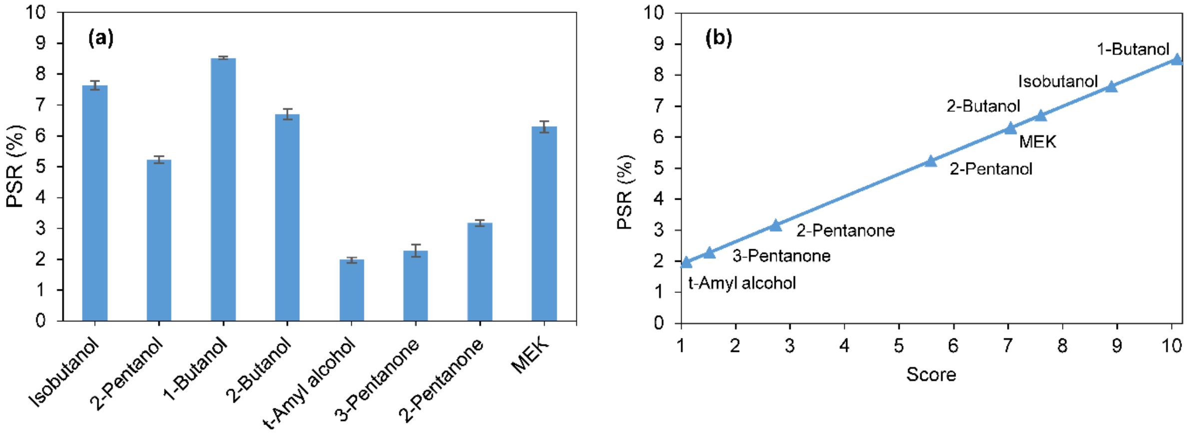


Figure 7.4. (a) PSR for different solvents (at solvent/oil ratio = 5/1; contact time = 20 min; T = 25 °C and mixing speed = 500 rpm), (b) PSR score assignment.

The same methodology used by GSK for assignment of scores and comparison of indicators was applied to the performance of extraction. Thus, to the lowest and highest PSR values, a score of 1 and 10 was assigned, respectively (Figure 7.4(b)). Then, the scores of each solvent are calculated by interpolation. More information can be consulted in the Supplementary Information. The scores of the efficiency extraction are shown in Table 7.2. The best performance score was obtained for 1-butanol, followed by isobutanol, 2-butanol and MEK.

7.2.2.3. COST

Most of the reported studies considering metrics for the selection of sustainable solvents account for EHS issues and their performances for a given application are seldom addressed. In addition, economic considerations are often ignored in sustainability assessments. A possible reason is that the cost and availability of solvents are variable with respect to time and geography. However, in this study, the assignment of scores to the acquisition costs (SA) was considered relevant. These scores may be updated at any time. Thus, a quotation from several suppliers was collected and the full dataset was scored, as demonstrated in the Supplementary Information, following the same methodology described in Section 7.2.2.2.

Furthermore, the energy involved in the solvent recovery system by distillation must be considered. The economics and operability of a deasphalting unit are critically dependent on the design of the solvent recovery system. A simple way of quantifying the costs related to solvent recovery (Re) is through the enthalpy of vaporization, since as the enthalpy increases more energy is required to recover the solvent. Enthalpy of vaporization of each solvent at its normal boiling point, and the respective scoring calculations are demonstrated in the Supplementary Information. Finally, the combined cost score was calculated based on the geometric mean, according to Eq. (7.11), and the values are reposted in Table 7.3.

$$\text{Cost score} = \sqrt{\text{SA} \times \text{Re}} \tag{7.11}$$

7.2.2.4. SUSTAINABILITY SCORE

Finally, the objective of Phase 2 is to rank the solvents based on greenness, efficiency, and cost through the calculation of the sustainability score, as described by Eq. (7.12).

$$\text{Sustainability score} = \text{GSK greeness score}^{w_1} \times \text{Performance score}^{w_2} \times \text{Cost score}^{w_3} \tag{7.12}$$

It should be noted that different weights can be attributed to the combined scores shown in Table 7.3, depending on the importance that is desired for each metric. Figure 7.5.(a) shows the sustainability scores giving similar significance to each metric, which were evenly weighted. The top sustainable solvents for the regeneration of waste oil are 1-butanol, isobutanol, MEK and 2-butanol.

Figure 7.5.(b) shows the sensitivity analysis of the sustainability score for each solvent when weights assigned to the individual scores vary. The results show that in general solvents with lower sustainability score are more sensitive to the assignment of weights. Nevertheless, the sensitivity analysis confirms that 1-butanol, isobutanol, MEK and 2-butanol are effectively the most sustainable solvents and variations on the given weights do not affect greatly the final score.

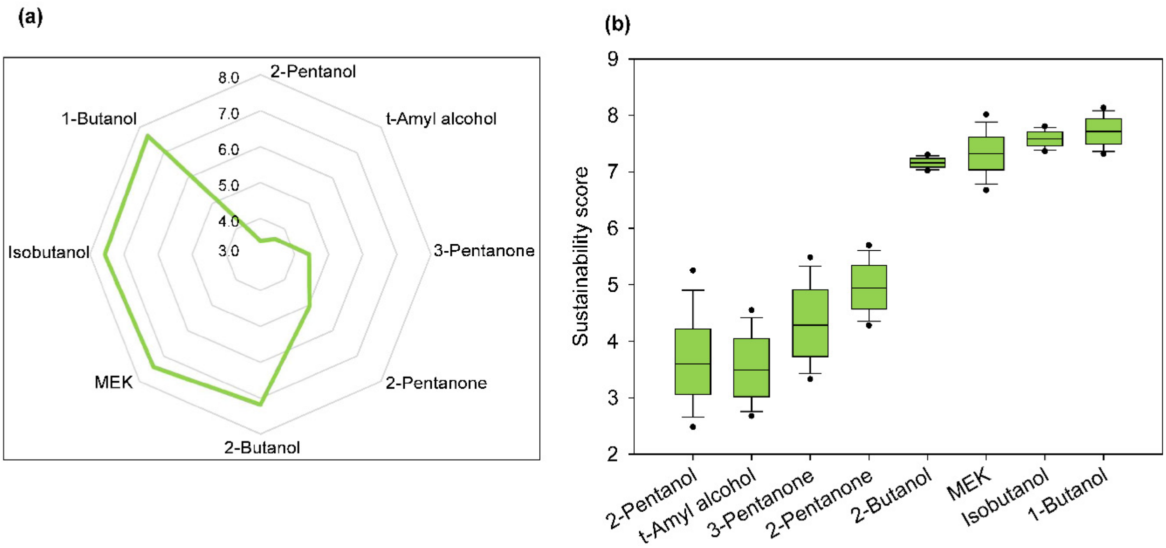


Figure 7.5. (a) Sustainability score for different solvents weighting evenly the greenness, performance and cost scores. (b) Sensitivity of the sustainability score to the variation of the weights assigned.

The present study does not account for the environmental impacts across the full life cycle of the solvents, from raw-material, manufacturing, use, recovery and disposal. Some research has been developed to consider the overall sustainability impact associated with solvent use. GSK has highlighted the importance of solvent optimization, recovery and recycling in reducing life cycle environmental impacts and the minimal use of complex solvent mixtures in chemical processes [13,17]. Amelio et al. indicated that solvents yielding a great environmental burden during the production step should always be recovered to minimize the total impact [53]. Thus, it would be interesting in the future work to include life cycle thinking into solvent selection decisions for the regeneration of WLO to ensure that the total business and environmental impacts are appropriately considered and verify the outcomes of the present methodology.

7.3. CONCLUSIONS

The methodology herein presented comprises a set of application-specific guidelines developed for the selection of solvents used in the treatment of WLO by extraction. The regeneration process contributes to the transition toward a circular economy and the selection of green solvents helps to boost the sustainability of the process.

The first phase of the methodology involved the screening of solvents through defined criteria. These included the selection of solvents meeting five process constraints: solvents are not constituted by water and acids, are selective for the extraction-flocculation process, have a number of carbon atoms between 3 and 5; have $T_m < 10$ ºC and T_{bp} between 60 and 130 ºC; and have a yield > 85%. The second phase of the selection methodology involves the scoring from 1 to 10 of sustainability metrics, namely greenness, efficiency of extraction and cost. In the end, a sustainability score is obtained for each solvent. The GSK solvent selection guide released in 2016 has been used as dataset for the greenness assessment, gathering data on environment, waste, health and process safety areas. From a list of 154 solvents, 8 passed the first screening criteria, meeting the defined process constraints. The main conclusion is that when weighting evenly the criteria of second phase, 1-butanol, isobutanol and MEK were the most sustainable solvents.

This methodology could be extended to other solvents, when information, mainly on greenness, is available. These guidelines for the selection of sustainable solvents can be used for other processes and applications, as long as proper screening criteria are defined.

7.4. REFERENCES

[1] M.A. Reis, M.S. Jerónimo, Waste lubricating oil rerefining by extraction-flocculation. 1. A scientific basis to design efficient solvents, Ind. Eng. Chem. Res. 27 (1988) 1222–1228.

[2] J.G. Speight, D.I. Exall, Rerefining of Used Lubricating Oils, CRC Press, Boca Raton, 2014.

[3] GEIR, An Environmental Review of Waste Oils Regeneration. http://www.geir-rerefining.org/documents/PositionpaperGEIR161104.pdf, 2004 (accessed September 15, 2017).

[4] R. Kerton, F. Marriott, Alternative Solvents for Green Chemistry, Royal Society of Chemistry, Cambridge, 2013.

[5] R. Gani, C. Jiménez-González, A. Ten Kate, P.A. Crafts, M. Jones, L. Powell, J.H. Atherton, J.L. Cordiner, A modern approach to solvent selection, Chem. Eng. J. 113 (2006) 30–43.

[6] P.G. Jessop, Green/Alternative solvents, in: M. Abraham (Ed.), Encyclopedia of Sustainable Technologies, Elsevier, Amsterdam, 2017, pp. 611–619.

[7] A. Kupareva, P. Mäki-Arvela, D.Y. Murzin, Technology for rerefining used lube oils applied in Europe: A review, J. Chem. Technol. Biotechnol. 88 (2013) 1780–1793.

[8] F. Awaja, D. Pavel, Design Aspects of Used Lubricating Oil Re-Refining, Elsevier, Amsterdam, 2006.

[9] F. Audibert, Waste Engine Oils. Rerefining and Energy Recovery, Elsevier Science & Technology Books, Amsterdam, 2006.

[10] J. Rincón, P. Cañizares, M.T. García, Regeneration of used lubricant oil by polar solvent extraction, Ind. Eng. Chem. Res. 44 (2005) 4373–4379.

[11] J.P. Martins, The extraction-flocculation re-refining lubricating oil process using ternary organic solvents, Ind. Eng. Chem. Res. 36 (1997) 3854–3858.

[12] D. Prat, O. Pardigon, H.W. Flemming, S. Letestu, V. Ducandas, P. Isnard, E. Guntrum, T. Senac, S. Ruisseau, P. Cruciani, P. Hosek, Sanofi's solvent selection guide: A step toward more sustainable processes, Org. Process Res. Dev. 17 (2013) 1517–1525.

[13] C. Jiménez-Gonzalez, A.D. Curzons, D.J.C. Constable, V.L. Cunningham, Expanding GSK's solvent selection guide - application of life cycle assessment to enhance solvent selections, Clean Technol. Environ. Policy. 7 (2004) 42–50.

[14] C.M. Alder, J.D. Hayler, R.K. Henderson, A.M. Redman, L. Shukla, L.E. Shuster, H.F. Sneddon, Updating and further expanding GSK's solvent sustainability guide, Green Chem. 18 (2016) 3879–3890.

[15] L.J. Diorazio, D.R.J. Hose, N.K. Adlington, Toward a more holistic framework for solvent selection, Org. Process Res. Dev. 20 (2016) 760–773.

[16] K. Alfonsi, J. Colberg, P.J. Dunn, T. Fevig, S. Jennings, T.A. Johnson, H.P. Kleine, C. Knight, M.A. Nagy, D.A. Perry, M. Stefaniak, Green chemistry tools to influence a medicinal chemistry and research chemistry based organisation, Green Chem. 10 (2008) 31–36.

[17] M. Sathish, S. Silambarasan, B. Madhan, J. Raghava Rao, Exploration of GSK'S solvent selection guide in leather industry: a CSIR-CLRI tool for sustainable leather manufacturing, Green Chem. 18 (2016) 5806–5813.

[18] K. Skowerski, J. Białecki, A. Tracz, T.K. Olszewski, An attempt to provide an environmentally friendly solvent selection guide for olefin metathesis, Green Chem. 16 (2014) 1125–1130.

[19] L. Soh, M.J. Eckelman, Green solvents in biomass processing, ACS Sustain. Chem. Eng. 4 (2016) 5821–5837.

[20] F.I. McGonagle, D.S. MacMillan, J. Murray, H.F. Sneddon, C. Jamieson, A.J.B. Watson, Development of a solvent selection guide for aldehyde-based direct reductive amination processes, Green Chem. 15 (2013) 1159–1165.

[21] J. Hildebrand, R.L. Scott, Regular Solutions, Prentice-Hall, Englewood Cliffs, New Jersey, 1962.

[22] G. Delmas, D. Patterson, T. Somcynsky, Thermodynamics of polyisobutylene–n-alkane systems, J. Polym. Sci. 57 (1962) 79–98.

[23] B. Efron, R. Tibshirani, An Introduction to the Bootstrap, Chapman & Hall/CRC, New York, 1994.

[24] Wolfram Research Inc., Mathematica, Version 11.3, Wolfram Research, Inc., Champaign, Illinois, 2018.

[25] C. Kajdas, Re-refining technologies, in: T. Mang (Ed.), Encyclopedia of Lubricants and Lubrication, Springer-Verlag Heidelberg, Berlin, 2014, pp. 1554–1568.

[26] I. Hamawand, T. Yusaf, S. Rafat, Recycling of waste engine oils using a new washing agent, Energies. 6 (2013) 1023–1049.

[27] D. Tsui, Society of tribologists and lubrication engineers - Why synthetics are leading the lubricants market. http://www.stle.org/files/TLTArchives/2017/06_June/Market_Trends.aspx, 2017 (accessed September 5, 2017).

[28] K. Izutsu, Electrochemistry in Nonaqueous Solutions, Wiley-VCH, Weinheim, 2009.

[29] J. Pöhler, M. Mödler, D. Bruhnke, H. Hindenberg, Method for reprocessing waste oils, US Patent 6712954 B1, 2004.

[30] J. Lukić, A. Orlović, M. Spiteller, J. Jovanović, D. Skala, Re-refining of waste mineral insulating oil by extraction with N-methyl-2-pyrrolidone, Sep. Purif. Technol. 51 (2006) 150–156.

[31] R.R. Mohammed, I.A.R. Ibrahim, A.H. Taha, G. McKay, Waste lubricating oil treatment by extraction and adsorption, Chem. Eng. J. 220 (2013) 343–351.

[32] M.A. Reis, M.S. Jeronimo, Waste lubricating oil rerefining by extraction-flocculation. 2. A method to formulate efficient composite solvents, Ind. Eng. Chem. Res. 29 (1990) 432–436.

[33] H. Burrell, The challenge of the solubility parameter concept, J. Paint Technol. 40 (1968) 197-208.

[34] S. Gryglewicz, M. Stankiewicz, F.A. Oko, I. Surawska, Esters of dicarboxylic acids as additives for lubricating oils, Tribol. Int. 39 (2006) 560–564.

[35] Peter-Greven, Your partner for ester lubricants. https://www.peter-greven.de/fileadmin/user_upload/dweber/PDFs/Broschueren/PG_LUBRICANTS_2016_erg.pdf, 2016 (accessed October 3, 2017).

[36] L.R. Rudnick, Synthetics, Mineral Oils, and Bio-Based Lubricants: Chemistry and Technology, CRC Press, Boca Raton, 2013.

[37] L. Lugo, V. Luna, J. García, E.R. López, M.J.P. Comuñas, J. Fernández, Prediction of the pressure dependence on the thermodynamic properties of dialkyl carbonate + alkane mixtures using Nitta-Chao model, Fluid Phase Equilib. 217 (2004) 165–173.

[38] A. Voelkel, J. Fall, Solubility parameter as polarity measure for high-boiling oil products, Fuel. 122 (2014) 310–315.

