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OPTIMIZATION OF FEEDSTOCK BLENDS TO IMPROVE BIODIESEL COST EFFECTIVENESS AND MANAGE ENVIRONMENTAL IMPACTS

PhD thesis in Sustainable Energy Systems,
supervised by Professor Fausto Miguel Cereja Seixas Freire and Professor Luis Miguel Cândido Dias,
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Universidade de Coimbra

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MINISTÉRIO DA EDUCAÇÃO E CIÊNCIA
POPH
PROGRAMA OPERACIONAL POTENCIAL HUMANO
QREN QUADRO DE REFERÊNCIA ESTRATÉGICO NACIONAL PORTUGAL 2007.2013
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ABSTRACT

The controversy raised around biofuels sustainability increased the pressure on biodiesel producers to be as cost efficient as possible and, simultaneously, ensure the sustainability of the biodiesel. As about 85% of biodiesel production costs are attributed to feedstock cost and each feedstock has a different environmental profile, operational level decision making about feedstock selection is crucial to reduce production costs and manage biodiesel environmental performance.

This thesis explores opportunities to improve biodiesel cost effectiveness at the operational level, particularly in the feedstock selection process, by assessing the use of waste-based feedstocks (Waste Cooking Oil, WCO) in blends with conventional feedstocks (palm, rapeseed and soya) and hedging feedstock purchase, whilst managing environmental impacts. For this purpose, an uncertainty-aware decision aiding tool to assess economic and environmental tradeoffs of decisions at the operational level, addressing feedstock compositional and price uncertainty, was developed. The model combines environmental life-cycle assessment (LCA) with blending models using multi-objective optimization to assess water scarcity (WSI), water degradability – acidification (AA), eutrophication (EU), ecotoxicity (FT) and human toxicity (HT) – and Greenhouse Gas (GHG) emissions (CC). Data from different crop cultivation locations were considered: Colombia and Malaysia for palm; Argentina, Brazil and the United States (US) for soybean; and, Germany, France, Spain, Canada and the US for rapeseed. An approach was developed to facilitate the decision process that enables the decision-maker to select the best compromise feedstock blend based on an explicit overall environmental performance.

Results show that incorporating feedstocks' compositional uncertainty allows the use of WCO in blends with conventional feedstocks without compromising biodiesel technical performance. A reduction of total feedstock cost was obtained for blends with WCO relatively to equivalent (similar technical performance) blends composed only of virgin oils. The percentage of cost reduction depends on the relation among the prices of the feedstocks. Moreover, the use of WCO in the blends allows a reduction in cost variation reduction relatively to virgin oils blends because the price of that feedstock presents lower volatility comparatively to the conventional feedstocks.

The differences observed in the environmental assessment of the various virgin oils systems are mainly related to water scarcity of the location, and the fertilization and pesticides schemes used in each crop/location. Results show that higher water scarcity footprint are due to both high water consumption and high water scarcity of the cultivation site. For the toxicity categories (HT and FT), the highest values are ascribed to the high quantity of pesticide used in the cultivation, while for CC, AA and EU the main contributor is the quantity of fertilizers. WCO presents the lowest values WSI, CC, EU and AA.

The multi-objective analysis showed that lower CC and WSI solutions (blends) can be obtained at a lower cost if WCO is included in the biodiesel blend. The same conclusion is obtained when more environmental objectives (AA, EU, FT and HT) are considered in the analysis. The decision-aiding approach developed allows for the visualization of the tradeoff between cost and environmental impacts, facilitating the decision process when more than three objectives are at stake.

This research shows that the inclusion of WCO in a diversified portfolio of feedstocks used in blending optimization models is an attractive approach to improve biodiesel cost effectiveness and environmental performance. The model developed can be further used to optimize the blending of alternative feedstocks and to assess the technical viability of other waste-based feedstock (e.g. animal fat) or emerging feedstocks such as algae. Although the tool was designed specifically for biodiesel production system, it can be adapted to other industries, particularly in the recycling sector, to support production planning at the operational level to enhance technical, economic and environmental performance of these industries.

Keywords: biodiesel, multi-objective optimization, blending models, waste cooking oils, production costs, water footprint, GHG emissions, price volatility, compositional uncertainty

RESUMO

A controvérsia gerada em torno da sustentabilidade dos biocombustíveis aumentou a pressão nos produtores de biodiesel para serem o mais eficientes possível em termos de custos e, simultaneamente, garantirem a sustentabilidade do biodiesel. Como cerca de 85% do custo total de produção é atribuído ao custo da matéria-prima, e cada uma apresenta um perfil ambiental diferente, decisões ao nível operacional acerca de selecção de matéria-prima são cruciais para melhorar a performance económica e ambiental do biodiesel.

Esta tese explora estratégias para reduzir custos de produção de biodiesel, particularmente no processo de selecção de matérias-primas, ao avaliar o uso de resíduos (Óleo Alimentar Usado, OAU) em misturas com óleos convencionais (soja, palma, colza) e planear a compra de matéria-prima, e, simultaneamente, gerir os impactes ambientais. Para tal, foi desenvolvida uma ferramenta de apoio à decisão para avaliar compromissos económicos e ambientais de decisões efectuadas ao nível operacional. Esta ferramenta tem em conta a incerteza associada à composição e ao preço da matéria-prima. O modelo desenvolvido combina Avaliação de Ciclo de Vida (ACV) ambiental com algoritmos de mistura através de optimização multiobjectivo para avaliar a escassez de água (WSI), degradabilidade da água – acidificação (AA), eutrofização (EU), ecotoxicidade (FT) e toxicidade humana (HT) – e, emissões de gases com efeito de estufa (CC). Diferentes locais de cultivo foram considerados: palma cultivada na Colômbia e Malásia; soja na Argentina, Brasil e Estados Unidos; e colza na Alemanha, França, Espanha, Canadá e Estados Unidos. Foi desenvolvida uma abordagem para facilitar o processo de decisão que permite ao decisor escolher a mistura com base na performance ambiental global.

Os resultados mostram que é possível utilizar OAU em misturas com óleos virgens sem comprometer a qualidade do biodiesel se a incerteza composicional dos óleos for tida em conta. Estas misturas apresentam menores custos relativamente a misturas de óleos virgens. A percentagem de redução depende da relação entre os preços dos diferentes óleos. Adicionalmente, o uso de OAU nas misturas permite obter também uma redução

na variação dos custos de produção porque o preço desta matéria-prima apresenta menor volatilidade relativamente à observada nos óleos convencionais.

As diferenças observadas na avaliação ambiental dos diferentes óleos virgens estão relacionadas com a escassez de água da região e o esquema de fertilização/pesticidas usados em cada cultura/local. Os resultados mostram que pegadas hídricas mais elevadas devem-se simultaneamente a maiores consumos de água e elevada escassez dos locais de cultivo. Para as categorias de toxicidade (HT e FT), os valores mais elevados são devido à elevada quantidade de pesticidas utilizados no cultivo, enquanto que para CC, AA e EU a maior contribuição provém da quantidade de fertilizantes. WCO apresenta os menores valores para WSI, CC, EU e AA.

Na análise multiobjectivo realizada, observou-se que soluções (misturas) com valores de CC e WSI mais baixos podem ser obtidos com menor custo se OAU for incluído nas misturas. A mesma conclusão é obtida quando mais objectivos ambientais (AA, EU, FT e HT) são considerados na análise. A ferramenta de apoio à decisão desenvolvida facilita o processo de decisão ao permitir a visualização do compromisso entre o objectivo económico e os ambientais quando mais do que três objectivos são considerados.

Nesta investigação é evidenciado que a inclusão de OAU num portfólio diversificado de matérias-primas usado em modelos de optimização de misturas é uma abordagem atractiva para melhorar a performance económica e ambiental do biodiesel. O modelo desenvolvido pode ser utilizado para optimizar a mistura de matérias-primas alternativas e avaliar a viabilidade técnica de utilizar outros resíduos (por ex. gorduras animais) nas misturas. Embora a ferramenta tenha sido desenvolvida especificamente para produção de biodiesel, pode ser aplicada a outras indústrias, nomeadamente de reciclagem, para apoio à decisão no planeamento de produção com vista a melhorar a performance técnica, económica e ambiental dessas indústrias.

Palavras-chave: biodiesel, optimização multiobjectivo, modelos de misturas, óleos alimentares usados, custos de produção, pegada hídrica, emissões GEE, volatilidade de preços, incerteza composicional

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ABBREVIATIONS AND NOTATION

AA: Aquatic Acidification

AD: Anderson-Darling

AWARE: Available Water REmaning

ARIMA: Autoregressive Integrated Moving Average

ASTM: American Society for Testing and Materials

CC: Climate Change

CCP: Chance-constrained Programming

CF: Characterization Factor

CFPP: Cold Filter Plugging Point

CN: Cetane Number

CO_2: Carbon dioxide

CTU: Comparative Toxic Units

DTA: Demand to Availability

EN: European Standard

EU: European Union

EWR: Environment Water Requirement

FA: Fatty Acid

FE: Freshwater Eutrophication

FT: Freshwater Ecotoxicity

FAME: Fatty Acid Methyl Ester

FFA: Free Fatty Acid

GHG: Greenhouse Gas

GWP: Global Warming Potential

HTc: Human Toxicity cancer

HTnc: Human Toxicity non-cancer

IPCC: Intergovernmental Panel on Climate Change

ISO: International Standardization Organization

IV: Iodine Value

LCA: Life-Cycle Assessment

LCMO: Life-Cycle Multi-Objective

LUC: Land-Use Change

MAPE: Mean Absolute Percent Error

MAD: Mean Absolute Deviation

ME: Marine Eutrophication

MO: Multi-Objective

N: Nitrogen

OS: Oxidative Stability

P: Phosphorus

PI: Performance Indicator

RED: Renewable Energy Directive

SO_2 : Sulfur Dioxide

TSA: Time Series Analysis

WCO: Waste Cooking Oil

WF: Water Footprint

WFA: Water Footprint Assessment

WSI: Water Stress Index

WTA: Water to Availability

WULCA: Water Use in Life-cycle Assessment

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1 INTRODUCTION

1.1 Context and Motivation

In the late 1990´s, biofuels emerged as a strategy to increase revenue of farmers, reduce GHG emissions, and improve energy independence. However, what seemed to be the solution for such critical problems has become a controversial subject. The demand for biofuels feedstock such as maize, soybeans, rapeseed and palm oil has increased food prices and also the environmental performance of these biofuels compared with fossil fuels has been ambiguous (Huo et al. 2008; Demirbas 2009; Chen et al. 2010; Malça and Freire 2010; Plevin et al. 2011; Castanheira and Freire 2013). A number of authors have argued that, to date, existing policies have been insufficient to ensure cost effectiveness and environmental sustainability of biofuels (Charles et al. 2013).

The controversy around biofuels has put pressure on governments to reform biofuel policies so as to reduce economic costs, to avoid increased food insecurity, and to ensure net decreases in GHG emissions. In 2015, the European Commission published Directive 2015/1513 recommending to cap the use of food crop-based biofuels and support the development of cost-effective alternate biofuels that do not compete with food production and are beneficial in terms of life-cycle GHG emissions (Elliott 2015; European Comission 2015). In the United States (US), although the Environmental Protection Agency had proposed in 2013 to cap the use of crop-based biofuels by 1.28 billion gallons per year, the final rule released in 2015 for volume standards for the Renewable Fuel Standard (RFS) program is above this value (1.9 billion gallons for 2016) (ICCT 2015).