[39] F.W. Billmeyer, J. Wiley, Textbook of Polymer Science, third ed., John Wiley and Sons, New York, 1984.

[40] M. Levin, P. Redelius, Determination of three-dimensional solubility parameters and solubility spheres for naphthenic mineral oils, Energy Fuels 22 (2008) 3395–3401.

[41] A.L. McClellan, Tables of Experimental Dipole Moments, W. H. Freeman and Company, San Francisco and London, 1963.

[42] C.M. Hansen, Hansen Solubility Parameters: A User's Handbook, second ed., CRC Press Taylor & Francis Group, Boca Raton, 2007.

[43] E. Epelle, Y. Lukman, A.J. Otaru, A comparative study of the solvent powers of phenol, furfural and NMP in improving the viscosity index of spent lubricating oil, Int. Res. J. Eng. 3 (2016) 8–24.

[44] J. Sherwood, M. De bruyn, A. Constantinou, L. Moity, C.R. McElroy, T.J. Farmer, T. Duncan, W. Raverty, A.J. Hunt, J.H. Clark, Dihydrolevoglucosenone (Cyrene) as a bio-based alternative for dipolar aprotic solvents, Chem. Commun. 50 (2014) 9650–9652.

[45] N.R. DeLue, W.R. Roberts, Fuel additive, US Patent 4718919 A, 1988.

[46] S. Ahn, S. Shin, S.I. Im, K.B. Lee, N.S. Nho, Solvent recovery in solvent deasphalting process for economical vacuum residue upgrading, Korean J. Chem. Eng. 33 (2016) 265–270.

[47] J.J. McKetta, Encyclopedia of Chemical Processing and Design: Volume 14 - Crystallization: Nucleation Systems to Design Data-Importance of Accuracy, CRC Press, New York and Basel, 1982.

[48] F. Audibert, Waste Engine Oils: Rerefining and Energy Recovery, Elsevier, Amsterdam, The Netherlands, 2006.

[49] J. Rincón, P. Cañizares, M.T. García, I. Gracia, regeneration of used lubricant oil by propane extraction, Ind. Eng. Chem. Res. 42 (2003) 4867–4873.

[50] C.T. Pinheiro, M.J. Quina, L.M. Gando-Ferreira, Efficiency of regeneration by solvent extraction for different types of waste oil, in: C. Vilarinho, F. Castro, M. de L. Lopes (Eds.), Wastes Solutions Treatments and Opportunities Vol II, CRC Press – Taylor & Francis Group, London, 2018, pp. 133–138.

[51] N.O. Elbashir, S.M. Al-zahrani, M.I.A. Mutalib, A.E. Abasaeed, A method of predicting effective solvent extraction parameters for recycling of used lubricating oils, 41 (2002) 765–769.

[52] J. Rincón, P. Cañizares, M.T. García, Waste oil recycling using mixtures of polar solvents, Ind. Eng. Chem. Res. 44 (2005) 7854–7859.

[53] A. Amelio, G. Genduso, S. Vreysen, P. Luis, B. Van der Bruggen, Guidelines based on life cycle assessment for solvent selection during the process design and evaluation of treatment alternatives, Green Chem. 16 (2014) 3045–3063.

8. REGENERATION OF WASTE LUBRICANT OIL WITH DIFFERENT PROPERTIES USING GREEN SOLVENTS

This work aimed at studying the effect of different characteristics of WLO on the extraction performance. 1-Butanol and methyl ethyl ketone (MEK) were selected as green solvents. The efficiency was evaluated for three WLO samples (class A, B, and C) with substantially different properties. Class A is the most common type of WLO; Class B corresponds to mineral oil with low level of contaminants (e.g. oxidation products and additives); Class C is mainly constituted by synthetic ester base oils. The analysis involved the response surface methodology and the desirability function to model two response variables (yield and percent sludge removal - PSR) and to find the best operating conditions for the most influent factors (solvent/oil ratio and KOH dosage).

The rates of contaminant removal were very dependent on the type of WLO. The maximum PSR achieved were 8.5 and 6.5% using 1-butanol for class A and C oils, respectively, while 6.3 and 4.7% were observed for MEK. Thus, 1-Butanol is a more efficient extracting agent than MEK for both classes A and C. The extraction process is not effective for class B oil (PSR ≈ 0%), and these oils can bypass the deasphalting stage, saving materials and energy. The addition of KOH as flocculation agent in class C oils is less effective due to the saponifiable matter content in the oil. Solvent extraction is a suitable treatment route for the regeneration of synthetic ester-based oils (class C). Reasonably accurate models regarding the response variables were obtained for both solvents and class A and C oils. Considering desirability functions, a solvent/oil ratio of 5 w/w and KOH dosage of 1.5 or 2 g/L were found as optimal conditions.

Keywords

Regeneration; extraction; waste oil segregation; green solvents; circular economy; optimization.

This chapter is based upon the publication:

Pinheiro, C.T., Pais, R.F., Quina, M.J., Gando-Ferreira, L.M., 2018. Regeneration of waste lubricant oil with different properties by extraction using green solvents, J. Clean. Prod. (Submitted and reviewed with minor revisions).

8.1. INTRODUCTION

Improper handling and disposal of waste lubricant oil (WLO) can cause severe damage to the environment, and to human health. Recently, Decision 2014/955/EU indicates clearly that WLO should be classified as hazardous waste, since it contains relevant hazardous substances that render them the hazardous properties HP 5 (specific target organ toxicity (STOT)/aspiration toxicity), HP 7 (carcinogenic) and HP 14 (ecotoxic) as listed in the Commission Regulation (EU) No 1357/2014 of 18 December 2014 [1].

Regeneration of WLO is the most interesting route to mitigate the negative environmental impact of this hazardous waste [2]. Regeneration aims at the recovery of the base oil to produce again fresh lubricants, improving resource efficiency, reducing the need for raw materials and aiming at closing the material flows [3]. This operation is clearly a worthy example of how to “close the loop” in a circular economy perspective, with minimal losses per cycle [4]. In general, the basic operations comprise the pre-treatment, the dewatering, and defueling, the de-asphalting, fractionation and finishing steps [5].

The de-asphalting stage is one of the most critical phases of the process since it allows the separation of impurities (additives, resinous and carbonaceous materials) from the base oil [6]. Vacuum distillation and solvent extraction are the common processes used to separate the base oil from heavier impurities [7]. One of the main problems associated with distillation processes is the formation of deposits and hot-spots caused by resinous materials. These deposits may induce coking and fouling of the internal surfaces, which makes continuous operation difficult and low-quality base oils [8]. To overcome this problem, thin film evaporator (TFE) or thermal deasphalting (TDA) units were suggested [5]. However, these equipment operate at high temperature and very high vacuum, requiring high investment and operating costs [9]. On the other hand, solvent extraction has been reported to be a simple, efficient, low energy consumption and economical technology that can be used as an alternative to vacuum distillation.

Supercritical propane is the typical solvent used in industry [10]. Recent studies showed that an alcohol or ketone can replace propane as extraction media, operating at room temperature and pressure and reducing coking and fouling problems downstream [11]. Mohammed and coworkers studied the performance of six solvents, showing that 1-butanol achieved the best percent sludge removal, followed by n-hexane, petroleum ether, 1-hexanol, carbon tetrachloride, and acetone [12]. Martins proposed a mixture of 0.25 waste oil/0.35 n-hexane/0.40 polar compound (80% 2-propanol + 20% 1-butanol) as an effective ternary solvent for the removal of contaminants [13]. Elbashir and coworkers highlighted the performance of three extracting solvents in recycling waste oil, showing that methyl ethyl ketone (MEK) achieved the lowest percent oil losses, followed by 2-propanol and 1-butanol [14].

Most technologies applied today are suitable for the treatment of different types of feedstock, including synthetic and bio-based oils, which are currently replacing the conventional mineral oils due to their enhanced performance characteristics. Bio-based lubricants have been found to exhibit superior lubricant properties over the conventional mineral lubricants, with great renewability and biodegradability [15]. However, when an alkaline treatment is applied, the amount of synthetic or semi-synthetic oils based on esters in the feedstock might be problematic, since these oils are less stable [10]. Application of strong alkali agents, such as potassium hydroxide (KOH), is a common treatment adopted to increase the removal of contaminants and reduce plant fouling. It allows the formation of low solubility metal salts, causing their precipitation [16]. The alkali is also an effective agent in neutralizing acids and free or bound chlorine [6].

However, given the wide variety of compounds that comprise a WLO, the alkali can interact with the oil in many different ways. WLO is considered colloidal multicomponent disperse systems comprising a dispersion medium (the base oil) and a dispersive phase (liquid or solid additives), which may accumulate impurities [17]. The stability of the colloidal system is mainly related to electrostatic repulsive forces between the particles. The addition of a strong electrolyte, such as KOH, results in a destabilization of the particles, i.e. the particles may interact with each other, resulting in aggregate formation (coagulation) by Van der Waals forces [18]. In addition, under certain operating conditions (e.g. temperature, the concentration of alkali solution, stirring, etc.), KOH promotes saponification reactions between long chain fatty acids or esters and the alkali, yielding a salt of the alkali, called soap [19]. Soaps impart a thickening effect on the oil, which can lead to the production of a gel-type matrix [20]. The occurrence of this phenomenon called coagulation phenomena is highly detrimental to the regeneration process. The production of a gel during separation steps reduces the lubricant's fluidity, possibly causing blocking problems in the plant [21]. Consequently, the deasphalting step by distillation is unfeasible for WLO with these characteristics which must be managed by alternative ways [22].

In this context, to the best of our knowledge, the effect of WLO with diverse properties in the extraction efficiency has not been reported in the literature. Thus, the main objective of this work is to evaluate the effect of different types of WLO in the performance of solvent extraction. In addition, the best process conditions for each system are assessed, based on the response surface methodology (RSM) and the desirability function approach.

8.2. MATERIALS AND METHODS

8.2.1. MATERIALS

Our previous study [22] revealed that WLO could be grouped into three main classes according to their stability to the alkaline pretreatment, namely: class A if the oil matrix remains unaffected by the addition of KOH; class B if a precipitate is formed; and class C if a gel-type oil occurs. Thus, three samples of WLO (one per class) were collected in Portugal. The samples were previously pre-treated by centrifugation and flash distillation to remove sediments, water, and light hydrocarbons, and then stored at room temperature in the dark to maintain their integrity until further use. Table 8.1 shows the physicochemical properties of each sample based on viscosity at 40 and 100 ºC, viscosity index, total acid number (TAN), and elemental composition, determined in accordance with the methods described in Section 8.2.3.

1-Butanol (Carlo Erba, > 99.5%) and methyl ethyl ketone - MEK (Sigma Aldrich, > 99.5%) were used as extraction solvents. These extracting agents were selected considering a screening methodology of our previous study, which indicated that 1-Butanol and MEK are the most sustainable solvents for the regeneration of waste oil [23].

Table 8.1. Properties of the analyzed waste oil classes A, B and C.

Parameter	Waste lubricant oil		
	Class A	Class B	Class C
Viscosity at 40 °C (cSt)	85.0	9.00	67.7
Viscosity at 100 °C (cSt)	10.7	2.33	10.50
Viscosity Index (VI)	110	56.4	143
TAN (mg KOH/g)	0.48	<QL	1.87
Elemental content			
P (ppm)	761	<QL	717
Ca (ppm)	1990	<QL	1620
Cl (ppm)	123	7.03	202
Zn (ppm)	1020	<QL	980
Fe (ppm)	142	<QL	212
S (%)	1.02	0.14	1.13

QL – Quantitation Limit for TAN = 0.05 mg KOH/g, P = 4.99 ppm, Ca = 11.8 ppm, Zn = 2.17 ppm and Fe = 9.24 ppm.

8.2.2. SOLVENT EXTRACTION PROCEDURE

The extraction procedure was adapted from Reis and Jeronimo, (1988). Previously weighed centrifugal tubes were filled with a mixture of 20 g of WLO sample (Wwaste oil) and solvent at a specified ratio. The samples were stirred by magnetic stirring at 500 rpm, for 20 min. The tubes were centrifuged at 4000 rpm for 20 min. Then, the wet sludge phase (additives and impurities) was separated from the mixture solvent/oil. The solvent was recovered by vacuum distillation (13 mbar) in a rotary evaporator. Distillation flasks were previously weighed, and the mass of the recovered oil (Wbase oil), and the solvent was calculated by difference. The yield was determined by Eq. (8.1).

$$Yield\ (\%) = \frac{W_{base\ oil}}{W_{waste\ oil}} \times 100 \tag{8.1}$$

The tubes were then placed in the oven for 1 h at 80 ºC to evaporate any remaining solvent. The wet sludge was redispersed by addition of 7 mL of n-hexane to separate the sludge, followed by 28 mL of isopropanol to produce again large flakes. The purpose of this washing phase is to reduce the interstitial oil content in the sludge that would not evaporate by simple drying. Finally, after centrifugation, the washing liquid was discarded, and the tubes were introduced into the oven and dried for 1 h at 80 ºC.

After cooling, the tubes with the sludge but without any oil were weighed (Wdry sludge) and the percent of sludge removal (PSR) was calculated according to Eq. (8.2).

$$PSR\ (\%) = \frac{W_{dry\ sludge}}{W_{waste\ oil}} \times 100 \qquad (8.2)$$

8.2.3. PHYSICOCHEMICAL CHARACTERIZATION

The WLO and extracted base oil samples were characterized based on viscosity (ASTM D7042), total acid number (TAN) (ASTM D664), saponification number (ASTM D94), elemental content by EDXRF, and FTIR. The experimental procedures are described in more detail in a previous work [25].

8.2.4. DESIGN OF EXPERIMENTS

In order to develop multiple linear regression models to relate important output parameters with input factors, a design of experiments (DoE) was performed. Among the process variables that influence the process are the temperature, the solvent/oil ratio, the concentration of flocculation agent, the mixing time, and speed. The contact time has been previously studied, revealing that equilibrium conditions are achieved within 5-10 min [26]. Rincón et al., (2005) tested the temperature increase from 25 to 60 ºC, which resulted in an insignificant increase in the yield of extraction [11]. The increase in the mixing speed from 400 to 1200 rpm showed little effect on the yield of extraction [27]. Thus, the selected operating variables (factors) are the solvent/oil ratio (X1) and the KOH dosage (X2). After determining the variation range of the input variables through the single-factor test, experiments were designed to find the interactions of the two factors. PSR and Yield were considered the target responses. A full factorial design of two variables at three levels was performed. The experimental matrix consisted of nine runs of different combinations, each run was performed in triplicate. The levels of the independent variables used in the experimental design are shown in Table 8.2.

Table 8.2. Full factorial design of experiments.

Factor	**Level**		
	-1	**0**	**+1**
$X1$: Solvent/oil ratio (w/w)	2	4	6
$X2$: KOH dosage (g/L)	0	1.5	3

The optimization strategy of the extraction process and the statistical analysis was carried out using JMP 13 PRO software [28]. A second-order polynomial regression model for describing the experimental responses was expressed according to Eq. (8.3),

$$\mathrm{Y} = \beta_0 + \sum_{i=1}^{n} \beta_i X_i + \sum_{i=1}^{n} \beta_{ii} X_i^2 + \sum_{1 \le i \le j}^{n} \beta_{ij} X_i X_j \tag{8.3}$$

were Y is the response, β_0 the intercept, X_i and X_j are the factors, and β_i, β_{ii}, and β_{ij} are regression coefficients of the linear, quadratic, and interactive terms, respectively. Regression coefficients were determined by employing standard least squares technique.

8.2.5. PROFILER AND DESIRABILITY FUNCTION APPROACH

In order to find the best conditions of extraction for different classes of WLO, the regression models based on Eq. (8.3) were used to generate a prediction profiler and then calculate the desirability functions using JMP 13 PRO software [29]. The prediction profiler is a two-dimensional illustration of the response surface function. In these plots, the responses (PSR and Yield) are plotted against each of the factors (solvent/oil ratio and KOH dosage), showing how changing one factor settings, while holding the other constant, impacts the responses in the model. The desirability function approach is one of the most widely used methods in the industry for dealing with the optimization of multiple response processes. The method finds operating conditions, X_i, that provide the "most desirable" response values [30].