Limiting the use of food crop-based biofuels puts pressure on biodiesel producers to be as cost-efficient as possible as the quantity of biodiesel covered by tax credit decreases (Kotrba 2014). This is particularly important as cost of biodiesel production is mainly attributed to feedstock costs (about 85%) (Haas et al. 2006). Another issue that compromises biodiesel cost effectiveness, by threatening the long-term financial stability of the producers, is the high volatility associated with the price of feedstocks conventionally used in biodiesel production. As such, operational level decision making about feedstock selection is crucial to achieve lower production costs and cost variation reduction. Nevertheless, this selection process cannot ignore the environmental impacts of these feedstocks. Although the main concerns of governmental bodies worldwide has been on limiting GHG emissions, other impact categories should not be neglected when assessing biodiesel sustainability, since biodiesel production entails other externalities. This thesis explores opportunities to improve biodiesel cost effectiveness at the operational level, particularly at the feedstock selection process, by assessing the use of waste-based feedstocks in biodiesel blends and hedging feedstock purchase, whilst managing environmental impacts.

1.2 PREVIOUS RESEARCH AND OPEN CHALLENGES

This work combines different issues to which several bodies of literature contributed. The following paragraphs present a brief state of the art for each of the issues addressed and the research gaps identified. More information related to these issues is provided at the beginning of corresponding chapters in the remainder of the thesis.

Biodiesel feedstocks and compositional uncertainty

Several authors have suggested that feedstocks from residues such as waste cooking oil (WCO) may represent an opportunity for biodiesel producers to reduce production costs (Talebian-Kiakalaieh et al. 2013). Although waste-based feedstocks have been widely discussed due to their potential economic and environmental advantages (Dufour and Iribarren 2012; Caldeira et al., 2015), the use of these feedstocks has been limited due to two main factors. One is related to the low available quantity. For example in Europe, in 2014 only 32% of the available WCO resource was collected and used for biodiesel production (Grennea 2014). The other factor is related to the low quality of these feedstocks (i.e., highly variable composition) that may lead to operational difficulties. The latter was addressed in this thesis using stochastic blending models to optimize the blend of WCO (secondary material) and virgin oils like palm, rapeseed and soya (primary material) to manage the quality variation, addressing feedstock compositional uncertainty.

Some authors have presented strategies to address feedstock uncertainty either within a linear performance constraint (Tintner 1960; Hartley et al. 1980; Bliss 1997; Dupacova and Popela 2005), or using a penalty function in the objective

(Evers 1967; Mihailidis and Chelst 1998; Karmarkar and Rajaram 2001), or using a chance-constrained programming (CCP) formulation of the performance constraints (Charnes and Cooper 1959). The advantages of the CCP approach in the development of blending models in relation to deterministic ones are presented by Olivetti et al. (2011). According to these authors, the CCP model formulation always performs better or equal to Linear Risk formulation (LR) and there are conditions where it can lead to increase the use of heterogeneous materials and lower production costs. The CCP formulation allows increase the variation while still meeting technical specifications because it identifies portfolios of raw materials whose uncertainty characteristics are superior to that of any individual raw material. The creation of these portfolios of raw materials allows to manage risk and cost simultaneously (Olivetti et al. 2011).

CCP has been applied in different problems showing the benefits of this technique in different case studies such as feed mixing (Panne and Popp 1963), materials production (Kumral 2003; Gaustad et al. 2007; Rong et al. 2008), coal blending, (Shih and Frey 1995) or brass (Sakallı et al. 2011; Sakallı and Baykoç 2013). Gülşen et al. (2014) applied CCP to develop a blend optimization model for biodiesel production considering the uncertainty of feedstocks chemical composition and pricing trends. The blending algorithm determines the recipe that minimizes cost having as constraints physical properties of the fuel. The results showed the potential for significant cost reduction through feedstock diversification, minimizing risks to producers from price fluctuations while still meeting technical fuel standards. The same CCP blend optimization method was used to analyze the impact of feedstock blending on the GHG emissions of biodiesel (Olivetti et al. 2014). Results showed that besides potential costs reduction, blending can be used to manage biodiesel GHG emissions uncertainty.

Gülşen et al. (2014) and Olivetti et al. (2014) focused on crop-based oils and although subject to compositional variability, this is not as high as the variability found in the in the WCO due to high diversity of sources and previous use (Knothe and Steidley 2009; Hoekman et al. 2012). To the author´s knowledge, no study in the literature explores the use of CCP formulation to assess the use of WCO in biodiesel blends.

Biodiesel feedstocks price volatility

Blending WCO with conventional feedstocks may also be advantageous to manage biodiesel cost variation because, according to WCO price information provided by an European broker, this feedstock presents lower price volatility (Grennea 2014) comparatively to conventional feedstocks like palm, rapeseed and soya oils (IndexMundi 2014). The WCO price data obtained refers to high quality WCO and for this reason it presents lower volatility than one would expect. Typically, as WCO have varying quality characteristics influencing its suitability for biodiesel production and depending on the oil quality the purchase price can vary significantly (Smith et al. 2013).

Conventional feedstocks prices present higher fluctuation over time because they are used in other industries, particularly in the food industry, and so they are influenced by several market conditions. Moreover, Hasanov et al. (2016) also showed strong evidence of causality from crude oil price volatility to conventional oils used in biodiesel production (rapeseed, soybean and sunflower) prices. The high uncertainty associated with the feedstock prices may compromise the biodiesel cost effectiveness, by threatening the long-term financial stability of the producers. For this reason, robust production planning that accounts for feedstock price uncertainty is of utmost relevance for biodiesel producers.

Methods have been developed to explicitly consider feedstock price uncertainty within an optimization framework. In the literature, the most used approach to deal with price volatility is the two stage stochastic programming with recourse model (Al-Othman et al. 2008; Khor et al. 2008; Lin and Wu 2014; Calfa and Grossmann 2015). Other approaches include the use of the Markowitz's Mean-Variance model (Khor et al. 2008), the geometric Brownian motion (GMB) to model price behavior over time (Chen et al. 2015) or the fuzzy sets theory (Moradi and Eskandari 2014).

Another body of literature can be found that investigates price commodities fluctuation using time series analysis (TSA) in different case studies (Caporale et al. 2014; Apergis et al. 2016; Gil-Alana et al. 2016; Hasanov et al. 2016; Lee et al. 2016; Nicola et al. 2016). Within an optimization context, Calfa and Grossmann (2015) developed a scenario-based two-stage stochastic programming framework to explicitly account for uncertainty in spot market prices of raw materials and the predictability of demand response models (DRM) where TSA was used to predict spot market prices scenarios. The objetive was to define optimal contract selection under uncertainty with suppliers and product selling price optimization. No study was found in the literature that addresses biodiesel feedstock price uncertainty within a blend optimization framework through planned feedstock prices hedging informed by predicted feedstock prices.

Biodiesel environmental life-cycle assessment

Although most of the studies reporting the environmental assessment of biodiesel are focused on the life-cycle assessment (LCA) of the biodiesel GHG emissions (e.g. Camobreco et al. 2000; Bozbas 2008; Fargione et al. 2008; Atabani et al. 2012), there are other relevant aspects to consider when evaluating the environmental impacts of biodiesel such as the freshwater use impacts. The majority of biodiesel is produced from vegetable oils feedstocks (Eisentraut 2010; OECD-FAO 2013; Issariyakul and Dalai 2014) such as soya, palm, rapeseed or sunflower that can require large quantities of freshwater depending on the location where the crops are cultivated (Pfister and Bayer 2014). If those areas present high water scarcity, the freshwater consumption impacts can be significant. Moreover, the use of fertilizers and pesticides in the crops cultivation can also impact freshwater quality (Emmenegger et al. 2011).

Over the last 5 years, water footprint (WF) based on LCA methodology has progressed rapidly, resulting in a complex set of methods for addressing different freshwater types and sources, pathways and characterization models, and with different spatial and temporal scales (Kounina et al. 2013; Tendall et al. 2014). The need to ensure consistency in addressing the impacts from freshwater consumption and degradation led to the development of the international standard ISO 14046 (ISO 2014), that provides guidelines on how to perform an assessment of freshwater related environmental impacts. According to this standard, the water footprint profile considers a range of potential environmental impacts associated with water, encompassing the consumption of freshwater (water scarcity assessment) and impact categories related to water pollution (e.g. freshwater and marine eutrophication, aquatic acidification, and human toxicity) (ISO 2014).

Some studies on WF of bioenergy systems based on LCA methodology can be found in the literature quantifying impacts due to freshwater consumption and degradation (impact assessment level) using different approaches (e.g. Emmenegger et al. 2011; Yeh et al. 2011; Chiu et al. 2011; Hagman et al. 2013). Nevertheless, none of those studies performs a comprehensive environmental assessment of crop and waste-based feedstocks used for biodiesel production, addressing impacts due to GHG emissions and water use (water consumption and degradability) according to the ISO 14046 guidelines.

Another body of literature can be found that assesses water use in bioenergy systems according to the water footprint assessment (WFA) manual (Hoekstra et al. 2009; Hoekstra et al. 2011) (e.g. Gerbens-Leenes et al. 2009; Elena and Esther 2010; Chiu and Wu 2012; Gerbens-Leenes et al. 2012; Chiu et al. 2015). Yet, this methodology is focused on accounting water at the inventory level and not the impacts.

Biodiesel life-cycle multi-objective assessment

In 1999, Azapagic and Clift (Azapagic and Clift 1999a; Azapagic and Clift 1999b) provided an approach that allowed the simultaneous assessment of economic and environmental performance of a system. The authors presented a method – "Optimum LCA Performance" that allows the simultaneous optimization of economic and environmental objective functions, generating optimum solutions that do not require a preference, allowing the analysis of the non-inferior solutions sets. Depending on the characteristics of the system, the problem can be formulated as Linear Programming (LP), Mixed Integer Linear Programming (MILP) or Mixed-Integer Nonlinear Programming (MINLP). The system is then optimized simultaneously on a number of environmental and economic objective functions to locate the multidimensional non-inferior or Pareto surface (Azapagic and Clift 1999a; Azapagic and Clift 1999b).

Since then, Life-Cycle Multi-Objective (LCMO) framework has been widely used to analyze tradeoffs between environmental and economic aspects (Pieragostini et al. 2012; Jacquemin et al. 2012) in different areas such as: processing (Capón-Garcia et al. 2011); recycling (Ponce-Ortega et al. 2011); energy systems (Gerber and Gassner

2011; López-Maldonado et al. 2011; Bamufleh et al. 2012; Cristóbal et al. 2012; Gutiérrez-Arriaga et al. 2012); or buildings (Carreras et al. 2015; Safaei et al. 2015).

In what concerns LCMO models for biofuels systems, the majority of the studies presented in the literature consider the supply chain (SC) in a well-to-tank (WTT) approach. Global Warming Potential (GWP) is the common denominator to all studies although some go further, including other environmental impact categories using mainly the Eco-indicator 99 method. A couple of studies include water assessment but only considering water consumption and not the impacts due to this consumption (Tan et al. 2009; Bernardi et al. 2012). The mathematical models are formulated in order to minimize costs or maximize profit and minimize environmental impacts and some consider spatial and multi-period issues. In most cases, the problem is solved using the CPLEX in GAMS software. **Table 1.1** summarizes the main characteristics of the consulted literature on LCMO applied to biofuels systems.