Each of the measured response $Y_i(X_i)$ is transformed into a dimensionless scale using the fitted models. The desirability function $d_i(Y_i)$ ranges between $d_i(Y_i) = 0$ for a completely undesired response, to $d_i(Y_i) = 1$ for a fully desired or ideal response value. Finally, the overall desirability *D* is calculated by applying Eq. (4),

$$D = (d_1(Y_1)\, d_2(Y_2) \ldots\, d_n(Y_n))^{1/n} \tag{8.4}$$

where *n* denotes the number of responses. Depending on whether a particular response Y_i is to be maximized, minimized, or assigned to a target value, different desirability functions can be used. In this work, the objective was to maximize both Y_1 *and* Y_2, which correspond to the PSR and Yield.

8.3. RESULTS AND DISCUSSION

8.3.1. SELECTION OF INPUT VARIABLES

Appropriate selection of the experimental domain for each of the factors was performed from the single-factor test for a wide range of the process variables.

8.3.1.1. EFFECT OF SOLVENT/OIL RATIO

The effect of solvent/oil ratio on the PSR using 1-butanol and MEK is shown in Figure 8.1 (a) and (b). Each solvent produces a different PSR response depending on the class of WLO. In general, similar trends are observed for class A and C oil. The sludge removal increases with the increase of the solvent/oil ratio up to a point where it stabilizes. At smaller ratios, the saturation of the solvent occurs, due to its inability to dissolve all base oil and flocculate most of the impurities. As the solvent/oil ratio increases, the amount of insoluble impurities that precipitate increases up to a ratio where the dissolution power is exhausted [11]. Consequently, further increase of solvent/oil ratio will not promote an increased removal of impurities. The maximum achieved PSR was 8.5 and 6.5% using 1-butanol and 6.3 and 4.7% using MEK for class A and C oils, respectively. MEK has clearly lower flocculation power when compared to 1-butanol. When using the same solvent, the variations on PSR achieved for different WLO is related to the intrinsic characteristics of the oil components. The lower PSR obtained for class C when compared to class A could be explained by the lower solubility of the base oil in the solvent. In addition, the contaminants could be more soluble in the solvent decreasing the antisolvent effect exerted on the impurities, or even the amount of impurities present is lower.

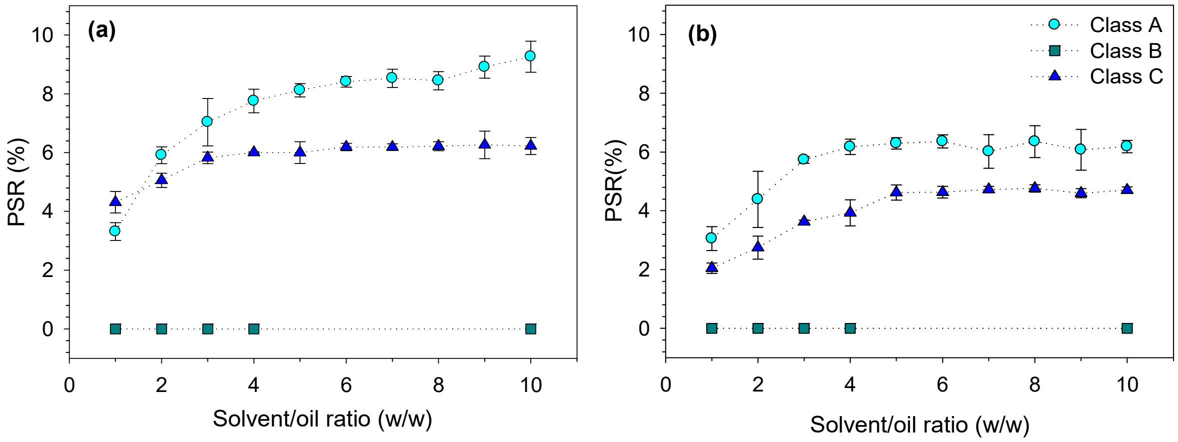


Figure 8.1. Effect of solvent/oil ratio on the sludge removal for different types of waste oil using (a) 1-butanol and (b) MEK.

In contrast, for class B oil, no flocculation was observed and no impurities were removed using both solvents. A previous study by Pinheiro et al. (2017) showed that class B oils have typically low TAN, saponification number and elements (P, Ca, Zn, S, Al, and Cl) which indicate the absence of additives and oxidation products [22]. These characteristics are confirmed for the class B oil studied in this work, which are shown in Table 8.1, Section 8.2.1. Thus, the deasphalting phase by solvent extraction for these oils could be avoided. In fact, this result supports the Waste Framework Directive 2008/98/EC, in particular, Article 21 which states that waste oils of different characteristics should not be mixed. The adoption of a prior WLO segregation methodology before regeneration would be desirable to avoid unnecessary use of materials and energy. Segregation can be performed to certain types of oils, such as hydraulic oils and cutting fluids, since they contain low level of contaminants and will give rise to class B oils. Consequently, WLO producers must be sensitized to separated and store these oils in specific containers, which can then be collected and treated separately. These changes in the management system may entail increased costs for the collection of WLO and should, therefore, be planned carefully.

Given that maximum PSR is achieved at a solvent/oil ratio of about 5 to 6 w/w for both solvents, the range of this variable in the subsequent tests was set from 2 to 6 w/w. Indeed, higher ratios will increase the operation and construction costs without promoting a significant increase in the efficiency of extraction. Solvent/oil ratios below 2 w/w might cause difficulties in sludge sedimentation. The critical clarifying ratio (CCR) was determined for class A and C oils, using 1-butanol and MEK. This parameter is defined as the minimum solvent/oil ratio to destabilize the dispersion contained in a column, producing aggregates that settle under centrifugal conditions equivalent to 24 h of gravity action and leaving a clear supernatant. The results shown in Table 8.3 show that the CCR for a particular solvent can be different depending on the type of WLO. Class A exhibit a CCR of 1.4 and 2.2 using 1-butanol and MEK, respectively, whereas for class C a CCR of 2.2 and 3.2 were observed. The results of Class A are comparable with the ones determined by Reis and Jerónimo (1988), but the same is not true for class C.

Table 8.3. Critical clarifying ratio for different types of waste oils.

Solvent	**Critical clarifying ratio**		
	Class A	**Class C**	**Literature***
1-Butanol	1.4	2.1	1.2
MEK	2.2	3.2	2.2

* Reference [24]

8.3.1.2. EFFECT OF KOH DOSAGE

The addition of an alkaline agent in the solvent enhances the flocculation and increases the removal of impurities from the WLO. Comparing to NaOH or LiOH, KOH was found to be the best degrading agent because it ionizes quickly, forming stronger nucleophile OH- ions to destabilize the particles [31]. As shown in Figure 8.2 (a) and (b), the effect of the KOH is more significant on class A oil, increasing by 32.9 % and 25.7% the PSR using 1-butanol and MEK, respectively. On the other hand, class C oil experienced a PSR increase of 13.1% and 15.2%, respectively. This can be explained by the fact that these oils are constituted by esters [22], which react with the KOH and decrease the flocculation action. The range of KOH dosage selected for the design of experiments varied from 0 to 3 g/L for both oils.

The effect of KOH on class B oil was also evaluated using 1-butanol. As shown in Figure 8.2 (a), little sludge was formed due to the precipitation of KOH added in the solvent. Thus, even in the presence of a flocculating agent, precipitation of impurities is not observed. The evaluation of the best extraction conditions for class B oil is not relevant and further experiments will exclude class B oils.

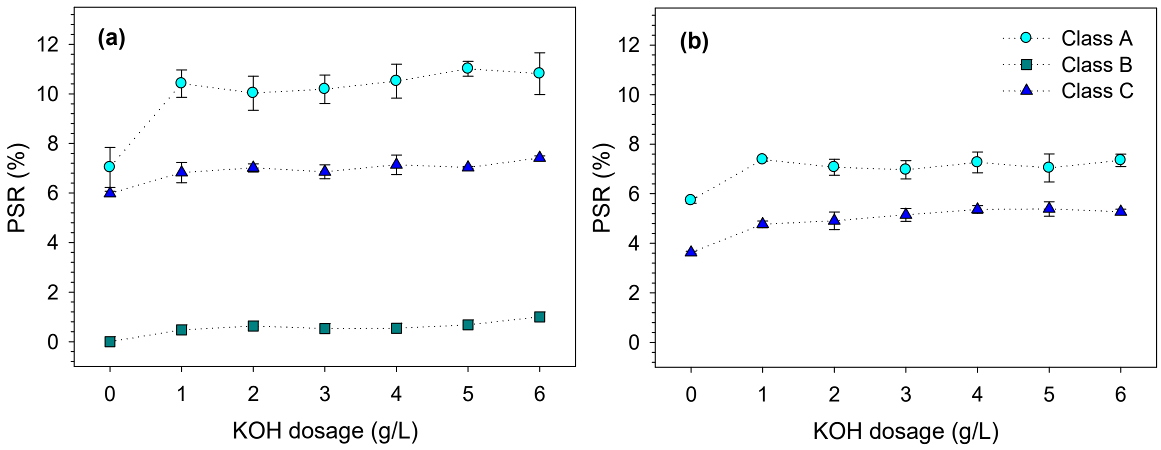


Figure 8.2. Effect of KOH dosage on the sludge removal for different types of waste oil using (a) 1-butanol and (b) MEK.

8.3.2. SURFACE RESPONSE MODELING

8.3.2.1. PREDICTED MODELS AND STATISTICAL ANALYSIS

The design of an extraction system for the regeneration of WLO depends on several operational variables. In the present work, the relationship between responses (PSR and Yield) and two independent factors (solvent/oil ratio and KOH dosage) were studied. The experimental results based on the full factorial design are shown in Table 8.4.

Table 8.4. Experimental sludge removal and yield obtained for class A and C, using 1-butanol and MEK.

Run	Solvent/oil ratio (w/w)	KOH Dosage (g/L)	Class A				Class C			
			Butanol		MEK		Butanol		MEK	
			PSR (%)	Yield (%)	PSR (%)	Yield (%)	PSR (%)	Yield (%)	PSR (%)	Yield (%)
1	**2**	**0**	4.9 ±0.6	84.8 ±1.7	4.4 ±1.0	90.3 ±0.4	4.6 ±0.3	86.9 ±0.7	2.7 ±0.4	90.2 ±0.3
2	**2**	**1.5**	7.4 ±0.6	85.4 ±0.4	5.7 ±0.2	91.5 ±0.3	5.8 ±0.2	88.7 ±0.6	3.3 ±0.1	91.9 ±0.1
3	**2**	**3**	7.5 ±0.2	86.3 ±0.1	6.4 ±0.4	92.1 ±0.1	5.8 ±0.3	89.9 ±0.2	3.2 ±0.0	93.6 ±0.1
4	**4**	**0**	6.7 ±0.8	87.5 ±0.6	6.2 ±0.3	92.3 ±0.8	5.9 ±0.0	90.7 ±0.2	4.1 ±0.2	92.4 ±0.3
5	**4**	**1.5**	10.1 ±0.2	88.9 ±0.1	7.8 ±0.4	93.1 ±0.8	6.8 ±0.1	92.1 ±0.3	4.7 ±0.1	94.1 ±0.1
6	**4**	**3**	10.2 ±0.1	89.5 ±0.1	8.2 ±0.2	93.8 ±0.2	6.9 ±0.1	92.9 ±0.3	4.7 ±0.1	95.7 ±0.3
7	**6**	**0**	8.4 ±0.2	88.9 ±0.2	6.4 ±0.2	92.8 ±0.6	6.2 ±0.1	91.8 ±0.5	4.4 ±0.2	93.1 ±0.5
8	**6**	**1.5**	11.1 ±0.3	90.1 ±0.2	8.1 ±0.1	93.7 ±0.5	7.5 ±0.1	93.3 ±0.4	4.8 ±0.2	94.9 ±0.2
9	**6**	**3**	11.1 ±0.2	91.0 ±0.1	8.5 ±0.1	94.3 ±0.3	7.5 ±0.3	94.1 ±0.2	4.9 ±0.1	96.4 ±0.1

The regression coefficients of the predicted response surface models and statistical analysis are shown in Table 8.5. The effects are centered by their mean when they are crossed with other effects, i.e.

interactions and polynomial terms, as exemplified in Eq. (8.5) for PSR response of class A tests using 1-butanol.

$$\text{PSR}\ (\%) = 4.7819 + 0.9044\,X1 + 0.9944\,X2 - 0.1397\,(X1-4)^2 + 0.0039\,(X1-4)\,(X2-1.5) - 0.6153\,(X2-1.5)^2 \tag{8.5}$$

Based on a 95% confidence level, the results indicated that for the PSR response both linear and quadratic parameters were statistically significant (p values < 0.05) for all types of oils and solvents tested. In addition, significant predicted variables are associated with reasonably large absolute t ratios (>2). In contrast, interactions between the solvent/oil ratio ($X1$) and KOH dosage ($X2$) did not produce a significant effect on this response (p values > 0.05). In respect to the Yield, the p value (<0.05) indicates that the solvent/oil ratio linear ($X1$) and quadratic ($X1^2$) effects, and linear KOH dosage ($X2$) are the effects that mostly influence the response.

Table 8.5. Regression coefficients of the predicted models.

Oil type	**Solvent**		**PSR**				**Yield**			
			Regression coefficient	**Std. Error**	***t* Ratio**	***p* Value**	**Regression coefficient**	**Std. Error**	***t* Ratio**	***p* Value**
Class A	**1-Butanol**	β_0	4.7819	0.3452	13.85	*<0.001*	83.3072	0.4942	168.57	*<0.001*
		β_1	0.9044	0.0598	15.12	*<0.001*	1.1231	0.0856	13.12	*<0.001*
		β_2	0.9944	0.0797	12.47	*<0.001*	0.6201	0.1141	5.43	*<0.001*
		β_{11}	-0.1397	0.0518	-2.70	*0.014*	-0.2254	0.0741	-3.04	*0.006*
		β_{12}	0.0039	0.0488	0.08	0.938	0.0476	0.0699	0.68	0.503
		β_{22}	-0.6153	0.0921	-6.68	*<0.001*	-0.0570	0.1318	-0.43	0.670
	MEK	β_0	4.5727	0.3237	14.12	*<0.001*	90.0576	0.3610	249.48	*<0.001*
		β_1	0.5370	0.0561	9.58	*<0.001*	0.5790	0.0625	9.26	*<0.001*
		β_2	0.6810	0.0748	9.11	*<0.001*	0.5427	0.0834	6.51	*<0.001*
		β_{11}	-0.2064	0.0486	-4.25	*<0.001*	-0.1540	0.0541	-2.84	*0.010*
		β_{12}	0.0050	0.0458	0.11	0.915	-0.0184	0.0511	-0.36	0.722
		β_{22}	-0.2356	0.0863	-2.73	*0.013*	-0.0741	0.0963	-0.77	0.450
Class C	**1-Butanol**	β_0	4.6811	0.1556	30.08	*<0.001*	86.3060	0.3275	263.51	*<0.001*
		β_1	0.4086	0.0270	15.16	*<0.001*	1.1472	0.0567	20.22	*<0.001*
		β_2	0.3853	0.0359	10.72	*<0.001*	0.8200	0.0756	10.84	*<0.001*
		β_{11}	-0.0749	0.0233	-3.21	*0.004*	-0.2801	0.0491	-5.7	*<0.001*
		β_{12}	0.0081	0.0220	0.37	0.715	-0.0660	0.0463	-1.42	0.169
		β_{22}	-0.2420	0.0415	-5.83	*<0.001*	-0.1561	0.0873	-1.79	0.088
	MEK	β_0	2.7465	0.1247	22.02	*<0.001*	89.5451	0.1837	487.38	*<0.001*
		β_1	0.4068	0.0216	18.83	*<0.001*	0.7300	0.0318	22.94	*<0.001*
		β_2	0.1775	0.0288	6.16	*<0.001*	1.1127	0.0424	26.22	*<0.001*
		β_{11}	-0.1494	0.0187	-7.98	*<0.001*	-0.1837	0.0276	-6.67	*<0.001*
		β_{12}	0.0025	0.0176	0.14	0.889	-0.0022	0.0260	-0.08	0.933
		β_{22}	-0.0965	0.0333	-2.90	*0.009*	-0.0368	0.0490	-0.75	0.461

The analysis of variance and goodness of fitting of the models are shown in Table 8.6. All models are significant (95% confidence level), as the computed p values are lower than 0.0001 and the F ratios are much higher than the critical value $F_{0.05(5,21)} = 2.685$ (NIST, 2017). Satisfactory coefficients of determination (R^2), which varied from 0.9051 to 0.9568 for PSR and from 0.8670 to 0.9836 for the Yield, indicated that the variation in the responses could be attributed to the considered effects rather than to random error. The R^2_{Adj} values, which adjust the R^2 to the number of parameters in the model, also indicated a goodness of fit in all cases. Therefore, there is strong evidence that the models will have a good predictive capability for PSR and Yield.