Table 1.1 LCMO studies on biofuels systems

Reference	System	System boundaries	Impact Assessment Method	Objective functions	Mathematical model /Solver	Application
Zamboni et al. 2009a; Zamboni et al. 2009b	Biofuel supply chain (SC)	Well to tank (WTT)	Intergovernmental Panel on Climate Change (IPCC)	Min Total daily cost (€/day) Min Total daily impact (kg CO_2 eq/day)	Spatially explicit MILP / CPLEX solver in GAMS	Corn-based ethanol in Italy
Tan et al. 2009	Biofuel production	WTT	Input–output-based life-cycle model	Max Satisfaction level - Max Biofuel production; Min Land use, water use and carbon emissions	Fuzzy linear programming	Integrated production of biodiesel, ethanol and electricity in Philippines
Zhang et al. 2010	Biofuel crop production	Biofuels Crops Cultivation	Environmental Policy Integrated Climate	Max Energy production Min GHG emissions, Soil erosion; and, N and P loss	Spatially explicit integrative modeling framework (SEIMF)/Genetically adaptive multi-objective method (AMALGAM)	Biofuel production in nine county in Michigan
Giarola et al. 2012	Bioethanol hybrid first/second generation SC	WTT	IPCC	Max Financial profitability (NPV) Min GHG emissions	Spatially explicit multi-period and multi-echelon bi-objective MILP/ CPLEX solver in GAMS	Bioethanol production in Northern Italy
You et al. 2012	Cellulosic ethanol SC	Field to wheel	IPCC	Min Total cost Min GHG emissions Max Number of accrued local jobs	Multi-period MILP / CPLEX solver in GAMS Ɛ-constraint method (Ɛ-c M)	Two county-level state case studies for the state of Illinois
Santibañez-Aguilar et al. 2011	Biorefinary	Cradle-to-Grave	Eco-indicator 99	Max Profit Min EI99 ecopoint	MOLP/ CPLEX solver in GAMS Ɛ-c M	Planning production of a biorefinary in Mexico
Mele et al. 2011	Ethanol and sugar SC	Cradle-to-gate	CML / Eco-indicator 99	Max NPV Min GWP and EI99 ecopoint	MILP / CPLEX solver in GAMS Ɛ-c M	Sugar industry in Argentina
Akgul et al. 2012	Bioethanol hybrid first/second generation SC	WTT	IPCC	Min Total daily cost Min GHG emissions	Multi-period MILP/ CPLEX solver in GAMS Ɛ-c M	Bioethanol production in the UK
Bernardi et al. 2012	Hybrid Bioethanol SC	WTT	IPCC /Water footprint (WF) network (inventory level)	Max NPV Min GHG emissions and Water Footprint	MILP /CPLEX solver in GAMS	Bioethanol production in Northern Italy
Wang et al. 2013	Biorefinary	Cradle-to gate	IPCC/ Eco-indicator 99	Max NPV Min GHG emissions	MINLP/ BARON 2.0 en GAMS Ɛ-c M	Hydrocarbon biorefinery
Murillo-Alvarado et al. 2015	Bioethanol SC	WTT	Eco-indicator 99	Max NPV Min EI99	MILP	Lignocellulosic residues from tequila processing industries in Mexico
Bairamzadeh et al. 2016	lignocellulosic bioethanol SC	WTT	Eco-indicator 99	Max Total Profit Min EI99 Max Number of jobs generated	Multi-objective Robust Possibilistic Programming/CPLEX solver in GAMS	Lignocellulosic supply chain established in Iran.

Life-cycle multi-objective under uncertainty

A few studies can be found in the literature that address uncertainty in LCMO models. Some of these studies are focused on the uncertainty of the LCA impact either by using CCP (Guille and Grossmann 2009; Guillén-Gosálbez and Grossmann 2010) or by describing the LCA uncertain parameters through scenarios with given probability of occurrence (Sabio et al. 2014). Others address uncertainty related to prices and demand uncertainty, using scenarios with given probability of occurrence in the design of sustainable chemical supply chains (Ruiz-Femenia et al. 2013) and chemical processes network (Alothman and Grossmann 2014); or, address uncertainty in several parameters expressed as fuzzy possibility distributions and probability distributions to help design better waste management strategies (Zhang and Huang 2013).

Among the LCMO models applied to biofuels systems presented in **table 1.1** only the ones developed by Tan et al. (2009) and Bairamzadeh et al. (2016) consider uncertainty. In the former case, fuzzy linear programming is used to determine the bioenergy system configuration given target values for both production and footprints (land use, water and carbon) levels. In the latter, uncertainties in the input data involving bioethanol demand and sale price, main crop selling price, and environmental impacts, as well as harvesting losses and deterioration of biomass during storage, are treated as fuzzy values and dealt with using a robust possibilistic programming approach.

Among the LCMO studies found in the literature, none of them developed a framework to optimize blends for biodiesel production using waste-based feedstocks (WCO) minimizing costs and environmental impacts addressing feedstocks compositional and price uncertainty.

1.3 RESEARCH QUESTIONS AND OBJECTIVES

The seminal research question that originated the work presented in this thesis is the following: **Can operational level decisions simultaneously reduce biodiesel cost and manage environmental impacts?**

In face of this question, the main goal of this thesis is to develop an uncertainty-aware decision aiding tool to assess economic and environmental tradeoffs of decisions at the operational level in biodiesel production, taking into account feedstock price and composition uncertainty. This tool allows exploring opportunities to improve biodiesel economic performance by assessing the use of WCO in biodiesel blends and hedging feedstock purchase, whilst managing environmental impacts.

Based on the gaps highlighted in section 1.1, the seminal research question is broken-down into four research questions. Specific objectives were established to help design the research strategy to answer to these questions. The research questions, the specific objectives and the corresponding chapter are presented in **table 1.2**.

Table 1.2 Research questions, objectives and corresponding chapter

Research Question	Objective	Chapter
1. Can biodiesel production cost be reduced by the incorporation of WCO in blends for biodiesel production without compromising the biodiesel technical performance?	1.1 Characterize the uncertainty in feedstocks (palm, rapeseed, soya and WCO)	2
	1.2 Evaluate existing prediction models that stablish a relation between the feedstocks chemical composition and biodiesel final quality	
	1.3 Develop an optimization blending model that addresses feedstocks compositional uncertainty	
	1.4 Evaluate the blends performance comparatively to virgin oils feedstocks blends	
2. Can production cost variation be reduced by planned prices hedging informed by forecasted feedstock prices?	2.1 Develop a time series analysis forecast model to predict feedstock prices	3
	2.2 Develop an optimization model to address price uncertainty using forecasted price information	
	2.3 Evaluate the influence on cost variation performance using the model developed	
3. What are the life-cycle GHG emissions and water use impacts associated with different feedstocks?	3.1 Build a LC model and inventory for virgin oils and WCO	4
	3.2 Calculate the GHG emissions and water use impacts of the feedstocks	
4. What are the environmental benefits of using WCO in biodiesel blends and the tradeoffs between costs and environmental impacts?	4.1 Integrate the environmental assessment results in a blending algorithm using multi-objective optimization	5
	4.2 Develop a tool to facilitate the assessment of the tradeoff between production costs and environmental impacts	
	4.3 Analyze the tradeoff between production costs and environmental impacts of blends composed with WCO and compare them with blends composed only by conventional feedstocks	

1.4 CONTRIBUTION

This thesis contributes to improve biodiesel cost effectiveness either by reducing production costs by using secondary material such as WCO in blends for biodiesel production without compromising technical performance or by addressing feedstock price uncertainty to reduce biodiesel production cost variation. Moreover, the integration of the feedstocks environmental assessment in a cost driven optimization tool facilitates the analysis between economic and environmental tradeoffs. The work developed enhances the technical, economic and environmental performance of biodiesel production, in particular by:

1. Demonstrating that by addressing feedstocks compositional uncertainty, secondary material such as WCO can be used in blends for biodiesel production without compromising technical performance and, consequently reduce production costs;
2. Showing that managing feedstock price uncertainty using forecasted feedstock price information can reduce biodiesel production cost variation;
3. Providing a life-cycle environmental assessment including GHG emissions and water use impacts of feedstocks used in biodiesel production;
4. Combining environmental assessment with blending models using multi-objective optimization towards novel engineering systems methodologies;
5. Supporting biodiesel producers in decision processes concerning economic and environmental tradeoffs.

The outcome of this research allows biodiesel industry to obtain blends that are efficient in terms of cost and environmental impact for biodiesel production in compliance with technical standards. The efficient solutions obtained allow the production planner to analyze the tradeoffs between the different objectives. Although applied specifically to biodiesel production, the uncertainty-aware decision tool developed in this work can be adapted and applied to other industries, namely recycling, to enhance their technical, economic and environmental performance.

The research in this PhD originated articles published or under review in ISI-JCR indexed journals. **Table 1.4** presents the articles and the corresponding chapter.

Table 1.3 Articles published or under review in ISI-indexed journals and corresponding chapter

Article	Corresponding Chapter
Caldeira, C., Freire, F., Olivetti, E., Kirchain, R. "Fatty Acid based prediction models for biodiesel properties addressing compositional uncertainty" Fuel 196C pp. 13-20	Chapter 2 (section 2.1)
Caldeira, C., Swei, O., Dias, L., Freire, F., Olivetti, E., Kirchain, R. "Planning strategies to manage production cost and cost variation of biodiesel production addressing operational and price uncertainty" (in final preparation)	Chapter 2 (section 2.2) and Chapter 3
Caldeira, C., Queirós, J., Freire, F. (2015). "Biodiesel from Waste Cooking Oils in Portugal: alternative collection systems". Waste and Biomass Valorization, vol. 6 (5), pp. 771-779.	Chapter 4
Caldeira, C., Queirós, J., Noshadravan, A., Freire, F. "Incorporating uncertainty in the Life-cycle Assessment of biodiesel from Waste Cooking Oil addressing different collection systems". Resources, Conservation and Recycling, vol. 112, pp. 83-92	Chapter 4
Caldeira, C., Quinteiro, P., Castanheira, E.G., Boulay, AM., Dias, A.C, Arroja, L., Freire, F. "Water footprint profile of crop-based vegetable oils and waste cooking oil" (submitted)	Chapter 4
Caldeira, C., Olivetti, E., Kirchain, R., Freire, F., Dias, L., "A life-cycle multi-objective decision aiding tool to assess the use of secondary material in biodiesel production" (in final preparation)	Chapter 5

Other related articles

Caldeira, C., Gülsen, E., Olivetti, E. A., Kirchain, R., Dias, L., Freire, F. (2014). "A Multiobjective model for biodiesel blends minimizing cost and Greenhouse Gas emissions". Computational Science and Its Applications. Lecture Notes in Computer Science. Vol. 8581, pp 653-666.

Caldeira, C., Dias, L., Freire, F., Kremmydas D., Rozakis, S. "Blends for biodiesel production: influence of technical constraints in GHG reduction and Cost effectiveness" (submitted)

Abstracts and keywords of the articles are presented in **Appendix I**. In addition, articles related to this PhD research published in conference proceedings with scientific refereeing are presented in the full list of publications in **Appendix II**.

1.5 THESIS OUTLINE

This thesis consists of six chapters including this introductory chapter, and it is structured as follows:

Chapter 2 presents firstly, a review and assessment of prediction models that relate the chemical composition of feedstocks to the final quality of biodiesel. Secondly, selected models were integrated in a chance-constrained optimization model to optimize blends for biodiesel production using WCO, addressing compositional uncertainty.

In **Chapter 3,** an approach to address feedstock price uncertainty is presented. Time series analysis models are used to forecast the feedstock prices and this information is integrated in a cost optimization model developed to minimize biodiesel production cost variation.

Chapter 4 presents the environmental life-cycle assessment of the virgin and WCO that include GHG emissions and water use (consumptive and degradative) impacts

Chapter 5 presents a multi-objective optimization model that works as a decision aiding tool to assess the incorporation of WCO in blends for biodiesel production and analyze the economic and environmental tradeoffs of operational decisions.

Finally, **Chapter 6** draws the conclusions, discusses the main limitations, and presents suggestions for future research.

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2 CHANCE-CONSTRAINED OPTIMIZATION TO ADDRESS COMPOSITIONAL UNCERTAINTY IN BIODIESEL BLENDING

The content of this chapter is presented in the following articles:

Caldeira, C., Freire, F., Olivetti, E., Kirchain, R. (2017) **Fatty Acid based prediction models for biodiesel properties incorporating compositional uncertainty** Fuel 196C pp. 13-20

Caldeira, C., Swei, O., Dias, L., Freire, F., Olivetti, E., Kirchain, R. **Planning strategies to manage production cost and cost variation of biodiesel production addressing operational and price uncertainty** (in final preparation)

2.1 INTRODUCTION

Biodiesel properties are intimately related to the vegetable oil chemical composition that originated it. As each vegetable oil presents a typical fatty acid (FA) profile , the modification of the final FA composition by blending different vegetable oils can lead to a specific value for a property, guaranteeing its compliance with quality standards (Moser 2008; Park et al. 2008; Knothe 2009). However, although blending can contribute to obtain required technical performance of biodiesel, if the compositional uncertainty of the oils is not considered, the risk of noncompliance with technical requirements exists. This risk is higher if the biodiesel producer intends to include in the blends secondary material such as WCO. To minimize this risk, stochastic optimization techniques such as chance-constrained programming (CCP) can be applied.

This chapter presents a model to optimize the blending of crop-based oils and WCO addressing oil compositional uncertainty (FA composition) using chance-constrained programing. The crop-based oils selected for this work are palm, rapeseed and soya as they are widely used in biodiesel production (OECD-FAO 2011). A review and assessment of biodiesel properties prediction models based on the FA composition is presented in section 2.2. Selected prediction models are then integrated in an optimization model described in section 2.3. The model was used to assess the use of WCO in blends with virgin oils. The blends are assessed in terms of costs and technical performance. Reference blends obtained having only virgin oils available in the model are also evaluated and used as a benchmark.

2.2 FATTY ACID BASED PREDICTION MODELS FOR BIODIESEL PROPERTIES ADDRESSING COMPOSITIONAL UNCERTAINTY

Biodiesel is globally produced from vegetable oils via a transesterification reaction using methanol (Balat and Balat 2010). Vegetable oils are mainly composed by triglycerides, an ester derived from glycerol and three fatty acids (FA). A FA is a carboxylic acid with a long aliphatic tail (chain), which is either saturated or unsaturated. Most naturally occurring FA have a chain of an even number of carbon atoms, from 4 to 28. A nomenclature "CX:Y" is associated with each FA, where X is the number of carbon atoms and Y the number of carbon–carbon double bonds in the FA chain. As schematically represented in **figure 2.1**, transesterification is the reaction of an alcohol with the FA (represented by R) in the presence of a catalyst to form the esters of fatty acids (biodiesel) and crude glycerol. The most commonly used alcohol is methanol and in this case, the biodiesel is a Fatty Acid Methyl Ester (FAME) (Knothe et al. 2010).

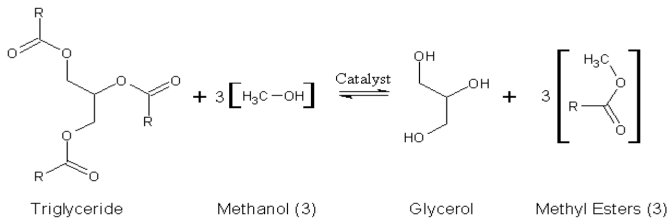

Figure 2.1 Scheme of the transesterification reaction

Transesterification can be used to produce biodiesel from triglyceride feedstock including oil-bearing crops, waste oils (waste cooking oil and animal fats) and algae lipids (Hoekman et al. 2012). It is generally assumed that FA compositional profiles remain unchanged during conversion of the feedstocks to fuels via transesterification For this reason, the biodiesel properties are directly related to the FA profile (Sajjadi et al. 2016). Structural features such as chain length, degree of unsaturation and branching of the FA chain determine the fuel properties (Hoekman et al. 2012).

Technically, the production of biodiesel from WCO is similar to conventional transesterification processes of crop-based oils (Knothe et al. 1997). Nevertheless, depending on the quality of the WCO, different catalyst (alkaline, acid or enzymatic) may present advantages. The quality of the WCO is associated with contaminants such as water and free fatty acids (FFA) and, depending on the quality of the oil, a pretreatment phase might be necessary so that the oil complies with standards required for the transesterification reaction (Diya'uddeen et al. 2012; Araújo et al. 2013). Another issue that may impact the quality of the WCO is the hydrogenation used to increase the oil useful cooking lifetime that may lead to the introduction of trans constituents (Moser 2009).

FFA are a problem in the transesterification process because they originate saponification reactions, while the high water content leads to the formation of bulk solids. If the FFA content is lower than 0.5%, the transesterification reaction can be performed directly. However, since the percentage of FFA in the WCO is usually more than 2% an acid esterification of the WCO previously to the transesterification reaction is necessary to reduce the % of FFA (Issariyakul et al. 2007; Diya'uddeen et al. 2012).

Although there are several parameters influencing the production of biodiesel from WCO, this work is focused only on the influence of the FA profile of the oils in the final quality of the biodiesel as they are the major indicators of the properties of the biodiesel (Chhetri et al. 2008). For this reason, it is assumed that the quality of the WCO is the required one for the transesterification reaction.

To ensure that the biodiesel has quality to be used as automotive diesel fuel, the standard organizations American Society for Testing and Materials (ASTM) in the US and European Committee for Standardization (CEN) in the EU have established standard specifications for biodiesel: ASTM D6751 (ASTM 2008) and EN 14214 (CEN 2008), respectively. Properties that are directly related to the FA profile are: viscosity, density, cetane number (CN), iodine value (IV), cloud point (CP), pour point (PP), cold filter plugging point (CFPP), and heating value (Martínez et al. 2014). Oxidative stability (OS) is related to the FA composition but it is also influenced significantly by the conditions that biodiesel is exposed to during storage, transport and handling (e.g. light, temperature). Moreover, anti-oxidant additives that some biodiesel samples contain modify the stability of the biodiesel (Knothe et al., 2010; Hoekman et al. 2012; Giakoumis 2013).

Models have been developed that express the relation between the FA composition and individual properties showing agreement with experimental data (Knothe and Steidley 2007; Bamgboye and Hansen 2008; Park et al. 2008; Demirbas 2008; Ramos et al. 2009; Pratas et al. 2010; Tong et al. 2010; Freitas et al. 2011; Knothe and Steidley 2011). These models provide deterministic results but do not explore the underlying variability associated with the FA composition. However, as FA sources are variable and because the attributes of a FA source are not always fully characterized, this variability translates into uncertainty for the production planner in determining quantity and types of oils to blend. The FA composition may vary due to different growing conditions and locations. This variability is even higher in cases of secondary feedstocks such as waste cooking oils (WCO) due to diverse origin sources (Knothe and Steidley 2009; Hoekman et al. 2012).

In this section, the results of existing prediction models for biodiesel properties that are directly based on the FA composition, integrating the FA compositional uncertainty are presented and discussed. Firstly, a review of existing prediction models that are directly related to the FA composition is presented (section 2.2.1); secondly, the procedure to integrate the FA compositional uncertainty in the models is described (section 2.2.2); and finally, the models results are compared with values found in the literature (section 2.2.3).

2.1.1 PREDICTION MODELS FOR BIODIESEL PROPERTIES

A review of existing biodiesel prediction models that are directly related to the FA composition is presented in this section. The following properties are addressed: density, cetane number (CN), iodine value (IV), cold filter plugging point (CFPP) and Oxidative stability (OS). These properties are also indicated by the industry as the most challenging to meet (Gülşen et al. 2014). Although viscosity and heating value also depend on the FA composition, these properties were not included in this study because no model that explicitly relates the property with the FA composition was found in the literature.

2.2.1.1 Density

The density of a fuel is critical to determine the quantity of mass injected and consequently, the air–fuel ratio and energy content within the combustion chamber. Density is limited to 860-900 kg m^{-3} at 15 ^{o}C in EN 14214 but there is no specification for density in ASTM D6751. Biodiesel density is affected by chain length (with higher chain length leading to lower fuel density) and degree of unsaturation (with higher unsaturation leading to increased density) (Knothe et al 2010).

Pratas et al. (2011) investigated three versions of Kay's mixing rules and two versions of the group contribution GCVOL model to predict biodiesel density, showing that Kay's mixing rules and the revised form of the GCVOL model suggested by the authors was able to predict biodiesel densities with average deviations of only 0.3%. Ramírez-Verduzco et al. (2012) also provided a model to predict density based on the correlation of experimental data and the molecular weight and the number of double bonds in a given FAME. The density of the biodiesel is then given by the weighed sum of the density of each FAME.

Giakoumis (2013) found a significant correlation (R^2 = 0.86) between density and the degree of unsaturation given by **equation 2.1**, where n_{FA} is the number of unsaturated bonds and x_{FA} the composition (percentage) of the FA in the oil.

$$\text{Density} = 9.17 \sum_{FA} n_{FA}\, x_{FA} + 869.25 \qquad \text{Eq. 2.1}$$

A linear correlation between the unsaturation degree and the density was also obtained by Martínez et al. (2014), but the equation is not provided. In this thesis the model given by Giakoumis (2013) was analyzed because it explicitly relates the property with the FA composition.

2.2.1.2 Cetane Number

The cetane number (CN) is a dimensionless number that reflects the auto ignition quality of the fuel. High CN means that there is a lower delay time between fuel ignition and ignition and this guarantees good start behavior and a smooth run of the engine. Studies have reported that fuels with higher CN have lower NOx and CO emissions (Knothe 2014; Sajjadi et al. 2016). This property is limited to a minimum of 51 in EN 14214 and a minimum of 47 in ASTM D6751.

The CN of biodiesel is affected by the degree of unsaturation (feedstocks with high concentration of unsaturated FA lead to lower CN) and chain length (higher chain length leads to higher CN values) (Refaat 2009; Giakoumis 2013).