Table 8.6. Analysis of variance and goodness of fit of the models for the responses PSR and Yield.

Oil type	**Solvent**	**PSR**				**Yield**			
		R^2	**R^2_{Adj}**	***F* ratio**	***p* value**	**R^2**	**R^2_{Adj}**	***F* ratio**	***p* value**
Class A	**1-Butanol**	0.9541	0.9431	87.25	*<0.001*	0.9097	0.8882	42.31	*<0.001*
	MEK	0.9051	0.8825	40.04	*<0.001*	0.8670	0.8354	27.39	*<0.001*
Class C	**1-Butanol**	0.9488	0.9366	77.83	*<0.001*	0.9641	0.9556	112.8	*<0.001*
	MEK	0.9568	0.9465	92.93	*<0.001*	0.9836	0.9797	251.8	*<0.001*

Figures 3 and 4 show the simultaneous effect of solvent/oil ratio and KOH dosage on the PSR and Yield for class A and C oils using 1-butanol and MEK. As aforementioned, the PSR increased both with the solvent/oil ratio and the KOH dosage. The increase of the Yield with the solvent/oil ratio is due to the decrease of oil loss in the sludge [33]. Regarding the effect of the KOH dosage on the Yield, it was expected to be similar to the PSR behavior, increasing initially and then stabilizing. However, the increase in the KOH dosage from 1.5 to 3 g/L produces a continuous increase in the Yield, while the PSR does not show a significant improvement. This can be explained by the fact that some excess KOH remains in the base oil after evaporation of the solvent, increasing the yield. In fact, an FTIR analysis was performed on the obtained base oil (class A) after extraction with 1-butanol and using 0, 1.5 and 3 g/L of KOH. The spectra indicated the presence of –OH bands when the KOH dosage increased to 3 g/L (see Figure A.4 in Annex A6).

Therefore, high Yield of extraction does not necessarily mean better efficiency. On the contrary, high PSR results in an improved quality of the regenerated oil, which will reduce downstream stages such as vacuum distillation and finishing phases.

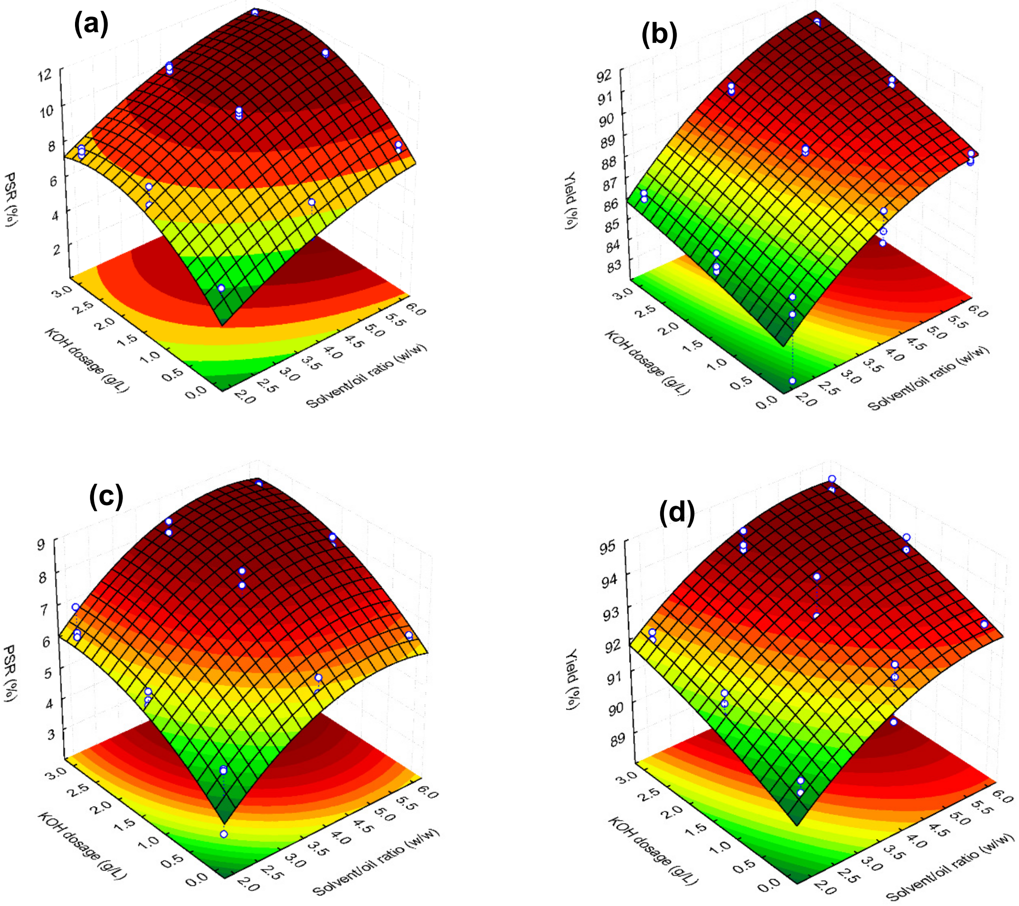
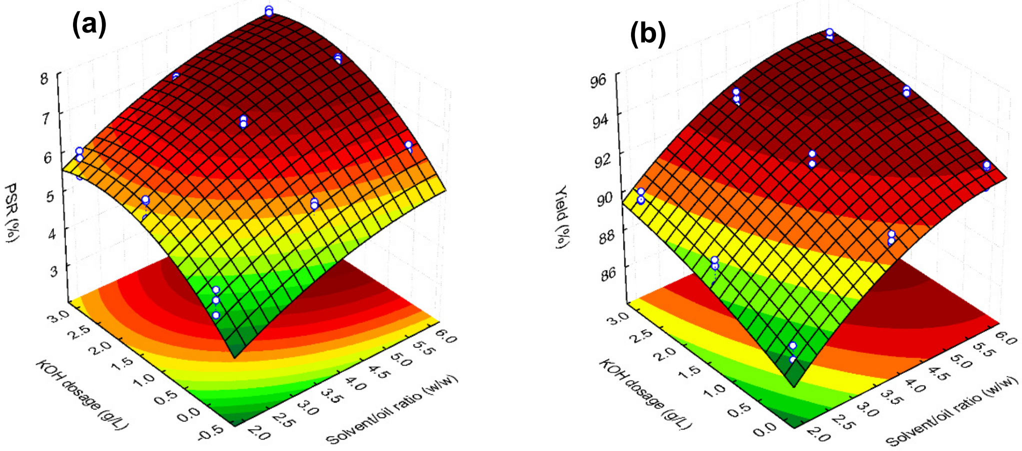


Figure 8.3. Response surface plots for WLO class A using (a) and (b) 1-butanol, and (c) and (d) MEK.



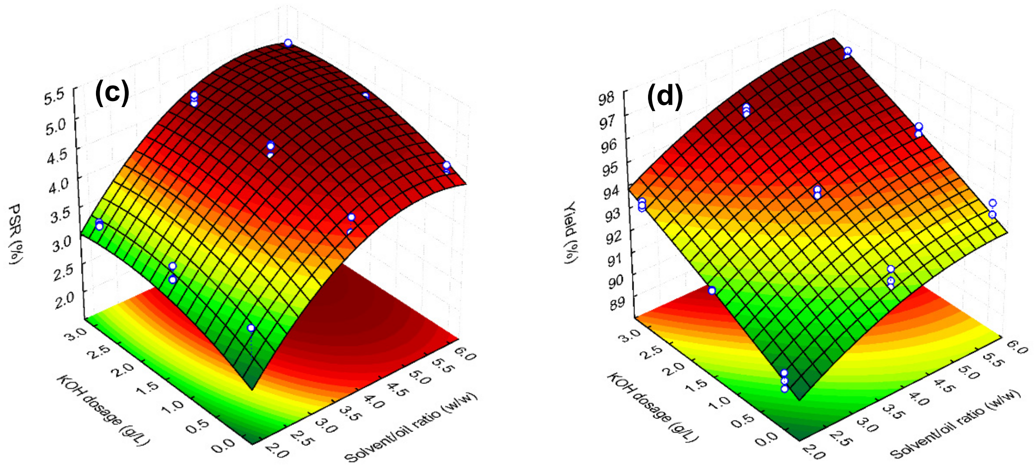


Figure 8.4. Response surface plots for WLO class C using (a) and (b) 1-butanol, and (c) and (d) using MEK.

8.3.2.2. DESIRABILITY ANALYSIS

In order to find optimal process conditions of extraction for different types of WLO, the above regression models were used to generate a prediction profiler and maximize the overall desirability function. The results indicated that optimal conditions are found near the maximum solvent/oil ratio and KOH dosage for all systems, as can be easily observed by the response surface plots shown in Figures 8.3 and 8.4. However, some practical trade-offs of the process could lead to an acceptable optimal solution different from the calculated one.

Figure 8.5 (a) and (b) illustrates the prediction profiler and desirability function for WLO class A using 1-butanol as an extraction solvent and for class C oil using MEK, respectively. The solid lines with shaded intervals show the predicted responses at 95% confidence intervals. The dotted vertical lines indicate the selected conditions for each of the factors and the dotted horizontal lines show the predicted value of both responses. The last column displays the desirability functions, d_1 and d_2, and the defined control points. In the last row, the desirability for each factor is illustrated, which combined give the overall desirability value, *D*. These curves represent the overall sensitivity of the combined desirability function to a variation of the factors.

In fact, since the increase in the KOH dosage causes the contamination of the extracted base oil and a misleading increase on the Yield, the best KOH dosage was determined by using the profiler to search the surface for maximum PSR. Another process restriction may be the use of high solvent/oil ratio, which will lead to increased solvent recovery costs and construction of the extraction units. As an example, for class A oil using 1-butanol (Figure 8.5 (a)), varying the solvent/oil ratio from 6 to 5 w/w allows savings of 16.7% of solvent use, while the PSR decrease just by 4.2% and the overall desirability decrease from 0.87 to 0.82. Thus, an overall desirability around 0.80 was established as an acceptable tradeoff between energy and material savings, and loss of extraction efficiency. The same procedure was applied for all systems and as a result, the best solvent/oil ratio was 5 w/w. The best KOH dosage was 1.5 g/L for oil class A extracted with MEK and 2 g/L for the other systems.

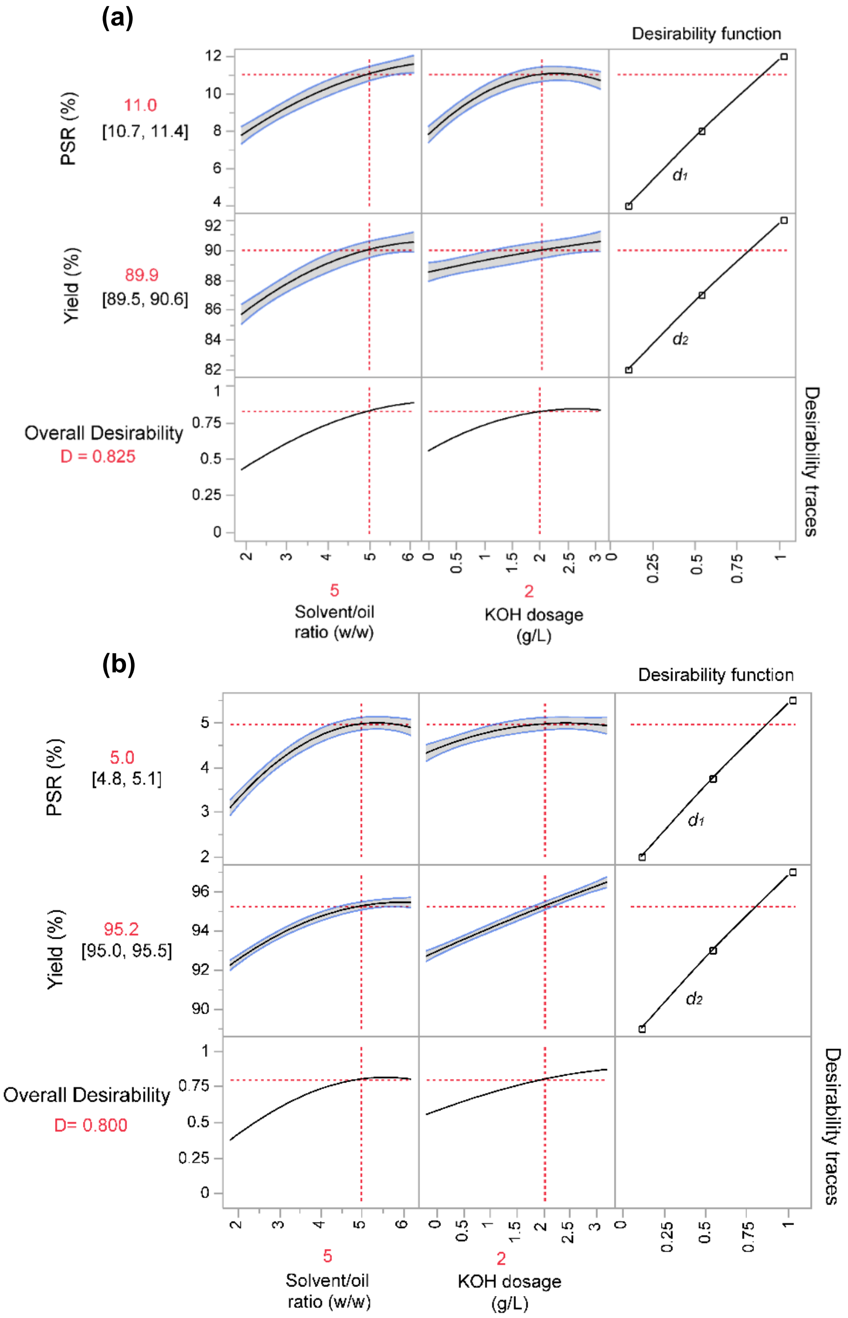


Figure 8.5. Prediction profiler and desirability function for (a) class A oil using 1-butanol and (b) class C using MEK.

8.3.2.3. VALIDATION OF PREDICTIVE MODELS

To ensure the predicted models were not biased, experimental verification was performed under different conditions within the experimental range. The results, shown in Table 8.7, demonstrated that experimental values of PSR and Yield were reasonably close to predicted values. The relative error (RE) varied from 0.4 to 9.7% for PSR and from 0.2 to 2.4% for Yield. The validation experiments confirmed that all multivariate models can satisfactorily predict the PSR and Yield.

Table 8.7. Experimental validation of predictive models.

Oil type	Solvent	Solvent/Oil ratio (w/w)	KOH dosage (g/L)	Experimental		Predicted		RE (%)[a]	
				PSR (%)	Yield (%)	PSR (%)	Yield (%)	PSR (%)	Yield (%)
Class A	**1-Butanol**	5	2	10.4 ±0.6	87.9 ±0.8	11.0	89.9	5.6	2.4
		3	1	7.5 ±0.2	87.4 ±0.2	8.2	87.1	8.6	0.4
	MEK	5	1.5	7.5 ±0.1	93.4 ±0.3	8.1	93.6	7.5	0.2
		3	1	7.1 ±0.1	91.4 ±1.8	6.6	92.2	6.6	0.8
Class C	**1-Butanol**	5	2	7.3 ±0.1	94.0 ±0.1	7.4	93.3	0.4	0.7
		3	1	6.8 ±0.4	89.8 ±1.0	6.2	90.2	9.7	0.5
	MEK	5	2	4.9 ±0.4	94.1 ±1.7	5.0	95.2	1.1	1.2
		3	1	4.3 ±0.2	92.0 ±0.7	4.0	92.7	7.6	0.7

[a] Relative error, determined as RE (%) = $\left|\frac{Experimental - Predicted}{Experimental}\right| \times 100$

8.3.2.4. PHYSICOCHEMICAL CHARACTERIZATION

The quality of the base oil after extraction using the best conditions was compared with the original waste oil. As shown in Table 8.8, the characteristics of the base oil are notably improved after extraction. The viscosity of both class A and C oils treated with 1-butanol and MEK decreases when compared to the original waste oil. This can be explained by the fact that oxidation products were removed, which are the cause of undesired viscosity increase during usage [34]. A decrease in the viscosity index (VI) of the treated base oils is also observed due to the removal of additives such as viscosity index improvers. TAN also decrease after treatment by about 50% using 1-butanol and 20% for MEK. Elements from additives (P, Ca, Zn and S) or from external contamination (Cl and Fe) are also removed during the treatment. Varying degrees of improvement were observed depending on the type of WLO and solvent, but in general, more than 50% of Ca is removed, 70% of Zn and 90% of Fe.

Table 8.8. Properties of different classes of waste oil and after extraction with 1-Butanol and MEK.

Parameter	Class A			Class C		
	Sample as received	After extraction		Sample as received	After extraction	
		1-Butanol	MEK		1-Butanol	MEK
Viscosity at 40 °C (cSt)	85.0	59.5	48.4	67.7	51.1	42.6
Viscosity at 100 °C (cSt)	10.7	7.60	6.60	10.50	7.97	6.45
Viscosity Index (VI)	110	87.7	83.3	143	125	100
TAN (mg KOH/g)	0.48	0.24	0.38	1.87	0.89	1.37
Elemental content						
P (ppm)	761	531	782	717	838	430
Ca (ppm)	1990	270	561	1620	507	817
Cl (ppm)	123	68.7	71.2	202	110	139
Zn (ppm)	1020	201	168	980	261	259
Fe (ppm)	142	2.22	14.4	212	1.49	18.4
S (%)	1.02	0.51	0.57	1.13	0.62	0.58

Figure 8.6 illustrates the FTIR spectra of WLO classes A, B and C before extraction and of classes A and C after extraction with 1-butanol and MEK. The spectra confirm the removal of major impurities from the base oil. Indeed, the extraction treatment reduces significantly peaks at 1750 cm^{-1}, which corresponds to the vibrational frequency of carbonyl groups (C=O), strongly present in oxidation products (ketones, aldehydes, etc.). In addition, sulfur-based additives such as ZDDP typically used in engines show S-O absorption bands at 1152 cm^{-1}, which are reduced after extraction [35]. A decrease of other additives such as polymethacrylates is revealed in a C-O stretch band that occurs at 1160 cm^{-1} [36].

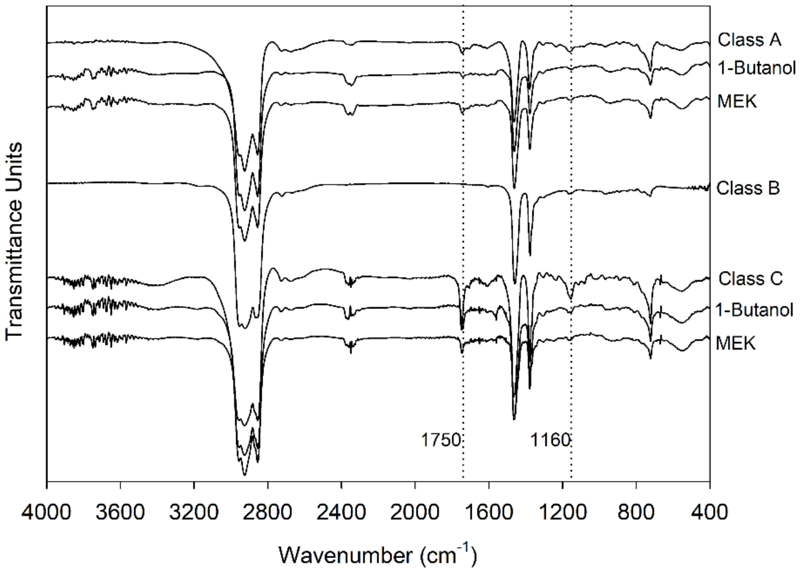


Figure 8.6. FTIR spectra of different classes of waste oil and after extraction with 1-Butanol and MEK.

8.4. CONCLUSIONS

The results showed that different performances are obtained when WLO with diverse physicochemical characteristics are treated by solvent extraction. Class A oil reached higher PSR and lower Yield than class C, while using the same solvent. WLO classified as class B should not be regenerated by solvent extraction due to the low level of contaminants. Therefore, class B oils can bypass the deasphalting stage, saving materials and energy. The addition of KOH as flocculation agent in class C oils is less effective due to the interference of saponification reactions with esters. In general, 1-butanol is more efficient for the removal of impurities than MEK. The increase in the KOH dosage from 2 to 3 g/L does not produce an increase on the PSR, but the yield increases due to undesirable sedimentation of excess KOH.

The extraction systems were reasonably modeled using response surface methodology (RSM). The best conditions of extraction were determined using the profiler and the desirability approach and based on acceptable process trade-offs. Consequently, a solvent/oil ratio of 5 w/w and a KOH dosage of 1.5 and 2 g/L were selected for all systems under analysis.

8.5. REFERENCES

[1] Environment Agency, How to find out if waste oil and wastes that contain oil are hazardous. https://www.hazwasteonline.com/marketing/media/Regulations/How_to_find_out_if_waste_oil_.pdf, 2017 (accessed January 23, 2018).

[2] F. Awaja, D. Pavel, Design Aspects of Used Lubricating Oil Re-Refining, Elsevier, Amsterdam, 2006.

[3] E. Loiseau, L. Saikku, R. Antikainen, N. Droste, B. Hansjürgens, K. Pitkänen, P. Leskinen, P. Kuikman, M. Thomsen, Green economy and related concepts: An overview, J. Clean. Prod. 139 (2016) 361–371.

[4] Y.M.B. Saavedra, D.R. Iritani, A.L.R. Pavan, A.R. Ometto, Theoretical contribution of industrial ecology to circular economy, J. Clean. Prod. 170 (2018) 1514–1522.

[5] F. Audibert, Waste Engine Oils: Rerefining and Energy Recovery, Elsevier, Amsterdam, The Netherlands, 2006.

[6] J.G. Speight, D.I. Exall, Rerefining of Used Lubricating Oils, CRC Press, Boca Raton, 2014.

[7] V. Monier, E. Labouze, Critical Review of Existing Studies and Life Cycle Analysis on the Regeneration and Incineration of Waste Oils. http://ec.europa.eu/environment/waste/studies/oil/waste_oil.pdf, 2001 (accessed January 15, 2018).

[8] C. Kajdas, Re-refining Technologies, in: T. Mang (Ed.), Encyclopedia of Lubricants and Lubrication, Springer-Verlag Heidelberg, Berlin, 2014, pp. 1554–1568.

[9] J. Rincón, P. Cañizares, M.T. García, I. Gracia, regeneration of used lubricant oil by propane extraction, Ind. Eng. Chem. Res. 42 (2003) 4867–4873.

[10] A. Kupareva, P. Mäki-Arvela, D.Y. Murzin, Technology for rerefining used lube oils applied in Europe: A review, J. Chem. Technol. Biotechnol. 88 (2013) 1780–1793.

[11] J. Rincón, P. Cañizares, M.T. García, Regeneration of used lubricant oil by polar solvent extraction, Ind. Eng. Chem. Res. 44 (2005) 4373–4379.

[12] R.R. Mohammed, I.A.R. Ibrahim, A.H. Taha, G. McKay, Waste lubricating oil treatment by extraction and adsorption, Chem. Eng. J. 220 (2013) 343–351.

[13] J.P. Martins, The Extraction-Flocculation Re-refining lubricating oil process using ternary organic solvents, Ind. Eng. Chem. Res. 36 (1997) 3854–3858.

[14] N.O. Elbashir, S.M. Al-zahrani, M.I.A. Mutalib, A.E. Abasaeed, A method of predicting effective solvent extraction parameters for recycling of used lubricating oils, 41 (2002) 765–769.

[15] A.Z. Syahir, N.W.M. Zulkifli, H.H. Masjuki, M.A. Kalam, A. Alabdulkarem, M. Gulzar, L.S. Khuong, M.H. Harith, A review on bio-based lubricants and their applications, J. Clean. Prod. 168 (2017) 997–1016.

[16] C. Kajdas, Major pathways for used oil disposal and recycling. Part 1, Tribotest. 7 (2000) 61-74.

[17] V.L. Lashkhi, I.G. Fuks, G.I. Shor, Colloid chemistry of lubricating oils (in the conditions of use), Plenum Publ. Corp. 1 (1992) 311–319.

[18] T. Cosgrove, Colloid Science: Principles, Methods and Applications, second ed., Wiley, Bristol, 2010.

[19] M.M. Chakrabarty, Chemistry and Technology of Oils and Fats, Allied Publishers Pvt. Ltd., New Delhi, 2003.

[20] J.E. Martín-Alfonso, G. Moreno, C. Valencia, M.C. Sánchez, J.M. Franco, C. Gallegos, Influence of soap/polymer concentration ratio on the rheological properties of lithium lubricating greases modified with virgin LDPE, J. Ind. Eng. Chem. 15 (2009) 687–693.

[21] F. Audibert, Les Huiles Usagées: Reraffinage et Valorisation Énergétique, Edition Technip, Paris, 2003.

[22] C.T. Pinheiro, V.R. Ascensão, M.S. Reis, M.J. Quina, L.M. Gando-Ferreira, A data-driven approach for the study of coagulation phenomena in waste lubricant oils and its relevance in alkaline regeneration treatments, Sci. Total Environ. 599–600 (2017) 2054–2064.

[23] C.T. Pinheiro, M.J. Quina, L.M. Gando-Ferreira, New methodology of solvent selection for the regeneration of waste lubricant oil using greenness criteria, ACS Sustain. Chem. Eng. 6 (2018) 6820−6828.

[24] M.A. Reis, M.S. Jeronimo, Waste lubricating oil rerefining by extraction-flocculation. 1. A scientific basis to design efficient solvents, Ind. Eng. Chem. Res. 27 (1988) 1222–1228.

[25] C.T. Pinheiro, R. Rendall, M.J. Quina, M.S. Reis, L.M. Gando-Ferreira, Assessment and prediction of lubricant oil properties using infrared spectroscopy and advanced predictive analytics, Energy Fuels 31 (2017) 179–187.

[26] C.T. Pinheiro, M.J. Quina, L.M. Gando-Ferreira, Efficiency of regeneration by solvent extraction for different types of waste oil, in: C. Vilarinho, F. Castro, M. de L. Lopes (Eds.), Wastes Solutions Treatments and Opportunities Vol II, CRC Press – Taylor & Francis Group, London, 2018, pp. 133–138.

[27] M. Hussein, A.A. Amer, A.S. Gaberah, Used lubricating oils re-refining by solvent extraction, Am. J. Environ. Eng. Sci. 1 (2014) 44–50.

[28] SAS Institute Inc, JMP® 13 Fitting Linear Models, second ed., SAS Institute Inc, Cary, NC, 2017.

[29] SAS Institute Inc, JMP® 13 Profilers, second ed., SAS Institute Inc, Cary, NC, 2017.

[30] E. Del Castillo, Process optimization: a statistical approach, Springer, New York, 2007.

[31] M. Diphare, E. Muzenda, Influence of solvents on the extraction of oil from waste lubricating grease: a comparative study, in: 2nd International Conference on Agricultural, Environment and Bioliogical Sciences (ICAEBS 2013), December 17-18, Pattaya, Thailand, 2013, pp. 76–78.

[32] NIST, Upper critical values of the F distribution. http://www.itl.nist.gov/div898/handbook/eda/section3/eda3673.htm, 2017 (accessed December 21, 2017).

[33] O.M. Nimir, M.I.A. Mutalib, R.Adnan, Recycling of used lubrication oil by solvent extraction — a guideline for single solvent design, in: Regional Symposium on Chemical Engineering in conjunction with 13th Symposium of Malaysian Chemical Engineers, October 13-15, Johor, Malaysia, 1997, pp. 420–427.

[34] J. Rincón, P. Cañizares, M.T. García, Waste oil recycling using mixtures of polar solvents, Ind. Eng. Chem. Res. 44 (2005) 7854–7859.

[35] D.L. Wooton, Applications of spectroscopy in the fuels and lubrication industry, Appl. Spectrosc. Rev. 36 (2001) 315–332.

[36] J. Zięba-Palus, P. Kościelniak, M. Łącki, Differentiation of used motor oils on the basis of their IR spectra with application of cluster analysis, J. Mol. Struct. 596 (2001) 221–228.

PART E – CONCLUSIONS AND FORTHCOMING WORK

A general overview of the most relevant conclusions of the work is presented in this part of the thesis. Moreover, some proposals for future work are suggested.

9. CONCLUSIONS AND FORTHCOMING WORK

The scope and motivation of this work was based on the improvement of the Portuguese waste lubricant oil management system and the boosting of the sustainability of the extraction process for the regeneration of this hazardous waste. The work involved several topics and the following main conclusions can be outlined:

- Several properties (density, viscosity, TAN, SN, percentage of aromatics, naphthenics and paraffinics) were determined for 62 fresh lubricant oil samples available in the Portuguese market, which were grouped into seven categories. Those properties among the categories may be diverse, and thus the WLO generated from spent lubricant is a very complex matrix.
- Robust and accurate models derived from advanced statistical methods (regression with variable selection, penalized regression, latent variable regression and tree-based ensemble methods) can be used to predict some of the properties based on FTIR spectra of fresh lubricant oil samples. The density and percentage of aromatics, naphthenics and paraffinics are well predicted;
- The viscosity of WLO samples is very well correlated with models that allow the estimation of low temperature properties such as the glass transition temperature, T_g. A new correlation between viscosity and density was found, enabling the calculation of viscosity with AARD of 7%. The surface tension of WLO can be calculated from the linear correlation between logarithm of surface tension and logarithm of density with relative deviations within ±2%;
- The analysis of data concerning the characterization of thousands of samples of WLO collected in Portugal from 2008 to 2015, have shown that 57.4% of the samples exceeding chlorine limits (> 2000 ppm). This contamination comes mainly from industrial producers.
- FTIR analysis suggested high contamination of WLO with glycol compounds. These molecules are mainly originated from brake fluids and antifreeze agents, which are chemically different from lubricant oils. Thus, whenever possible, these fluids must be segregated in the WLO producer to increase the efficiency of the management system.
- The application of an empirical test method (involving addition of KOH) to evaluate the regenerability of WLO prior to entering a regeneration plant revealed three different classes of WLO: class A – the addition of KOH does not affect the oil matrix; class B – precipitates are formed; class C – the oil forms a gel-type oil that hinders regeneration;
- The physicochemical properties of WLO revealed that coagulation classes A and B may be very different, namely the former class has lower values for TAN, SN, water content, viscosity at 40°C and concentration of major elements (P, S, Ca and Zn). Class C oil samples display SN values statistically different and in a higher range than the other classes. Another distinct feature of class C samples spectra is the intense peaks at 1750 cm^{-1} and 1250 – 1100 cm^{-1}, which indicates the presence of ester type oils;
- The classification analysis applied to FTIR spectra based on chemometric methods correctly classified 83% of the waste oils according to their coagulation class;

- Spectral discriminating analysis revealed that class A oils do not have any compounds that affect negatively the alkaline treatment. Class B oils may be constituted by gear or hydraulic lubricants, which are mineral based oils, have low concentration of additives and oxidation products. Class C WLO are mainly composed by synthetic ester type base oils, which form a gel-type oil after the addition of KOH and hamper regeneration processes using alkaline treatments;
- A set of application-specific guidelines were developed for the selection of solvents used in the treatment of WLO by extraction. From a list of 154 solvents, the main conclusion is that 1-butanol, isobutanol and MEK were the most sustainable solvents. This methodology could be extended to other solvents, if information related to greenness is available.
- Waste lubricant oil management systems should implement segregate collection according to the physicochemical characteristics of WLO. The results indicated that class B oils can not be improved by deasphalting phase based on solvent extraction. In addition, class A oil reached higher PSR and lower Yield than class C for a specific solvent. In general, 1-Butanol revealed to be more efficient than MEK for the removal of impurities. KOH has lower flocculation power in class C due to the saponification reaction with esters;
- An increase on the KOH dosage from 2 to 3 g/L do not produce an increase on the PSR, but the yield rises due to undesirable sedimentation of excess KOH. Thus, the best conditions of extraction were selected based on acceptable process trade-offs. As a result, a solvent/oil ratio of 5 w/w and a KOH dosage of 1.5 and 2 g/L were selected for all systems under analysis.