Bamgboye and Hansen (2008) proposed **equation 2.2** to predict the CN of biodiesel based on the composition (percentage) of specific FAMEs (x).

$$\begin{aligned} CN = 61.1 + 0.088x_{C14:0} + 0.133x_{C16:0} + 0.152x_{C18:0} - 0.101x_{C16:1} - 0.039x_{C18:1} - 0.243x_{C18:2} \\ - 0.395x_{C18:3} \end{aligned} \qquad \text{Eq. 2.2}$$

According Gopinath et al. (2009a) and Piloto-Rodríguez et al. (2013), CN can be predicted using **equations 2.3 and 2.4**, respectively.

$$CN = 62.2 + 0.017x_{C12:0} + 0.074x_{C14:0} + 0.115x_{C16:0} + 0.177x_{C18:0} - 0103x_{C18:1} - 0.279x_{C18:2} - 0.366x_{C18:3} \quad \text{Eq. 2.3}$$

$$CN = 56.16 + 0.007x_{C12:0} + 0.1x_{C14:0} + 0.15x_{C16:0} - 0.05x_{C16:1} + 0.23x_{C18:0} - 0.030x_{C18:1} - 0.19x_{C18:2} - 0.31x_{C18:3} + 0.08x_{C20:1} + 0.18x_{C22:1} - 0.1x_{\text{sum of residual FAME}} \quad \text{Eq. 2.4}$$

Lapuerta et al. (2009) proposed the predictive **equation 2.5** based on statistical analysis for FAME CN that is largely driven by the number of double bonds (db) and the carbon number (n) in the FAME.

$$CN = -21.157 + (7.965 - 1.785db + 0.235db^2) - 0.099n^2 \quad \text{Eq. 2.5}$$

Tong et al. (2010) and Knothe (2014) predicted the CN of biodiesel based on the CN of each FAME. The biodiesel CN is given by the sum of the relative percentage of the FAME multiplied by the CN FAME value.

The Bamgboye and Hansen (2008), Lapuerta et al. (2009), Gopinath et al. (2009a) and Piloto-Rodríguez et al. (2013) models were compared in the analysis.

2.2.1.3 Iodine value

Iodine value (IV) is a parameter used to determine the degree of unsaturation (number of double bonds) in a molecule of oil. It is determined by measuring the amount of iodine (I_2) in grams that reacts by addition to carbon–carbon double bonds, since one molecule of iodine is consumed by every double bond. EN 14214 restricts the value of IV to a maximum of 120 g I_2/100 g of biodiesel, while ASTM D6751 does not present any specification for this parameter. The European standard provides a procedure to calculate IV according to which, the sample's IV is the sum of the contributions of each methyl ester, obtained by multiplying the methyl ester percentage (x_{FA}) by its respective factor according **equation 2.6** (CEN 2008).

$$IV = 0.95x_{C16:1} + 0.860x_{C18:1} + 1.732x_{C18:2} + 2.616x_{C18:3} + 0.785x_{C20:1} + 0.723x_{C22:1} \qquad \text{Eq. 2.6}$$

2.2.1.4 Cold Flow Properties

The performance of biodiesel in cold weather is a critical issue. At low temperatures, the saturated esters begin to nucleate and form solid crystals that can restrict flow in fuel lines and filters, which can lead to fuel starvation and engine failure (Knothe et al. 2010). Cooling temperatures cause formation of wax crystal nuclei invisible to the human eye. These crystals grow with decreasing temperature until they become visible. The temperature at which this happens is defined as the cloud point (CP). Bellow the CP, larger crystals fuse together and form agglomerates that can restrict or cut-off flow through fuel lines and filters causing operability problems. This happens when the pour point (PP) is reached. Since non of these parameters are suitable for predicting cold flow operability of diesel fuels under field conditions, an alternative bench-scale tests parameter, the cold filter plugging point (CFPP), was developed to predict overnight temperatures at which start-up or operability problems may occur (Moser 2008; Knothe et al. 2010).

The three metrics (CP, PP, and CFPP) are highly correlated amongst themselves and although the European and US standards do not include explicit specifications for cold flow properties. The CP is required by report only in ASTM D6751. In EN 14214, climate-dependent requirements options are given to allow for seasonal grades to be defined for each country. There are six CFPP grades for temperate climates and five different classes for arctic climates.

The cold flow properties are influenced by all the factors that influence close packing of highly ordered molecules. This factors are: i) chain length, the longer the carbon chain, the higher the melting point, and poorer the low temperature performance; ii) unsaturation degree, double bond disrupts the close packing of molecules and consequently lower the crystallization temperatures. Furthermore, differences in double bond orientation have been noted, with the “cis” configuration providing better low temperature test performance than “trans”; and, iii) branching of the FA chain or of the alcohol portion of FAME, replacing methanol with ethanol to produce FAEE results in slightly improved low temperature performance, as ethyl esters typically have melting points 5 –10 ◦C lower than the comparable methyl esters (Knothe et al. 2010).

Park et al. (2008) studied the effects of the total content (percentage) of unsaturated FA ($x_{\text{unsat FA}}$) in CFPP and obtained a good correlation expressed by **equation 2.7** if the total content of unsaturated FA is lower than or equal to 88% and by **equation 2.8** if the total content of unsaturated FA is higher than 88%.

$$\text{CFPP} = -0.488 \sum_{\text{unsat FA}} x_{\text{unsat FA}} + 36.0548 \text{ , if } x_{\text{unsat FA}} \leq 88\% \qquad \text{Eq. 2.7}$$

$$\text{CFPP} = -2.7043 \sum_{\text{unsat FA}} x_{\text{unsat FA}} + 232.0036 \text{ , } \quad \text{if } x_{\text{unsat FA}} > 88\% \qquad \text{Eq. 2.8}$$

Moser (2008) reported a prediction model based on the quantity of saturated FA ($x_{\text{sat FA}}$) expressed by **equation 2.9** to be applied if the content of saturated FA is lower than or equal to 48%.

$$\text{CFPP} = 0.438 \sum_{\text{sat FA}} x_{\text{sat FA}} - 8.93 \qquad \text{Eq. 2.9}$$

Ramos et al. (2009) analyzed the correlation between CFPP and the Long Chain Saturated Factor (LCSF) parameter. LCSF is an empiric parameter determined taking into account the composition of saturated FA and giving more weight to the composition of FA with long chain. The results show a strong correlation (R^2 = 0.966) that is described by **equation 2.10**.

$$\text{CFPP} = 3.1417(0.1x_{\text{c16:0}} + 0.5x_{\text{C18:0}} + x_{\text{C20:0}} + 1.5x_{\text{C22:0}} + 2x_{\text{C24:0}}) - 16.477 \qquad \text{Eq. 2.10}$$

2.2.1.5 Oxidative Stability (OS)

Oxidative stability is one of the most important fuel properties with respect to in-use performance of biodiesel. Unstable fuel can lead to increased viscosity, as well as formation of gums, sediment, and other deposits. Although OS is influenced by the FA composition, several other factors such as natural antioxidant content, the level of contaminants and the conditions of fuel storage (temperature, exposure to light and air and tank material) can also affect this property (Refaat 2009). OS is limited to 8 hours in EN 14214 and 3 hours ASTM D6751.

The removal of a hydrogen atom from an allylic position (removed from a carbon adjacent to a double bond) initiates the oxidative degradation processes. After this, rapid reaction with molecular oxygen leads to formation of allylic hydroperoxides. Subsequent reactions involving isomerization and radical chain propagation produce numerous secondary oxidation products such as aldehydes, alcohols, and carboxylic acids (Knothe et al. 2010; Hoekman et al. 2012). Considering the chemical composition, OS is influenced by: i) degree of unsaturation, higher unsaturation leads to poorer stability; ii) number and position of the double bonds, esters composed of linoleic and linolenic acids that contain a carbon atom that is adjacent to two double bonds (a bis-allylic group) are particularly susceptible to oxidative instability; and iii) double bond orientation, trans- configuration generally presents more stability than cis, what may favor the WCO biodiesel (Moser 2009).

Oxidation is a complex process to understand because FAs usually occur in complex mixtures, with minor components in these mixtures catalyzing or inhibiting oxidation (Refaat 2009). The presence of water and other compounds derived from external contamination or thermal degradation (the case of WCO) may also promote oxidation. Also the reduction in the natural anti-oxidants when the oil is subjected to a frying process contributes to the lower oxidation stability of waste cooking oils esters (Giakoumis 2013).

Park et al. (2008) studied the relationship between the content (percentage) of unsaturated FAMEs: Linoleic (C18:2) and linolenic (C18:3) and the stability of the biodiesel and developed the predictive **equation 2.11** for biofuel stability based on the content of these two FAMEs.

$$\mathrm{OS} = \frac{117.9295}{\mathrm{x}_{\mathrm{C18:2}} + \mathrm{x}_{\mathrm{C18:3}}} + 2.5905 \qquad \text{Eq. 2.11}$$

In the analysis performed by Gülşen et al. (2014), besides the two FAMEs considered in Park´s model, the presence of natural antioxidants (tocopherol- γT and tocotrienol-TT) in the oil was also taken into account by representing them as dummy variables. A multiple regression analysis on these factors was performed and the regression equation is given by **equation 2.12**.

$$\mathrm{OS} = 7.41 - 0.092(\mathrm{x}_{\mathrm{C18:2}} + \mathrm{x}_{\mathrm{C18:3}}) + 2.76\gamma\mathrm{T} + 4.12\mathrm{TT} \qquad \text{Eq. 2.12}$$

2.2.2 INTEGRATION OF COMPOSITIONAL UNCERTAINTY IN THE PREDICTION MODELS

To integrate the FA compositional uncertainty in the prediction models the following steps were performed: i) data collection about the FA composition of vegetable oils; ii) selection of the adequate uncertainty representation of the parameters (FA composition); iii) integration of the FA compositional uncertainty in the models and estimate the range of results given by the models; and, iv) comparison of the results with reference values obtained from the literature.

The FA compositional data of vegetable oils were obtained from 27 studies that reported compositional information for palm, 20 for rapeseed, 39 for soya and 19 for WCO (Hoekman et al. 2012). The main FA for these feedstocks are palmitic (C16:0); stearic (C18:0), oleic (C18:1) and linoleic (C18:2) as presented in **table 2.1**. For the FA with higher percentage in each oil (e.g. C16:0 and C18:1 for palm) the coefficient of variation (CV) ranges from 7% to 13% for the virgin oils and 21% to 41% in the WCO. WCO presents the highest variation due to high diversity of sources associated with this type of feedstock.

Table 2.1 Main Fatty Acids average composition (μ), standard deviation (σ) and coefficient of variation (CV) in percentage in palm, rapeseed, soya, and WCO (adapted from Hoekman et al. 2012)

Fatty Acid		**Palm**			**Rapeseed**			**Soya**			**WCO**		
Common Name	**Nom**	**μ**	**σ**	**CV**	**μ**	**σ**	**CV**	**μ**	**σ**	**CV**	**μ**	**σ**	**CV**
Palmitic	C16:0	**42.5**	**3.2**	**8**	4.2	1.1	26	11.6	2	17	16.5	5.6	34
Stearic	C18:0	4.2	1.1	26	1.6	0.7	44	3.9	0.8	21	7.1	3.9	55
Oleic	C18:1	**41.3**	**2.9**	**7**	**59.5**	**7.8**	**13**	**23.7**	**2.4**	**10**	**44.6**	**9.3**	**21**
Linoleic	C18:2	9.5	1.8	19	**21.5**	**2.8**	**13**	**53.8**	**3.5**	**7**	**25.1**	**10.3**	**41**
Composition share (%)		98			87			93			93		

The average values and standard deviation of the FA compositional data are presented in **Appendix III** and the histograms of the data collected in **Appendix IV.**

To determine an appropriate representation of the uncertainty (distribution) associated with the FA composition, we used the Anderson-Darling (AD) goodness-of-fit statistic. The AD test provides a statistic that represents the probability that random data generated from the fitted distribution would have originated a value as low as that calculated for the observed data (Anderson and Darling 1952; Vose 2010). The lower the value of these statistics, the more likely is that the data has origin in the hypothesized distribution. The distributions attributed to each FA are presented in **Appendix IV.** Some FAs are reported only in some studies and the number of observations was not enough to apply the test. In these cases, a normal distribution was assumed.