FORTHCOMING WORK

The studies conducted in the thesis could entail more in-depth analysis to complete specific issues. The following topics are proposed as future studies:

- to obtain more robust and reliable predictive models based on advanced statistics and infrared spectroscopy, a larger and more equitable number of fresh oil samples between categories (engine oil, gear fluid, hydraulic fluids, etc.) should be assessed;
- the possibility of segregation of industrial WLO to prevent contaminations of other type of oils with chlorine should be investigated. The future implementation of these improvements in the current collection system should consider logistic and economic viability analysis;
- identify the type, applications or even brands of lubricant oils that will give rise to the coagulation phenomena. Recognize the most commonly used additives in the lubricant design that are prone to react under alkaline conditions. This would allow a better understanding of the type of oils that prevent the regeneration and that should be segregated;
- investigate in detail the effect of specific additives in the oil during the alkaline treatment, namely the concentration, temperature gradient, stirring conditions, cooling temperature gradient, etc.;

- evaluate the possibility of perform extraction/distillation process for the removal of additives or other compounds identified as coagulating agents, in order to avoid this phenomenon;
- study the economic and logistic feasibility of the segregation of oils classes A, B and C;
- the multivariate statistical analysis indicates a very interesting prediction capacity of physicochemical properties based on FTIR. This tool should be explored in the future for application in waste lubricant oils. Preliminary tests have been performed, indicating that it would be possible to correlate the FTIR of matrices as complex as the WLO with specific properties;
- develop a computer tool in order to apply the predictive models based on FTIR for a rapid determination of the coagulation test, and other physicochemical properties in the refining plants;
- evaluate the possibility of using portable infrared sensors to obtain spectra and to predict the coagulation phenomena on collection sites. This would allow a quick decision about the possibility of mixing the waste oils during collection.
- scale-up studies of the extraction process studied and evaluate its economic viability aiming at the commercialization of the oil base in the European market. For scale-up purposes, the data obtained should be described with appropriate mathematical models to enable the simulation of the treatment of the waste oil with the integration of the regeneration processes (e.g. distillation, extraction and adsorption), at an industrial scale, using the simulator Aspen Plus;
- analyze the potential of ionic liquids or eutectic solvents for the treatment of waste oils by extraction. These liquids have been reported in the literature as interesting alternatives to conventional solvents for several phases of the crude refining process. Preliminary studies in the present work have been performed using two low temperature ionic liquids (TESA/TESAC and P6,6,6,14Cl) as extraction solvents, showing that there is potential for the recovery of base oil from WLO. However, further studies should be carried out. In addition, it would be interesting to compare the sustainability of ionic liquids with the alcohols and ketones studied in this work.

ANNEX A. SUPPLEMENTARY MATERIAL

In this final section, the supplementary material of Chapters 3 to 8 is presented.

A.1. CHAPTER 3

The analytical results obtained for the characterization of 62 lubricant oils according to density at 15 ºC, viscosity at 40 and 100 ºC, viscosity index, TAN, sap. number and aromatic, naphthenic and paraffinic contents are presented in Table A.1.

Table A.1. Physicochemical characteristics of lubricant oil samples used for model development.

Sample Reference	Density @ 15°C (kg/m^3)	Viscosity @ 40°C (cSt)	Viscosity @ 100°C (cSt)	Visc. Index	TAN (mg KOH/g)	Sap. Number (mg KOH/g)	Arom. (%)	Napht. (%)	Paraff. (%)
1	817	4	1	---	<LQ	0.8	1.0	59.0	40.0
2	891	22	5	126	1.3	20.8	0.2	55.0	44.8
3	906	398	29	111	1.1	6.5	8.8	21.3	69.9
4	861	38	8	168	1.1	3.3	4.7	37.4	57.9
5	893	156	15	99	0.9	3.1	4.5	47.0	48.6
6	885	53	8	110	2.2	2.8	5.2	28.2	66.6
7	1068	491	86	262	0.4	4.3	0.6	75.5	23.9
8	909	381	29	106	2.0	7.7	7.1	36.6	56.3
9	856	170	28	204	0.9	32.2	0.8	23.9	75.4
10	885	120	16	139	0.6	4.9	5.9	39.6	54.5
11	870	40	8	168	0.9	1.7	5.0	50.4	44.6
12	829	19	6	314	1.5	3.1	2.3	46.7	51.0
13	871	42	8	158	0.6	4.1	6.2	37.6	56.2
14	1063	8	2	48	20.5	33.1	1.0	70.1	28.9
15	1069	7	2	123	31.3	16.4	1.2	70.6	28.3
16	1073	7	2	107	20.4	4.6	1.1	70.6	28.3
17	1041	9	2	96	20.9	33.0	0.9	70.6	28.5
18	1073	7	2	145	27.3	20.4	1.1	70.6	28.3
19	1057	8	2	88	19.0	24.9	1.1	70.7	28.2
20	878	48	7	104	0.6	1.0	4.9	42.4	52.7
21	875	46	8	146	0.5	1.2	6.4	25.1	68.5
22	845	22	5	135	2.1	0.7	0.7	49.7	49.6
23	868	37	7	173	0.3	0.6	5.5	43.3	51.2
24	895	101	13	125	2.4	2.8	9.4	22.0	68.6
25	885	98	14	141	3.0	3.6	6.9	33.2	60.0
26	875	92	14	152	3.1	4.0	4.0	37.6	58.4
27	885	110	15	137	3.3	1.8	4.7	41.5	53.8
28	887	105	14	135	3.4	5.2	4.6	43.5	51.9
29	875	93	14	158	5.3	5.0	2.6	48.7	48.7
30	858	84	14	174	2.8	1.7	3.5	40.4	56.1
31	859	93	14	157	2.6	5.5	5.4	39.6	55.0
32	849	56	11	184	2.9	4.5	3.5	28.7	67.9
33	875	101	14	146	2.4	3.0	3.5	48.4	48.1
34	870	98	14	153	2.6	2.4	3.3	50.2	46.5
35	856	86	15	179	2.7	3.4	3.3	42.2	54.5
36	871	149	20	153	2.6	2.2	2.5	52.9	44.6
37	873	100	14	149	2.5	2.6	3.3	47.9	48.8
38	871	98	15	153	2.6	1.3	3.0	52.4	44.6
39	854	66	12	175	2.2	6.8	5.3	41.5	53.3
40	852	88	15	174	2.9	1.6	3.4	45.3	51.2
41	853	68	12	179	1.5	4.9	3.8	46.5	49.7
42	875	94	14	150	2.5	0.1	3.2	47.6	49.2

Table A.1 (continued). Physicochemical characteristics of lubricant oil samples used for model development.

Sample Reference	Density @ 15°C (kg/m^3)	Viscosity @ 40°C (cSt)	Viscosity @ 100°C (cSt)	Visc. Index	TAN (mg KOH/g)	Sap. Number (mg KOH/g)	Arom. (%)	Napht. (%)	Paraff. (%)
43	883	102	14	139	2.7	5.0	3.2	54.0	42.9
44	846	70	13	184	3.3	5.3	2.1	41.7	56.3
45	857	73	12	167	1.6	13.7	6.5	44.7	48.8
46	875	100	15	159	2.9	3.0	4.5	43.2	52.3
47	885	99	14	138	2.6	4.0	5.6	40.5	53.8
48	845	82	13	168	3.1	3.0	6.4	31.5	62.1
49	866	95	14	157	3.3	2.0	6.0	35.6	58.4
50	869	105	15	143	2.8	4.9	3.3	42.9	53.8
51	843	51	10	192	2.0	2.1	4.4	37.4	58.2
52	875	99	15	164	2.6	1.7	6.4	43.9	49.8
53	887	94	13	140	3.3	3.8	5.3	38.3	56.4
54	893	145	15	100	0.9	2.3	6.0	49.1	44.9
55	895	141	15	107	2.0	2.8	5.0	41.9	53.2
56	898	109	12	140	1.2	2.7	5.4	37.6	57.1
57	953	70	8	68	0.4	64.2	19.3	45.9	34.8
58	839	33	6	138	0.1	23.5	4.0	36.1	59.9
59	870	45	5	-13	<LQ	1.7	18.6	51.8	29.6
60	913	77	9	91	<LQ	2.8	4.6	46.3	49.1
61	874	10	3	67	0.2	1.3	3.2	61.3	35.5
62	882	11	3	46	<LQ	1.4	2.5	63.4	34.2

In the first stage of the comparison study, as described in Section 3.2.3, no extreme samples nor regression methods were discarded. The decision to remove tree-based regression methods was partially based on the results presented in Table A.2, where it can be seen that they had poorer performances compared to the remaining methods. However, the large residuals of samples 7, 57 and 59 can only be observed when plotting the prediction errors for each sample. An example is given in Figure S3.1, which shows the predicted and measured density values in all iterations of double cross-validation, using the elastic net method. These samples are outliers in terms of prediction errors and similar results were obtained for other physicochemical properties. Furthermore, Table A.2 presents larger prediction errors and higher variations in prediction performance when compared to Table 3.2, a consequence of including these samples in the analysis.

Table A.2. Prediction results for nine oil properties, including all samples and regression methods initially considered. [a]

Oil properties	**Predictive analytical methods** [b]											
	variable selection	**penalized regression**				**patent variable**				**tree-based ensembles**		
	FSR	**RR**	**LASSO**	**EN**	**SVR**	**PCR**	**PCR_FS**	**PLS**	**iPLS**	**BRT**	**RF**	**BT**
Density @ 15°C (kg/m^3)	0.88 (0.83)	**0.91** **(0.34)**	0.9 (0.35)	0.89 (0.31)	0.81 (0.52)	0.89 (0.11)	0.87 (0.15)	**0.94** **(0.09)**	0.84 (0.76)	**0.9** **(0.09)**	0.86 (0.05)	0.85 (0.22)
Viscosity @ 40°C (cSt)	<0 (>1)	**0.33** **(0.93)**	**0.38** **(0.99)**	**0.4** **(1)**	<0 (>1)	<0 (>1)	<0 (1)	0.19 (0.86)	<0 (0.69)	0 (0.96)	<0 (0.77)	0.03 (>1)
Viscosity @ 100°C (cSt)	0.11 (>1)	0.1 (>1)	**0.51** **(0.58)**	**0.5** **(0.48)**	<0 (>1)	0.07 (0.51)	<0 (0.97)	**0.26** **(0.45)**	0.02 (>1)	0.06 (0.54)	0.15 (0.48)	<0 (0.59)
Viscosity Index	<0 (>1)	0.15 (>1)	**0.11** **0.96)**	0.06 (0.84)	<0 (>1)	0.09 (0.7)	<0 (0.22)	0.05 (0.67)	<0 (>1)	**0.13** **(0.53)**	**0.1** **(0.42)**	0.04 (0.68)
TAN (mg KOH/g)	**0.85** **(0.7)**	**0.82** **(0.6)**	0.68 (0.87)	0.65 (>1)	**0.84** **(0.53)**	0.64 (0.95)	0.66 (>1)	0.69 (0.74)	0.21 (>1)	0.72 (0.28)	0.76 (0.33)	0.67 (0.55)
Sap. Number (mg KOH/g)	0.14 (>1)	0.32 (>1)	**0.57** **(0.46)**	**0.57** **(0.52)**	0.49 (>1)	0.28 (0.55)	0.05 (0.71)	0.28 (0.61)	0.13 (1)	0.28 (0.31)	0.22 (0.39)	**0.31** **(0.54)**
Arom. (%)	0.78 (0.62)	0.72 (0.33)	**0.81** **(0.2)**	0.77 (0.35)	0.7 (0.33)	0.66 (0.38)	0.09 (0.62)	**0.78** **(0.2)**	**0.91** **(0.12)**	0.24 (0.4)	0.18 (0.49)	0.3 (0.43)
Napht. (%)	**0.94** **(0.14)**	0.92 (0.11)	**0.95** **(0.09)**	**0.94** **(0.11)**	0.89 (0.23)	0.87 (0.7)	0.66 (0.3)	0.91 (0.41)	0.94 (0.24)	0.9 (0.24)	0.9 (0.28)	0.93 (0.2)
Paraff. (%)	**0.97** **(0.03)**	0.92 0.09	**0.97** **(0.03)**	**0.97** **(0.04)**	0.89 (0.11)	0.91 (0.5)	0.55 (0.24)	0.92 (0.18)	0.97 (0.05)	0.82 (0.17)	0.79 (0.19)	0.9 (0.13)

[a] The value at the top of each cell represents the $\tilde{R}^2_{dvc}$ and the value inside parenthesis is the respective interquartile range. The best 3 regression methods for each property are identified in boldface. [b] FSR – Forward Stepwise Regression; RR – Ridge Regression; LASSO – Least Absolute Shrinkage and Selection Operator; EN – Elastic Nets; SVR – Support Vector Regression; PCR – Principal Component Regression; PCR_FS – PCR with Forward Stepwise; PLS – Partial Least Squares; iPLS – interval PLS; BRT – Bagging of Regression Trees; RF – Random Forests and BT – Boosted Trees.

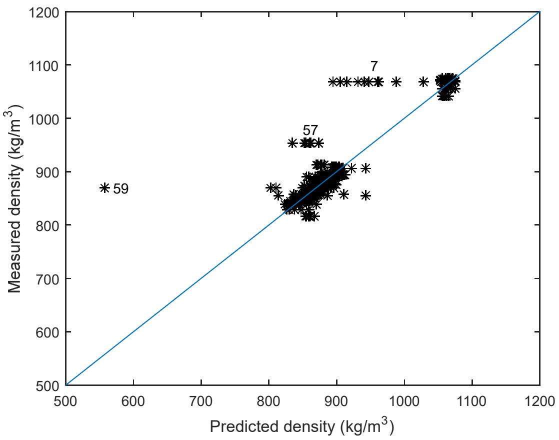


Figure A.1. Predicted and measured density values for all samples (samples 7, 57 and 59 are identified since they were removed from the results presented in the paper). Note that there are multiple instances of samples 57 and 7, representing different double-cross validation iterations where they were in the left-out fold.

A.2. CHAPTER 4

In Table A.3 are listed the experimental results of mean viscosity, η, at shear rates, $\dot{\gamma}$ = (200, 400 and 800) s^{-1} and temperatures ranging from 298.15 K to 343.15 K. Density, ρ, at temperatures between 298.15 K and 343.15 K and surface tension, σ, measured at temperatures ranging from 303.15 K to 343.15 K are also listed.

Table A.3. Viscosity, density and surface tension determined experimentally for waste lubricant oil samples at temperature T and pressure P = 101.86 kPa.[a]

T / K	S1	S2	S3	S4	S5	S6	S7	S8	S9	Range
	η / mPa.s									
298.15	151.7	151.3	136.3	112.7	129.0	-	154.3	97.8	145.3	97.8–154.3
303.15	119.3	116.7	105.7	88.3	100.9	102.3	115.3	77.6	111.3	77.6–119.3
308.15	95.4	91.9	83.8	70.2	80.3	81.3	91.4	62.7	86.6	62.7–95.4
313.15	77.3	73.1	67.2	57.4	64.5	65.0	72.8	51.8	71.6	51.8–77.3
318.15	63.4	59.4	54.8	48.0	52.7	52.8	58.8	42.4	58.7	42.4–63.4
323.15	52.5	48.4	44.9	40.2	43.5	43.6	48.9	35.5	48.9	35.5–52.5
328.15	43.7	40.4	37.5	34.0	37.5	36.3	40.4	29.9	40.8	29.9–43.7
333.15	37.0	34.0	31.7	28.9	31.1	30.6	33.9	25.5	34.7	25.5–37.0
338.15	31.4	29.0	27.0	24.8	26.6	25.9	28.8	21.9	29.5	21.9–31.4
343.15	26.9	24.8	23.3	21.6	22.9	22.3	24.4	19.1	25.5	19.1–26.9
	ρ / kg.m^{-3}									
298.15	882.9	896.6	879.7	881.9	885.3	-	886.8	868.6	887.6	868.6–896.6
303.15	879.8	893.2	876.5	878.6	882.1	885.0	883.4	865.4	884.4	865.4–893.2
308.15	876.3	889.5	873.2	875.0	878.6	881.4	879.9	862.0	880.9	862.0–889.5
313.15	872.6	885.8	869.7	871.4	874.9	877.8	876.2	858.4	877.1	858.4–885.8
318.15	868.8	881.9	866.0	867.5	871.0	873.9	872.3	854.7	873.1	854.7–881.9
323.15	864.9	877.8	862.2	863.5	867.0	870.0	868.5	850.4	867.8	850.4–877.8
328.15	860.9	873.7	858.2	857.0	862.9	865.9	864.3	845.2	862.2	845.2–873.7
333.15	856.4	869.4	854.0	854.8	858.3	861.6	860.1	840.4	856.0	840.4–869.4
338.15	851.5	864.8	849.4	850.2	853.5	857.1	855.3	835.5	850.3	835.5–864.8
343.15	846.2	860.1	844.6	845.3	848.8	852.4	850.3	830.7	844.5	830.7–860.1
	σ / mN.m^{-1}									
303.15	25.28	28.90	25.79	25.83	27.01	26.98	29.08	26.41	26.28	25.3–29.1
313.15	23.94	27.16	23.94	24.80	25.38	25.60	27.33	25.19	25.10	23.9–27.3
323.15	23.23	25.95	23.80	24.12	24.77	24.32	26.29	23.79	23.86	23.2–26.3
333.15	22.07	24.71	22.70	23.13	23.42	23.11	24.91	22.48	22.30	22.1–24.9
343.15	21.16	23.18	21.90	22.24	21.46	22.66	23.43	20.99	21.02	21.0–23.4

[a] Standard uncertainties u are $u_c(\eta)$ = 2%, $u_c(\rho)$ = 0.45 kg·m^{-3}, $u_c(\sigma)$ = 0.3 mN.m^{-1}, $u(p)$ = 0.23 kPa, and $u(T)$ for η measurements are $u(T)$ = 0.2 K, for ρ measurements, $u(T)$ = 0.01 K and for σ, $u(T)$ = 0.1 K.

A.3. CHAPTER 5

The analytical results obtained for the dataset characterization of 60 lubricant oils according to density at 15ºC, viscosity at 40 ºC, TAN, SN and elemental analysis are presented in Table A.4. FTIR spectra of the samples is are illustrated in Figure A.2. Samples from industry correspond to I1 to I12; from garage to G1 to G38 and for other producers from O1 to O10.

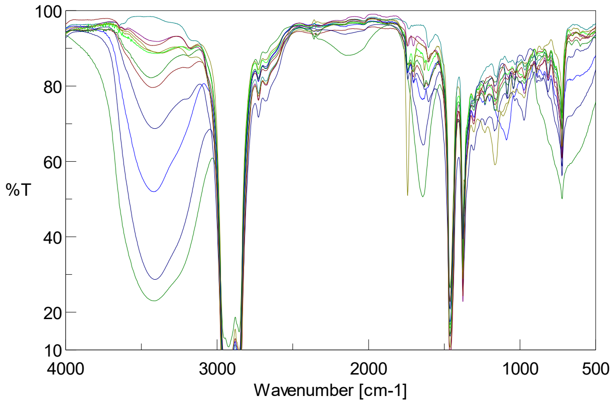
Table A.4. Physicochemical characteristics of WLO sub-dataset analyzed.

Reference Sample	Density @ 15 °C (kg/m^3)	Viscosity @ 40 °C (cSt)	TAN (mg KOH/g)	SN (mg KOH/g)	P (ppm)	Ca (ppm)	Zn (ppm)	Si (ppm)	S (%)	Fe (ppm)
I1	923.6	205.7	2.17	7.0	683	2280	964	194.0	0.5	451
I2	885.3	79.2	1.81	5.0	936	2680	1220	74.2	0.8	135
I3	882.0	80.1	3.22	12.0	1200	2780	1530	54.8	0.7	128
I4	869.3	97.6	3.56	14.6	678	2000	788	17.7	0.3	198
I5	884.5	86.8	0.43	2.4	294	124	236	190.0	0.9	99
I6	884.4	67.5	1.20	5.1	728	1390	754	48.2	1.1	135
I7	881.4	57.6	1.97	10.8	953	2230	1210	30.9	0.7	223
I8	890.6	85.7	2.44	12.3	966	3110	1260	146.0	0.6	132
I9	878.1	76.8	2.73	13.2	1130	2480	1440	56.3	0.6	230
I10	892.4	97.2	2.60	11.4	904	2710	1140	14.2	0.7	90
I11	870.3	34.5	0.42	2.9	306	4030	1560	373.0	0.5	1060
I12	874.0	65.3	1.22	19.4	1010	1450	762	70.7	1.0	125
G1	911.2	146.1	2.32	6.3	682	1520	859	765.0	0.5	437
G2	893.1	111.0	3.97	13.8	853	2440	1140	205.0	0.5	335
G3	870.2	86.0	2.28	14.0	708	1650	876	12.7	0.4	134
G4	877.1	96.8	2.99	13.0	915	2340	1140	23.1	0.6	98
G5	863.0	78.6	3.32	17.3	672	1660	911	11.4	0.2	144
G6	889.2	114.0	3.35	13.9	1040	2540	1420	23.4	0.6	168
G7	887.4	109.6	2.73	11.1	1100	3460	1530	39.4	1.0	73
G8	878.3	116.3	2.63	11.4	803	2430	1130	12.0	0.5	133
G9	880.8	69.7	2.49	10.8	1220	2750	1670	32.1	0.7	145
G10	882.0	68.1	1.75	13.4	1050	2750	1280	44.2	0.6	218
G11	887.7	67.5	1.44	8.5	797	2490	1100	66.3	0.5	83
G12	906.0	133.2	1.19	6.0	253	548	524	38.7	0.8	837
G13	879.9	71.7	2.28	12.3	883	2500	1170	40.8	0.5	129
G14	875.7	75.3	2.70	9.9	929	2400	1280	17.1	0.5	148
G15	887.9	92.1	3.00	11.1	899	2460	1180	35.2	0.5	377
G16	916.2	140.7	2.86	10.6	845	2480	1140	228.0	0.4	623
G17	885.9	92.6	2.28	12.5	930	2320	1080	22.3	0.6	269
G18	890.8	14.5	0.33	2.1	57	341	91	335.0	0.0	183
G19	872.3	74.9	2.83	12.2	774	2050	1060	24.8	0.3	138
G20	891.9	89.1	2.44	9.5	956	2780	1230	74.9	0.7	145
G21	894.0	105.7	3.08	14.5	893	2600	1200	320.0	0.6	684

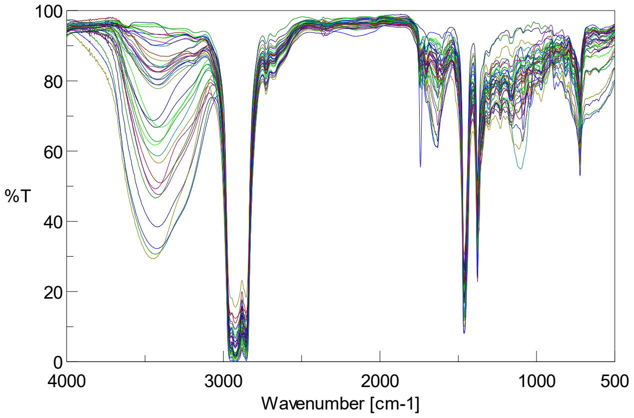
Table A.4 (continued). Physicochemical characteristics of WLO sub-dataset analyzed.

Reference Sample	Density @ 15 °C (kg/m^3)	Viscosity @ 40 °C (cSt)	TAN (mg KOH/g)	SN (mg KOH/g)	P (ppm)	Ca (ppm)	Zn (ppm)	Si (ppm)	S (%)	Fe (ppm)
G22	887.2	85.2	2.13	11.7	889	2320	1080	44.2	0.6	173
G23	878.5	65.6	1.12	9.3	900	1680	841	36.9	1.1	139
G24	881.6	63.1	1.26	7.8	858	2210	1110	163.0	0.9	153
G25	890.7	94.3	2.65	11.2	100	2430	1300	94.0	0.7	157
G26	888.5	89.4	2.53	11.4	1180	3120	1670	31.6	0.9	297
G27	872.1	7.1	2.51	10.7	872	2450	1180	23.8	0.6	195
G28	870.7	65.8	3.16	17.7	767	1910	1050	16.3	0.3	231
G29	956.5	0.8	0.33	2.8	78	90	24	233.0	0.2	80
G30	873.9	77.4	2.94	10.4	828	1790	1020	15.9	0.5	142
G31	851.2	90.6	0.26	20.1	138	255	125	74.2	0.1	20
G32	881.9	85.0	1.60	13.5	748	2710	935	94.9	0.6	322
G33	866.2	68.4	3.41	15.7	670	1810	899	10.8	0.3	198
G34	874.7	98.7	3.41	12.5	1010	3560	1270	16.7	0.8	95
G35	887.2	84.8	2.18	11.9	1000	2730	1260	128.0	0.5	288
G36	881.8	62.7	0.95	3.4	470	724	574	181.0	0.8	187
G37	879.7	67.0	2.77	11.9	832	2330	1140	31.2	0.6	140
G38	891.3	93.5	3.59	11.3	1220	3420	1510	356.0	0.8	142
O1	932.3	323.6	2.19	6.0	481	1370	670	46.6	0.3	145
O2	873.7	77.5	2.79	10.7	1040	2650	1240	28.2	0.5	214
O3	971.7	96.7	4.60	5.2	695	2260	670	133.0	0.4	1210
O4	876.4	50.6	1.78	11.1	897	2780	1230	50.2	0.7	79
O5	883.8	78.4	0.86	4.9	715	1510	999	11.4	0.8	23
O6	886.7	84.2	2.83	13.5	749	2010	1030	32.2	0.3	147
O7	879.2	69.0	3.44	14.8	1090	4190	1350	233.0	0.6	197
O8	908.0	108.2	4.48	14.4	702	3370	1040	879.0	0.4	1080
O9	910.2	145.9	2.03	8.5	737	2020	980	591.0	0.5	466
O10	887.1	48.3	1.02	8.0	322	1430	515	202.0	0.3	895

(a) Industry



(b) Garage



(c) Others

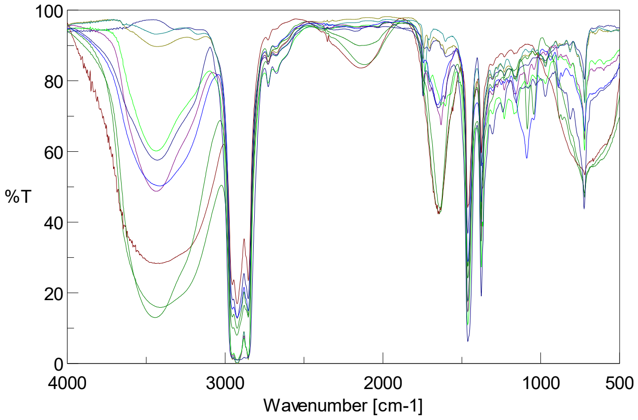


Figure A.2. FTIR spectra of WLO samples from a) Industry, b) Garage and c) Others.

A.4. CHAPTER 6

Fig. A.3 illustrates the FTIR spectrum of the precipitate formed in a coagulation class B2 oil.

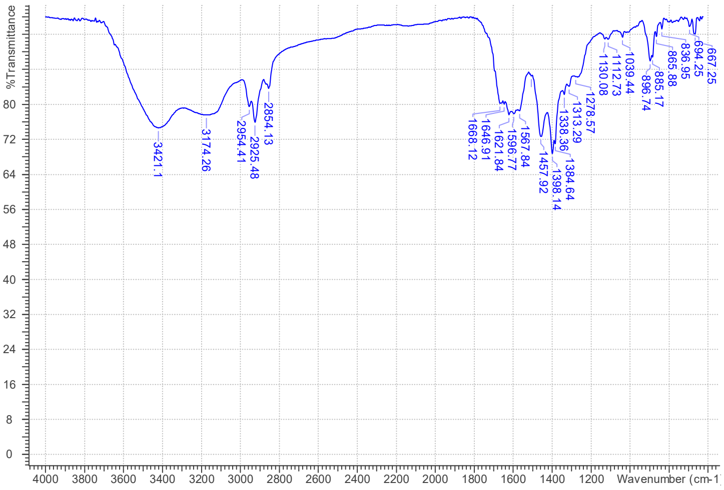


Figure A.3. FTIR spectrum of coagulation class B2 precipitate.

In Table A.5 are identified the bands illustrated in Figure 6.6 as discriminant for each coagulation class, identifying the associated functional groups and possible origin.

Table A.5. Discriminant bands of coagulation classes B1, B2 and C

Class	Frequency (cm^{-1})	Assignment	Possible Origin
B1	970	P–O–C aliphatic asymmetric stretching N–H second overtone stretching O–H second overtone stretching	Phosphate-based antiwear (ZDDP)
	1230	C–N aromatic stretching C–N aliphatic stretching C–C–O stretching	Succinimides Poly(methacrylates)
	1390	C–N aromatic stretching NO_2 aliphatic symmetric stretching SO_2 asymmetric stretching	Succinimides
	1470	N–H first overtone stretching, O–H first overtone stretching C–H methyl asymmetrical bending CH_2 scissoring	Carbonates of overbased sulfonates
	1550	NO_2 aliphatic asymmetric stretching N–H secondary amide bending C–N secondary amide stretching	Nitro compounds Amine antioxidant
	1710	C=O aliphatic stretching C=O aromatic stretching C–H first overtone stretching	Oxidation products (ketones, aldehydes, etc.) Poly(methacrylates)
	2550-2700	O–H stretching	Esters Phosphorus acid
	2850	C–H symmetric stretching (methylene)	
	2890	C–H asymmetric stretching (methyl)	
	2970-2990	C–H symmetric stretching (methyl) =C–H stretching C–H aromatic stretching O–CH_3 stretching	Poly(methacrylates)

Table A.5 (cont.). Discriminant bands of coagulation classes B1, B2 and C.

Class	Frequency (cm^{-1})	Assignment	Possible Origin
B2	730	CH_2 rocking	Additives
	980	P–O–C aliphatic asymmetric stretching N–H second overtone stretching O–H second overtone stretching C–CH_3 bending	Phosphate-based antiwear (ZDDP) Poly(methacrylates)
	1240	Si–CH_3 symmetric bending P=O aliphatic stretching C–O stretching (Carboxylic acids) C–O aromatic stretching (Esters) C–N aromatic stretching C–N aliphatic stretching	Succinimides
	1390	C–N aromatic stretching NO_2 aliphatic symmetric stretching SO_2 asymmetric stretching C–CH_3 bending	Poly(methacrylates)
	1430	C–O–H in-plane bending	Carboxylic acids
	1470	N–H first overtone stretching O–H first overtone stretching C–H asymmetrical bending CH_2 scissoring	Carbonates of overbased sulfonates
	1530	NO_2 aliphatic asymmetric stretching N–H secondary amide bending C–N stretching	Nitro compounds Amine antioxidant
	1570	N–H secondary amide bending C–N stretching	
	1710	C=O aliphatic stretching C=O aromatic stretching	Oxidation products (ketones, aldehydes, etc.)
	1790	C–H first overtone stretching	Poly(methacrylates)
	2540	S–H stretching	
	2690	O–H stretching	Esters
	2800	C–H symmetric stretching N–CH_2 stretching	Methylene Aldehydes
	2990	C–H symmetric stretching =C–H stretching C–H aromatic stretching O–CH_3 stretching	Poly(methacrylates)

Table A.5 (cont.). Discriminant bands of coagulation classes B1, B2 and C.

Class	Frequency (cm^{-1})	Assignment	Possible Origin
C	1020	P–O–C aliphatic asymmetric stretching N–H second overtone stretching O–H second overtone stretching S=O stretching P–OH stretching	Phosphate-based antiwear (ZDDP) Sulfonate detergent Phosphorus ester
	1110	C–O aliphatic stretching Si–O–Si asymmetric stretching Si–O–C stretching Si–C_6H_5 stretching	Esters Silicone Polysilicone oils
	1160	C–O–C bending C–O aliphatic stretching P–O aromatic stretching C–H second overtone stretching SO_2 symmetric stretching	Poly(methacrylates) Phosphate esters Sulfonate detergent
	1250	Si–CH_3 symmetric bending P=O aliphatic stretching C–O stretching (Carboxylic acids) C–O aromatic stretching (Esters) C–N aromatic stretching C–C–O stretching	Esters Succinimides Poly(methacrylates)
	1450	P–C aromatic stretching N–H first overtone stretching O–H first overtone stretching	Carbonates of overbased sulfonates
	1540	NO_2 aliphatic asymmetric stretching N–H secondary amide bending C–N stretching	Nitro compounds Amine antioxidant
	1750	C=O aliphatic stretching C–H first overtone stretching	Esters, Anhydrides Poly(methacrylates)
	2360-2550	O–H stretching P–H stretching S–H stretching C–H combination stretching	Carboxylic acids Esters Phosphorus acids

A.5. CHAPTER 7

GSK LIST OF SOLVENTS

Table A.6. List of solvents from the 2016 GSK solvent selection guide.