A Monte Carlo simulation with 10 000 runs was performed to determine the potential range given by the models of each property for each feedstock. The range given by the model is compared graphically with the range of reference values obtained from the literature (Hoekman et al. 2012; Giakoumis 2013). The average values and standard deviation of the literature reported data are presented in **Appendix V.** Additionally, the deviation of the model median value relatively to the median reference value normalized by the reference value standard deviation was calculated according **equation 2.13**. This metric allows us to know how many standard deviations the median value is off relatively to the reference median value.

$$\text{ModDev} = \frac{\text{Model median} - \text{Reference median}}{\text{Reference } \sigma} \qquad \text{Eq. 2.13}$$

Another source of uncertainty that should be considered when performing this analysis is the uncertainty that stems from standard errors in the prediction models coefficients. However, since none of the studies presenting prediction models reported information concerning the uncertainty of the coefficients, this was not considered in this thesis.

2.2.3 SELECTION OF MODELS FOR BLEND OPTIMIZATION

Figures 2.2 to 2.6 depict the results obtained by the prediction models and reference values for density, cetane number, iodine value, cold filter plugging point and oxidative stability, respectively. Each data point in a plot depicts the 5^{th}, 25^{th}, 50^{th} (median), 75^{th}, and 95^{th} percentiles. The relative deviation (%) of the model median to the reference median was calculated according **equation 2.13** and it is presented in the figures.

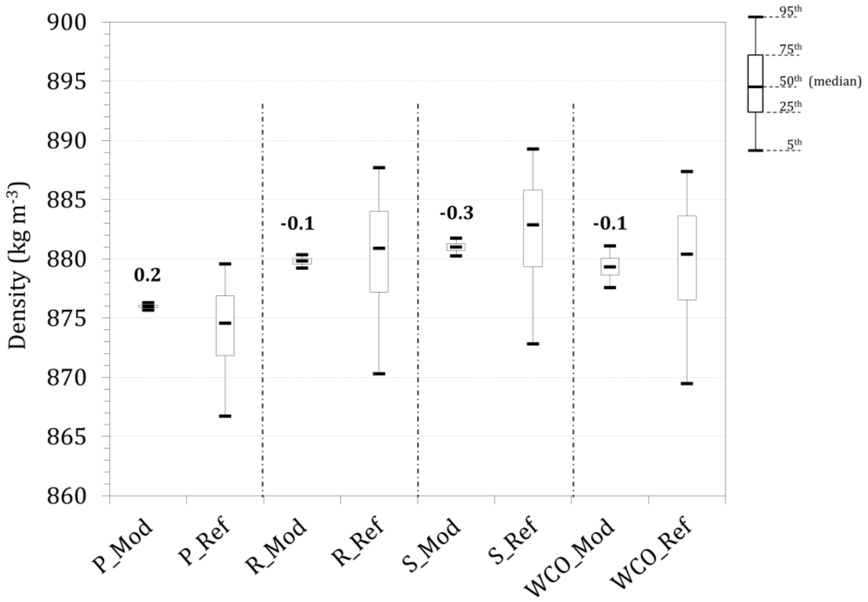

Figure 2.2 Density (kg m^{-3}) of biodiesel from palm (P), Rapeseed (R), Soya (S) and WCO obtained from the correlation established in (Giakoumis 2013) (_Mod) and reference values (_Ref). The figure above the model result is the ModDev metric

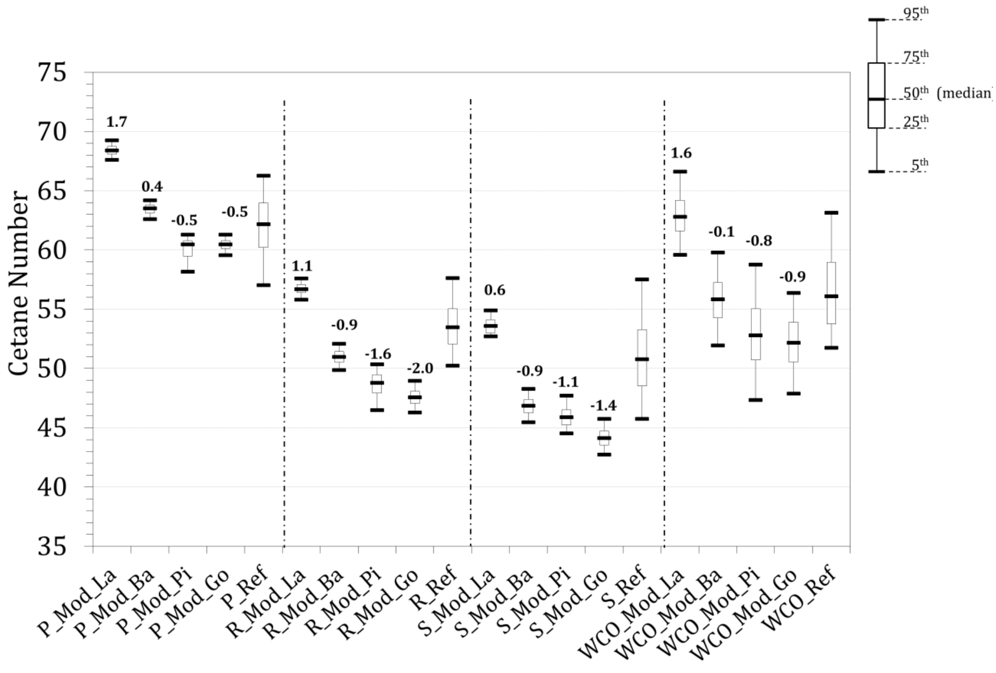

Figure 2.3 Cetane number of biodiesel from palm (P), Rapeseed (R), Soya (S) and WCO obtained from the Bamgboye and Hansen (2008)(_Mod_Ba), Lapuerta et al. (2009)(_Mod_La), Gopinath et al. (2009a) (_Mod_Go) and Piloto-Rodríguez et al. (2013)(_Mod_PI) models and reference values (_Ref). The figure above the model result is the ModDev metric.

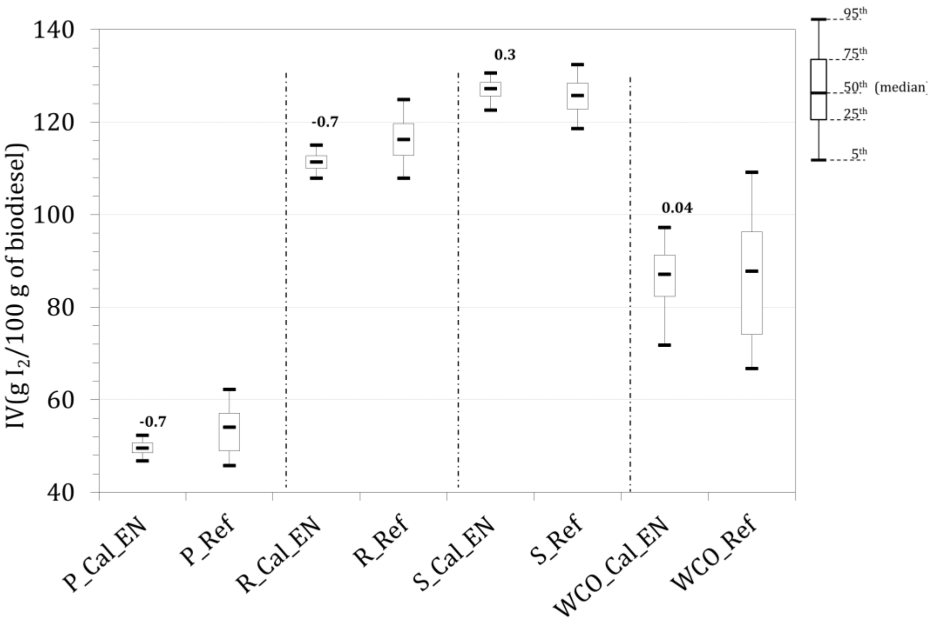

Figure 2.4. Iodine value (g iodine/100 g of biodiesel) from palm (P), Rapeseed (R), Soya (S) and WCO obtained from the procedure presented in EN 14214 model (_Cal_EN) and the reference values (_Ref). The figure above the model result is the ModDev metric.

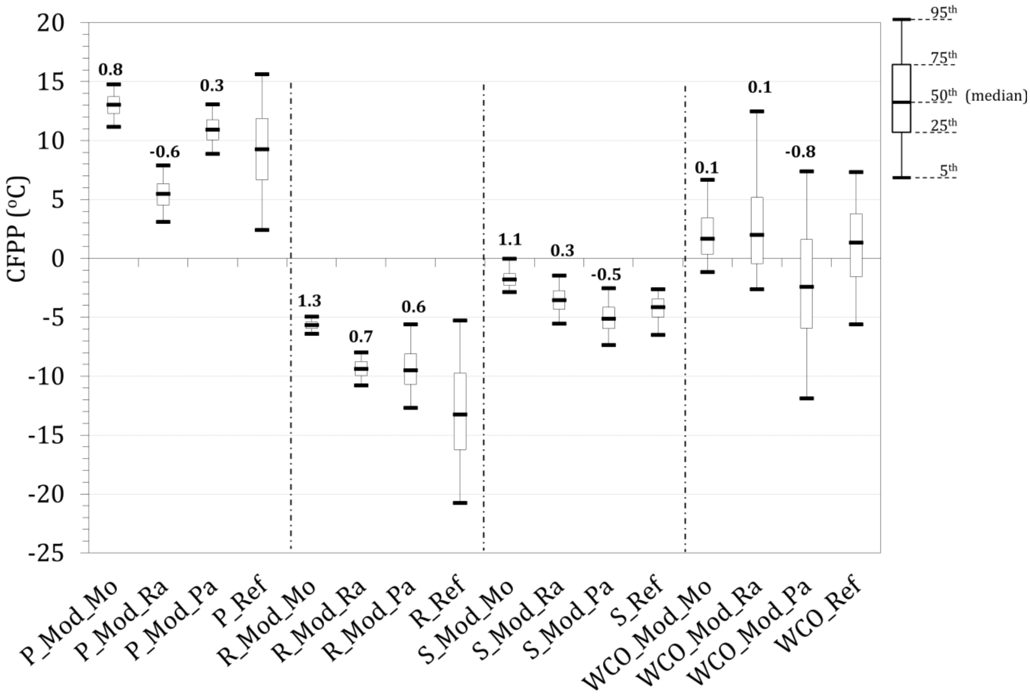

Figure 2.5 Cold filter plugging point (°C) of biodiesel from palm (P), Rapeseed (R), Soya (S) and WCO obtained from the models Moser (2008) (_Mod_Mo), Ramos et al. (2009) (_Mod_Ra), Park et al. (2008) (_Mod_Pa) and reference values (_Ref). The figure above the model result is the ModDev metric.