Classification	#	Solvent	CAS Number	T_{bp} (°C)	T_m (°C)
Water & Acids	WA1	Water	7732-18-5	100	0
	WA2	Lactic acid	50-21-5	122	18
	WA3	Propionic acid	79-09-4	141	-24
	WA4	Methanesulfonic acid	75-75-2	167	19
	WA5	Formic acid	64-18-6	101	8
	WA6	Acetic acid	64-19-7	118	16
Alcohols	A1	1,3-Propanediol	504-63-2	214	-32
	A2	1-Pentanol	71-41-0	137	-78
	A3	2-Ethyl hexanol	104-76-7	185	-76
	A4	1-Heptanol	111-70-6	178	-36
	A5	Ethylene glycol	107-21-1	197	-13
	A6	Di(ethylene glycol)	111-46-6	246	-10
	A7	Tri(ethylene glycol)	112-27-6	285	-7
	A8	1,2-Propanediol	57-55-6	188	-60
	A9	Benzyl alcohol	100-51-6	205	-15
	A10	Isoamyl alcohol	123-51-3	131	-117
	A11	1-Octanol	111-87-5	195	-15
	A12	Glycerol	56-81-5	290	20
	A13	1,4-butanediol	110-63-4	235	20
	A14	Cyclohexanol	108-93-0	161	23
	A15	Isobutanol	78-83-1	108	-108
	A16	2-Pentanol	6032-29-7	119	-50
	A17	1-Hexanol	111-27-3	157	-52
	A18	1-Butanol	71-36-3	118	-89
	A19	1-Propanol	71-23-8	97	-127
	A20	Ethanol	64-17-5	78	-114
	A21	2-Butanol	78-92-2	100	-115
	A22	2-Propanol	67-63-0	82	-90
	A23	*t*-Amyl alcohol	75-85-4	102	-12
	A24	1,2-Isopropylidene glycerol	100-79-8	192	-27
	A25	*t*-Butanol	75-65-0	82	23-26
	A26	IMS (ethanol, denatured)	64-17-5	78	-114
	A27	Methanol	67-56-1	65	-98
	A28	Tetrahydrofurfuryl alcohol	97-99-4	178	-80
	A29	2-Methoxyethanol	109-86-4	124	-85
Esters	Es1	Glycerol triacetate	102-76-1	259	3
	Es2	Glycerol diacetate	111-55-7	187	-41
	Es3	Isobutyl acetate	110-19-0	116	-99
	Es4	Amyl acetate	628-63-7	146	-100
	Es5	2-Ethylhexyl acetate	103-09-3	199	-92
	Es6	Butyl acetate	123-86-4	126	-78
	Es7	Methyl oleate	112-62-9	218	-20
	Es8	Isoamyl acetate	123-92-2	142	-78
	Es9	Isopropyl acetate	108-21-4	89	-73
	Es10	Propyl acetate	109-60-4	102	-95
	Es11	Dimethyl succinate	106-65-0	200	16-19
	Es12	*n*-Octyl acetate	112-14-1	210	-38.5
	Es13	Ethyl acetate	141-78-6	77	-84
	Es14	Ethyl lactate	97-64-3	154	-26
	Es15	Diethyl succinate	123-25-1	218	-20
	Es16	Dimethyl adipate	627-93-0	110	8
	Es17	γ-Valerolactone	108-29-2	207	-31
	Es18	Diisopropyl adipate	6938-94-9	136	-1
	Es19	Methyl lactate	547-64-8	144	35
	Es20	*t*-Butyl acetate	540-88-5	95	-62
	Es21	Ethyl formate	109-94-4	54	-80
	Es22	Methyl acetate	79-20-9	57	-98

Table A.6 (cont.). List of solvents from the 2016 GSK solvent selection guide.

Classification	#	Solvent	CAS Number	T_{bp} (°C)	T_m (°C)
Esters	Es23	Methyl propionate	554-12-1	79	-88
	Es24	Ethyl propionate	105-37-3	99	-73
	Es25	Methyl formate	107-31-3	33	-100
Carbonates	C1	Propylene carbonate	108-32-7	242	-49
	C2	Ethylene carbonate	96-49-1	248	35-38
	C3	Diethyl carbonate	105-58-8	126	-43
	C4	Dimethyl carbonate	616-38-6	91	2-4
	C5	Butylene carbonate	4437-85-8	250	-45
Ketones	K1	Cyclopentanone	120-92-3	131	-51
	K2	Cyclohexanone	108-94-1	155	-47
	K3	3-Pentanone	96-22-0	102	-40
	K4	Methylisobutyl ketone	108-10-1	117	-84
	K5	2-Pentanone	107-87-9	102	-78
	K6	Methylethyl ketone	78-93-3	80	-87
	K7	Acetone	67-64-1	56	-94
Aromatics	Ar1	2,4,6-Collidine	108-75-8	171	-43
	Ar2	Anisole	100-66-3	154	-37
	Ar3	Ethoxybenzene	103-73-1	170	-30
	Ar4	*p*-Xylene	106-42-3	138	12-13
	Ar5	Mesitylene	108-67-8	165	-45
	Ar6	*p*-Cymene	99-87-6	177	-68
	Ar7	Cumene	98-82-8	152	-96
	Ar8	Toluene	108-88-3	111	-95
	Ar9	Trifluorotoluene	98-08-8	102	-29
	Ar10	Pyridine	110-86-1	115	-42
	Ar11	Benzene	71-43-2	80	5.5
Hydrocarbons	HC1	Isooctane	540-84-1	99	-107
	HC2	*cis*-Decalin	493-01-6	196	-43
	HC3	Heptane	142-82-5	98	-91
	HC4	L-Limonene	5989-54-8	175	-74
	HC5	Cyclohexane	110-82-7	81	4-7
	HC6	D-Limonene	5989-27-5	175	-74
	HC7	Methyl cyclohexane	108-87-2	101	-126
	HC8	Methyl cyclopentane	96-37-7	72	-143
	HC9	Pentane	109-66-0	36	-130
	HC10	2-Methylpentane	107-83-5	60	-154
	HC11	Hexane	110-54-3	69	-95
	HC12	Petroleum spirit	8032-32-4	55	5
Ethers	Et1	Diethylene glycol monobutyl ether	112-34-5	231	-68
	Et2	Dimethyl isosorbide	5306-85-4	236	-70
	Et3	Dibutyl ether	142-96-1	140	-98
	Et4	t-Amyl methyl ether	994-05-8	86	-80
	Et5	1,2,3-Trimethoxypropane	20637-49-4	143	-60
	Et6	Diphenyl ether	101-84-8	258	26
	Et7	*t*-Butyl ethyl ether	637-92-3	70	-97
	Et8	1,3-Dioxolane	646-06-0	75	-95
	Et9	Cyclopentyl methyl ether	5614-37-9	106	-140
	Et10	Diethoxymethane	462-95-3	88	-66.5
	Et11	2-Methyltetrahydrofuran	96-47-9	78	-136
	Et12	*t*-Butylmethyl ether	1634-04-4	55	-110
	Et13	Diisopropyl ether	108-20-3	68	-85.5
	Et14	Dimethoxymethane	109-87-5	42	-105
	Et15	Tetrahydrofuran	109-99-9	65	33-36
	Et16	Bis(2-methoxyethyl) ether	111-96-6	162	-64
	Et17	1,4-Dioxane	123-91-1	102	12
	Et18	Diethyl ether	60-29-7	35	-116
	Et19	1,2-Dimethoxyethane	110-71-4	85	-69
	Et20	Dimethyl ether	115-10-6	-25	-141
Dipolar Aprotics	DA1	Dimethylpropylene urea	7226-23-5	247	-20
	DA2	Dimethyl sulphoxide	67-68-5	189	18
	DA3	1,3-Dimethyl-2-imidazolidinone	80-73-9	225	8

Table A.6 (cont.). List of solvents from the 2016 GSK solvent selection guide.

Classification	#	Solvent	CAS Number	T_{bp} (°C)	T_m (°C)
	DA4	Acetonitrile	75-05-8	82	-42
	DA5	Propanenitrile	107-12-0	97	-93
	DA6	Sulfolane	126-33-0	282	27.4
	DA7	Formamide	75-12-7	220	2-3
	DA8	*N*-Methyl pyrrolidone	872-50-4	202	-24
	DA9	Dimethyl acetamide	127-19-5	165	-20
	DA10	*N*-Ethylpyrrolidone	2687-91-4	212	-77
	DA11	*N*-Methylformamide	123-39-7	200	-3
	DA12	Dimethyl formamide	68-12-2	153	-61
	DA13	Tetramethylurea	632-22-4	177	-1
	DA14	Carbon disulfide	75-15-0	46	-112
Halogenated	Hal1	1,2,4-Trichlorobenzene	120-82-1	214	16
	Hal2	Chlorobenzene	108-90-7	132	-45
	Hal3	1,2-Dichlorobenzene	95-50-1	180	-15
	Hal4	Trichloroacetonitrile	545-06-2	83	-42
	Hal5	Perfluorotoluene	434-64-0	104	-66
	Hal6	Fluorobenzene	462-06-6	85	-42
	Hal7	Perfluorocyclic ether	335-36-4	103	-88
	Hal8	Dichloromethane	75-09-2	40	-97
	Hal9	1,2-Dichloroethane	107-06-2	84	-35
	Hal10	Perfluorocyclohexane	355-68-0	53	51
	Hal11	Chloroform	67-66-3	61	-63
	Hal12	Trichloroacetic acid	76-03-9	197	54-58
	Hal13	Chloroacetic acid	79-11-8	189	61
	Hal14	Trifluoracetic acid	76-05-1	72	-15
	Hal15	Perfluorohexane	355-42-0	57	-4
	Hal16	Carbon tetrachloride	56-23-5	77	-23
	Hal17	2,2,2-Trifluoroethanol	75-89-8	74	-44
Other	O1	Furfural	98-01-1	162	-36
	O2	*N*,*N*-Dimethyldecanamide	14433-76-2	291	-7
	O3	Dihydrolevoglucosenone	1087696-49-8	203	-20
	O4	*N*,*N*-Dimethyloctanamide	1118-92-9	261	-21
	O5	*N*,*N*-Dimethylaniline	121-69-7	194	2
	O6	Acetic anhydride	108-24-7	140	-71.3
	O7	Nitromethane	75-52-5	101	-29
	O8	Triethylamine	121-44-8	89	-115

Note: The orange values highlighted in the Table correspond to solvents with $T_m < 10$ ºC and $50 < T_{bp} < 130$ ºC

GSK GREENNESS METRICS

Table 9.7. GSK solvent selection guide metrics, categories and areas of assessment.

Metric	Category	Area of assessment
Waste (Wm)	Incineration (Ic)	Water solubility Emissions to air Enthalpy of combustion
	Recycling (Rc)	Water solubility Boiling point Ease of drying Flammability & explosion Reactivity & stability
	Biotreatment (Bc)	Nitrogen content Theoretical oxygen demand Vapor pressure Halogen content Water solubility
	VOC emissions (Vc)	Vapor pressure Boiling point
Environment (Em)	Aquatic impact (Aqc)	Acute and chronic ecotoxicity (GHS) Partition coefficient (Log K_{ow}) Biodegradation
	Air impact (Aic)	Photochemical ozone creation potential (POCP) Odor threshold Vapor pressure
Human Health (HHm)	Health hazard (HHc)	GHS hazard phrases OEL values Carcinogenicity Mutagenicity Reprotoxicity
	Exposure potential (EPc)	Vapor hazard ratio (Occupational exposure limits & sat. concentration)
Process safety (PSm)	Flammability & explosion (FEc)	Flash point Boiling point Vapor pressure Electrical conductivity/Static charge Autoignition temperature
	Reactivity & stability(RSc)	Peroxide formation potential Explosion risk (NFPA) Self-reactive hazard assessment Acidity

DETERMINATION OF SCORES

Data scores assessed for the categories of this work are based on the range of known values within the dataset. The full set of data is gathered in Table A.8.

Table 9.8. Percent sludge removal (PSR), solvent acquisition cost [(a)], enthalpy of vaporization[(b)].

Solvent	PSR (%)	Solvent acquisition cost (US$/Ton)	ΔH_{vap} (kJ/mol)
Isobutanol	7.6	1197	41.8 [(c)]
2-Pentanol	5.2	1200	51.2
1-Butanol	8.5	1210	43.3
2-Butanol	6.7	2100	40.8
***t*-Amyl alcohol**	2.0	3500	39.0
3-Pentanone	2.3	5900	33.5
2-Pentanone	3.2	9354	33.4
Methylethyl ketone	6.3	21200	31.3

[(a)] 99% purity

[(b)] Reference: V. Majer, V. Svoboda, Enthalpies of vaporization of organic compounds: A critical review and data compilation; Blackwell Scientific Publications, Oxford, 1985.

[(c)] Reference: J.F. Counsell, J.O. Fenwick, E.B. Lees, Thermodynamic properties of organic oxygen compounds 24. vapour heat capacities and enthalpies of vaporization of ethanol, 2-methylpropan-1-ol, and pentan-1-ol, J. Chem. Thermodyn. 2 (1970) 367–372.

Minimum and maximum values for each category are assigned to scores of 1 and 10. This approach is employed for the categories shown in Table A.9.

Table 9.9. List of data values from which the scores are calculated.

Category	Score	Data value for score = 1	Data value for score = 10
Performance	PSR	1.97%	8.52%
Cost	Solvent acquisition cost	1197 US$/Ton	21 200 US$/Ton
Cost	Recovery cost (ΔH_{vap})	51.2 kJ/mol	31.3 kJ/mol

The data values and respective scores are then plotted, and the corresponding equation calculated (Eqs. A.1-A.3). These equations are used to calculate the scores for the full dataset.

$$\text{Performance score} = 1.3752 \times \text{PSR} - 1.7158 \tag{A.1}$$

$$\text{Solvent acquisition score} = -0.0004 \times \text{solvent acq. cost} + 10.5386 \tag{A.2}$$

$$\text{Recovery cost score} = -0.4523 \times \Delta H_{vap} + 24.1558 \tag{A.3}$$

A.6. CHAPTER 8

Figure A.4 illustrates the effect of increasing KOH dosage in the extraction solvent for the treatment of WLO. The FTIR spectra show the arising of a –OH band in the WLO when the KOH dosage in the solvent increases to 3 g/L.

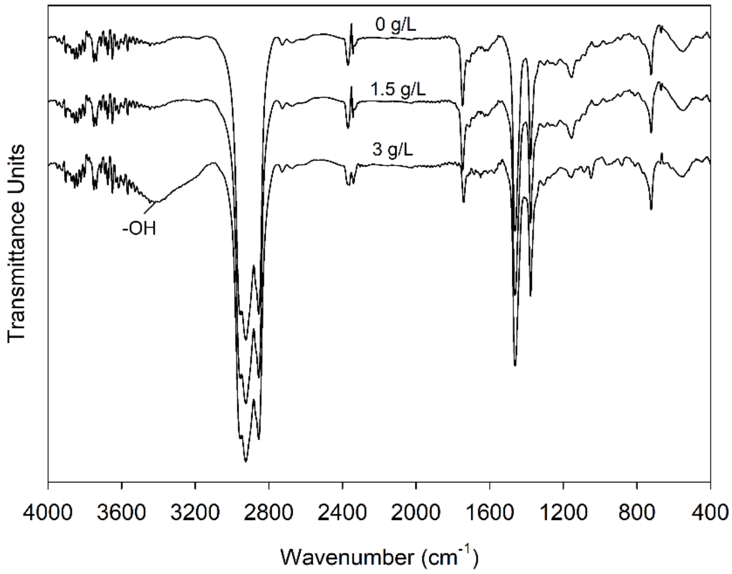


Figure A.4. FTIR spectra of waste oil class C treated with 1-butanol and a KOH dosage of 0, 1.5 and 3 g/L.