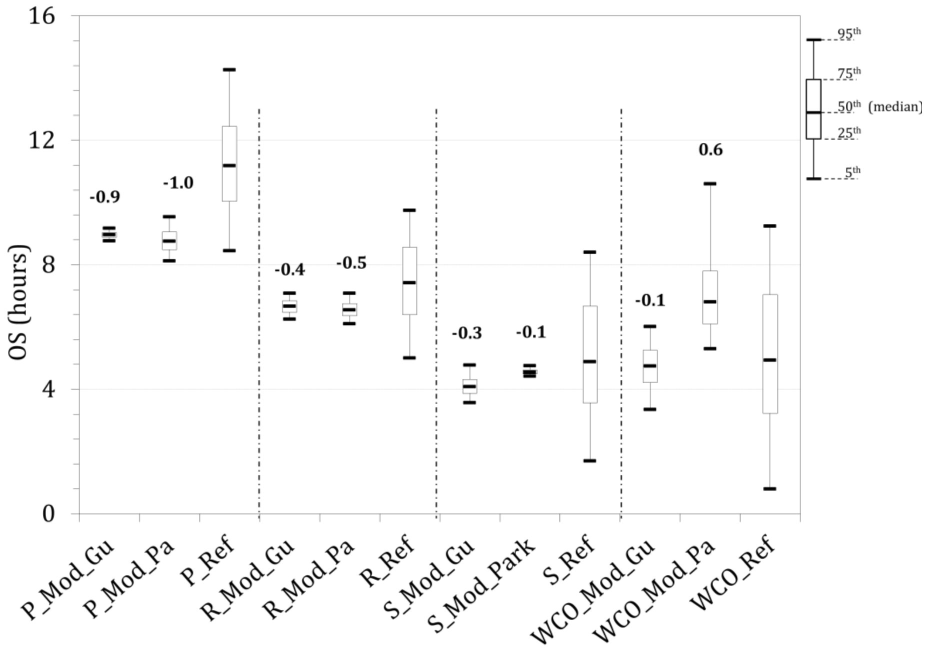

Figure 2.6 Oxidative Stability (hours) of biodiesel from palm (P), Rapeseed (R), Soya (S) and WCO obtained from the models Gülşen et al. (2014) (_Mod_Gu), Park et al. (2008) (_Mod_Pa) and reference values (_Ref). The figure above the model result is the ModDev metric.

The variation of the results provided by the model incorporating FA uncertainty is lower than the variation observed in the reference values. According to Hoekman et al. (2012), the variation observed in the reference values may be due to several factors such as water contamination, the chemical process and conditions used to produce FAME, the clean-up process used to purify raw FAME, the storage time (and conditions) prior to analysis and even different equipment and skills of the analysts performing the analyses. For the WCO the variation is higher comparatively to virgin oils (palm, rapeseed and soya). This is a consequence of the high compositional variability due the diversity of oil and origin associated with this feedstock.

For density, the deviation ranges from -0.3 to 0.1. For both properties, the results provided by the model are within the range of the reference values. The model provided by Lapuerta et al. (2009) to predict CN appears to have a systematic deviation since it provides results above the median of the reference values or even out of the range of reference values, as is the case for palm. The deviation of the median value obtained by this model ranges from 0.6 to 1.7 standard deviations. Also the results obtained using the models provided by Piloto-Rodríguez et al. (2013) and Gopinath et al. (2009a) present a deviation as they provide results always below the median value of the reference values. The deviation varies from -1.6 to -0.5 for Piloto-Rodríguez et al. (2013) model and from -2.0 to -0.5 for Gopinath et al. (2009a) model. For Bamgboye and Hansen (2008) model this value ranges from -0.9 to 0.4.

For IV, the procedure presented by EN 14214 provide results are in the range of the reference values with a deviation of the median value ranging from -0.7 to 0.3. For CFPP, similarly to what was observed for the Lapuerta et al. (2009) model for CN, also the model presented by Moser (2008a) provides results above the median of the reference values. The deviation of the median value of the results obtained with this model ranges from 0.1 to 1.3 standard deviations. For Ramos et al. (2009) model the deviation varies from -0.6 to 0.7 and for Park et al. (2008) from -0.8 to 0.6.

For OS, the deviation of the median value of the models presented by Gülşen et al. (2014) and Park et al. (2008) ranges from -0.9 to -0.1 and from -1.0 to 0.6, respectively. Although the values provided by the models are within the range of the reference values, OS can be difficult to predict using composition-based prediction models because it is significantly influenced by the conditions that biodiesel is exposed to during storage, transport and handling.

The selection of which models to use in the blending model was made based on the comparison of the range of values given by the prediction models results incorporating FA uncertainty with the range of references values. For CN, CFPP and OS, since more than one model was assessed, the one selected was that with results presenting lower deviation to the references values (median value) and a higher overlapping of the range of results given by the model and the reference values spread. For CN the model selected was the one presented by Bamgboye and Hansen (2008), for CFPP it was the one presented by Ramos et al. (2009) and for OS by Park et al. (2008).

2.3 CHANCE-CONSTRAINED OPTIMIZATION

Chance-constrained programming (CCP) is a technique used to tackle uncertainty in optimization models. It considers the system feasibility under uncertain environments focusing on the reliability of the system, which is expressed as a minimum requirement on the probability of satisfying constraints (Sahinidis 2004). This formulation allows the user to decide about the confidence level at which the constraint must be complied adding flexibility to the model reflecting the reality under consideration (Kampempe 2012). The method was firstly presented by Charnes & Cooper (1959) and several applications of this technique have been made to consider more explicitly the feedstock variation in blending model (Kumral 2003; Li et al. 2006; Gaustad et al. 2007; Rong et al. 2008; Sakallı et al. 2011; Gülşen et al. 2014).

The CCP formulation ensures that the constraint is realized with a minimum probability of $1 - \alpha$ having the form described by **equation 2.14**. a_i is the stochastic parameter, x_i the decision variable and b the constraint level:

$$P\left\{\sum_{i=1}^{N} a_i x_i \leq b\right\} \geq 1 - \alpha, \qquad x_i \geq 0 \text{ and } 0 < \alpha < 1 \qquad \text{Eq. 2.14}$$

If a_i is a normally distributed parameter, $a_i \sim N(\mu_i, \sigma_i^2)$ and all a_i are independent, the constraint is converted as follows:

$$P\left\{\frac{\sum_{i=1}^{N} a_i x_i - \sum_{i=1}^{N} \mu_i x_i}{\sqrt{\sum_{i=1}^{N} \sigma_i^2 x_i^2}} \leq \frac{b - \sum_{i=1}^{N} \mu_i x_i}{\sqrt{\sum_{i=1}^{N} \sigma_i^2 x_i^2}}\right\} \geq 1 - \alpha, \qquad \text{Eq. 2.15}$$

Where $\frac{\sum_{i=1}^{N} a_i x_i - \sum_{i=1}^{N} \mu_i x_i}{\sqrt{\sum_{i=1}^{N} \sigma_i^2 x_i^2}}$ represents a standard normal variate with a mean of zero and a variance of one. Then, the stochastic chance-constraint is transformed into the following inequality:

$$\varphi\left(\frac{b - \sum_{i=1}^{N} \mu_i x_i}{\sqrt{\sum_{i=1}^{N} \sigma_i^2 x_i^2}}\right) \geq \varphi\left(K_{1-\alpha}\right) \qquad \text{Eq. 2.16}$$

Where $K_{1-\alpha} = 1 - \alpha$ and $\varphi(\cdot)$ represents the standard normal cumulative distribution function (Sakallı et al. 2011). This yields the nonlinear deterministic constraint described by **equation 2.17**.

$$\sum_{i=1}^{N} \mu_i x_i + K_{1-\alpha} \sqrt{\sum_{i=1}^{N} \sigma_i^2 x_i^2} \leq b \qquad \text{Eq. 2.17}$$

Assuming Gaussian distributions for the stochastic parameter, $K_{1-\alpha}$ is the test coefficient usually denoted as z-value corresponding to the chosen confidence value level.

2.3.1 BIODIESEL BLENDING OPTIMIZATION MODEL

In the biodiesel blending model, the goal is to determine the optimal blend that minimizes production costs that are calculated according **equation 2.18** by multiplying the quantity of each feedstock used in the blend (QU_i) by its market price (P_i). The decision variables of the model are the proportion of each feedstock used in the blend. The model is subject to technical specification constraints that the final properties of the biodiesel blend shall conform to. These technical constraints are the prediction models selected in section 2.2.3 for the following biodiesel proprieties: density (Den), cetane number (CN), cold filter plugging point (CFPP), iodine value (IV) and oxidative stability (OS). In the deterministic version, these technical constraints are given by **equations 2.19 and 2.20**. To analyze the proportions of each feedstock in the blend, an additional constrained is added: the sum of the various oil feedstocks shall be equal to the demand (D) (**equation 2.24**). since the goal is to analyze the proportions of each feedstock in the blend, the demand (D) was set equal to 1 and considered no supply limitations. We implicitly considered that biodiesel production is fully consumed by the oil refinery industry and that the supply of feedstocks is unlimited. This model can be found in Caldeira et al. (2014). The mathematical formulation of the deterministic biodiesel blending problem is presented below and the nomenclature is described in **table 2.2**. The model was implemented in GAMS 24.4.2 (GAMS 2011) and the problems solved using the non-linear solver CONOPT (Arne 2014).

Table 2.2 Biodiesel blending optimization problem nomenclature

Indices and sets	$i \in I$	I = {soya, rapeseed, palm, WCO}, feedstock oils
	$j \in J$	J = {1, 2,..., 18}, Fatty Acids (FA) index
	$l \in L$	L = {DenLB, CN, OS}, set of properties with lower bound
	$m \in M$	M = {DenUB, IV, CFPP}, set of properties with upper bound
Parameters	P_i	Price of feedstock i
	D	Demand
	S_i	Supply of feedstock i
	$\overline{q_{i,j}}$	Average quantity (%) of FA-j in feedstock i
	$\sigma_{i,j}$	Standard deviation of the quantity (%) of FA-j in feedstock i
	$PropCoef_{l,j}$	Coefficient of FA-j in the prediction model for property l
	$PropCoef_{m,j}$	Coefficient of FA-j in the prediction model for property m
	$PropConst_l$	Constant in the prediction model for property l
	$PropConst_m$	Constant in the prediction model for property m
	$PropGT_l$	Threshold for property l
	$PropLT_m$	Threshold for property m
	β	Test coefficient for normal distribution, one tailed
Decision Variables	QU_i	Quantity of feedstock i to use in the blend

$$\text{Minimize:}\quad Z = \sum_{i \in I} P_i\, QU_i \qquad \text{Eq. 2.18}$$

Subject to:

$$\sum_{j \in J}\left(PropCoef_{l,j} \sum_{i \in I} QU_i\, \overline{q_{i,j}}\right) + PropConst_l \geq PropGT_l\,, \quad \forall_{l \in L} \qquad \text{Eq. 2.19}$$

$$\sum_{j \in J}\left(PropCoef_{m,j} \sum_{i \in I} QU_i\, \overline{q_{i,j}}\right) + PropConst_m \leq PropLT_m, \quad \forall_{m \in M} \qquad \text{Eq. 2.20}$$

$$\sum_{i \in I} QU_i = D \qquad \text{Eq. 2.21}$$

$$QU_i \geq 0 \quad \forall_{i \in I} \qquad \text{Eq. 2.22}$$

$$QU_i \leq S_i \quad \forall_{i \in I} \qquad \text{Eq. 2.23}$$

Using CCP formulation to address the compositional uncertainty associated with parameter $q_{i,j}$ (quantity of FA j in feedstock i), equations 2.19 and 2.20 are replaced by **equations 2.24 and 2.25**, respectively. β represents the risk tradeoff parameter that determines the maximum accepted non-compliance rate level chosen by the user. Assuming a normal distribution of the uncertain parameter ($q_{i,j}$), β is the normal distribution test coefficient (z-value), one-tailed.

$$\sum_{j\in J}\left(\text{PropCoef}_{l,j}\sum_{i\in I}\text{QU}_i\overline{q_{i,j}}\right)+\text{PropConst}_l-\beta\left(\sqrt{\sum_{j\in J}\text{Prop Coef}_{l,j}{}^2\sum_{i\in I}\text{QU}_i{}^2\,\sigma_{i,j}{}^2}\right) \geq \text{PropGT}_l \quad \forall_{l\in L} \tag{Eq. 2.24}$$

$$\sum_{j\in J}\left(\text{PropCoef}_{m,j}\sum_{i\in I}\text{QU}_i\,\overline{q_{i,j}}\right)+\text{PropConst}_m+\beta\left(\sqrt{\sum_{j\in J}\text{Prop Coef}_{m,j}{}^2\sum_{i\in I}\text{QU}_i{}^2\,\sigma_{i,j}{}^2}\right) \leq \text{PropLT}_m \quad \forall_{m\in M} \tag{Eq. 2.25}$$

The technical constraints target was stablished according to EN 14214. For CFPP, EN 14214 climate-dependent requirements options are given to allow for seasonal grades to be defined for each country. There are six CFPP grades for temperate climates and five different classes for arctic climates. Level B, with a maximum of 0ºC was selected for this work. All the parameters used in the model are presented in **Appendix VI**.

To assess the use of WCO in the blends, reference blends obtained having only virgin oils available in the model were established as a benchmark. The blends were evaluated in terms of cost and technical performance and cost. The latter was assessed through the blends error rate (ER). This parameter was calculated using Monte Carlo simulations. The Monte Carlo method statistically simulates random variables, in this case oil compositions, using pseudo-random numbers (Gaustad et al. 2007). We calculated the ER for each property and also a global ER that accounts for failure in all properties. The former was assessed calculating the WCO-blends cost reduction relatively to equivalent (same ER) blends composed only with virgin oils (VO-blend) according **equation 2.26**.

$$\text{WCO blend CR (\%)}=\frac{\text{VO blend cost} - \text{WCO blend cost}}{\text{VO blend cost}} * 100 \tag{Eq. 2.26}$$

Price information for palm, rapeseed and soya oils was taken from (IndexMundi 2014) and for WCO from a European broker (Grennea 2014). **Figure 2.7** depicts the monthly prices for the four feedstocks (palm, rapeseed, soya and WCO) from January 2011 to May 2014 that were used in this study.

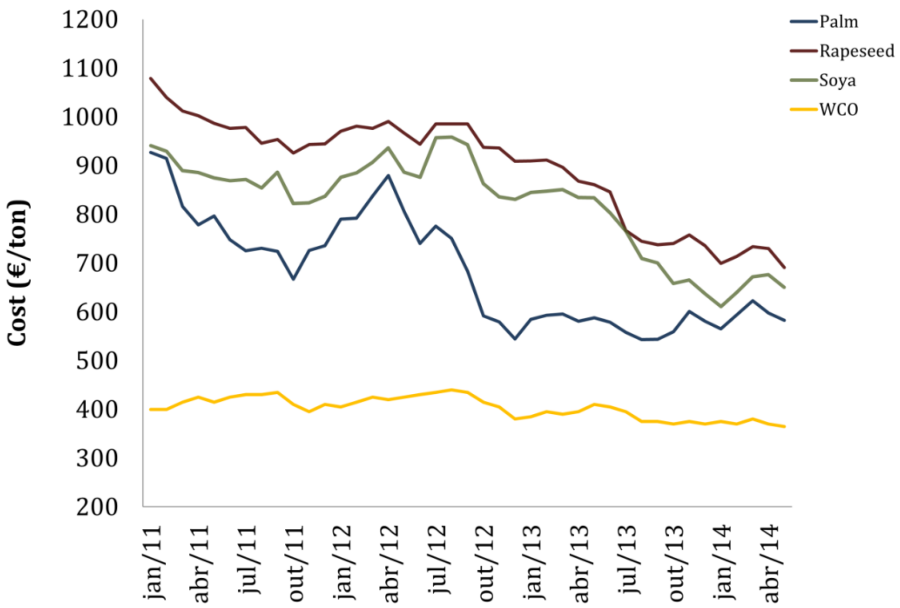

Figure 2.7 Monthly prices (€/ton) for palm, rapeseed, soya and WCO

The behavior of the model was first analyzed for a single period. For July 2013, the prices were 559 €, 767 €, 765 € and 400 € per ton of palm, rapeseed, soya and WCO, respectively. A reference blend (Blend A in **figure 2.8**) was obtained by setting the WCO availability in the model to zero and a confidence level set to 80%. This blend is composed of about 50% of palm and rapeseed and has a cost of 666 €/ton. The error rate (ER) for each property is shown in **figure 2.9**; blend A presents an error rate of about 1% for the property CFPP.

If one considers WCO as available feedstock in the model without considering the compositional uncertainty (β set to 0% confidence level), the optimal blend obtained (Blend B in **figure 2.8**) is mainly composed of WCO (about 65%) and a cost reduction of 23% relatively to Blend A is obtained. However, the blend behaves poorly in terms of technical performance. As shown in **figure 2.9**, this blend has about 20% probability of being out of specification for CN, about 6% for IV and OS, and about 50% for CFPP.

Increasing the confidence level to the value established for blend A (80%), the WCO share in the optimal blend reduces to about 40% (Blend C in **figure 2.8**); the increase in the confidence level reduces the quantity of secondary material. However, although it was obtained with the same confidence level as Blend A, Blend C has worst technical performance than blend A: 10% ER for CN, 4% for IV, 9% for OS and 4% for CFPP. To achieve the same technical behavior as virgin material blends, the confidence level has to be increased. The optimal blend obtained with a confidence level of 90% (Blend D in **figure 2.8**) has an ER similar to Blend A: 1% for CFPP. The quantity of WCO in the blend is about 20% and the blend cost is 654 €/ton representing a cost reduction of about 2% when compared to the reference blend.

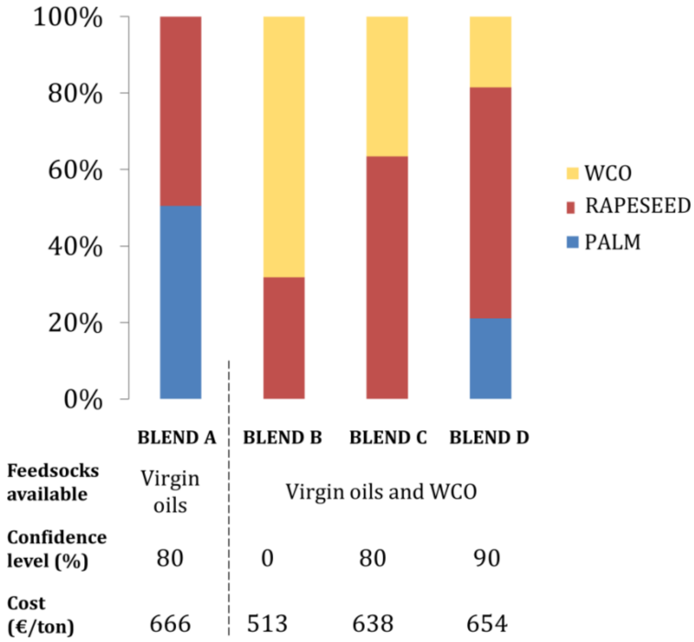

Figure 2.8 Blends composition and cost (€/ton) obtained with different feedstocks available and different confidence level

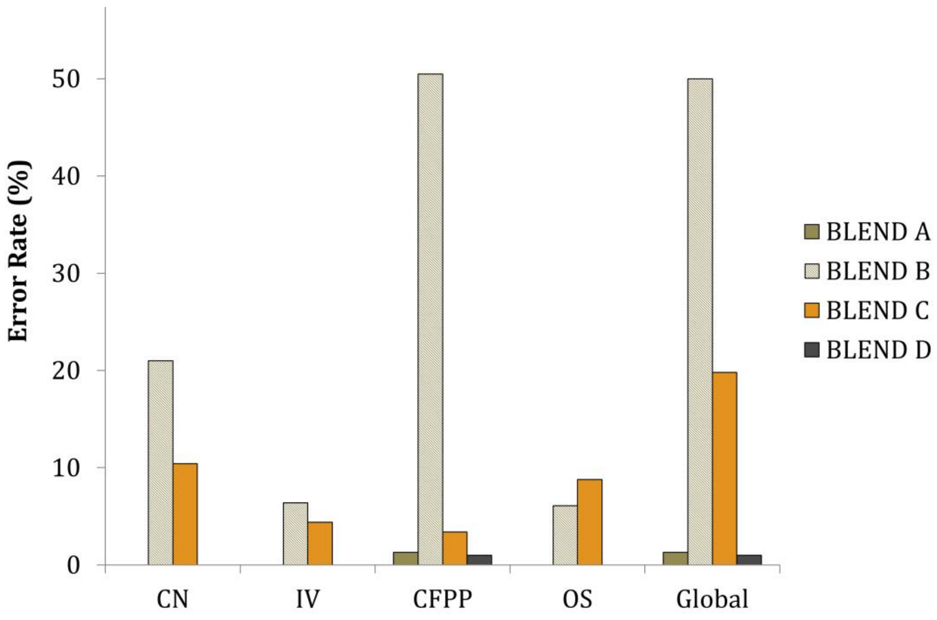

Figure 2.9 Error rate (%) of each blend for CN, IV, CFPP and OS

Depending on the confidence level, the quantity of WCO used in the blend is different; the increase in the confidence level reduces the quantity of secondary material and, consequently, the cost reduction obtained relatively to a blend composed only with virgin oils is lower. Another factor that influences the costs of the blends is the relation among the feedstock prices. To illustrate this, optimal blends were obtained for each month (from January 2011 to May 2014) and compared with optimal blends obtained without WCO available. To ensure the comparability of the blends in terms of technical performance, the confidence level was adjusted so that the ER of the blends with and without WCO is similar. If WCO is not available, the confidence level was set to 80% and, when WCO is available, set to 90%. Since the WCO present higher compositional uncertainty, the confidence level has to be increased in order to obtain the same technical performance as blends of virgin oils. **Figure 2.10** depicts the blends composition obtained when WCO is available (on the left side) and when it is not (right side). The dashed line is the ER of each of the blends. The solid line represented in the left graph is the cost reduction obtained relatively to the equivalent blend (obtained in the same month and with similar ER) with no WCO available.

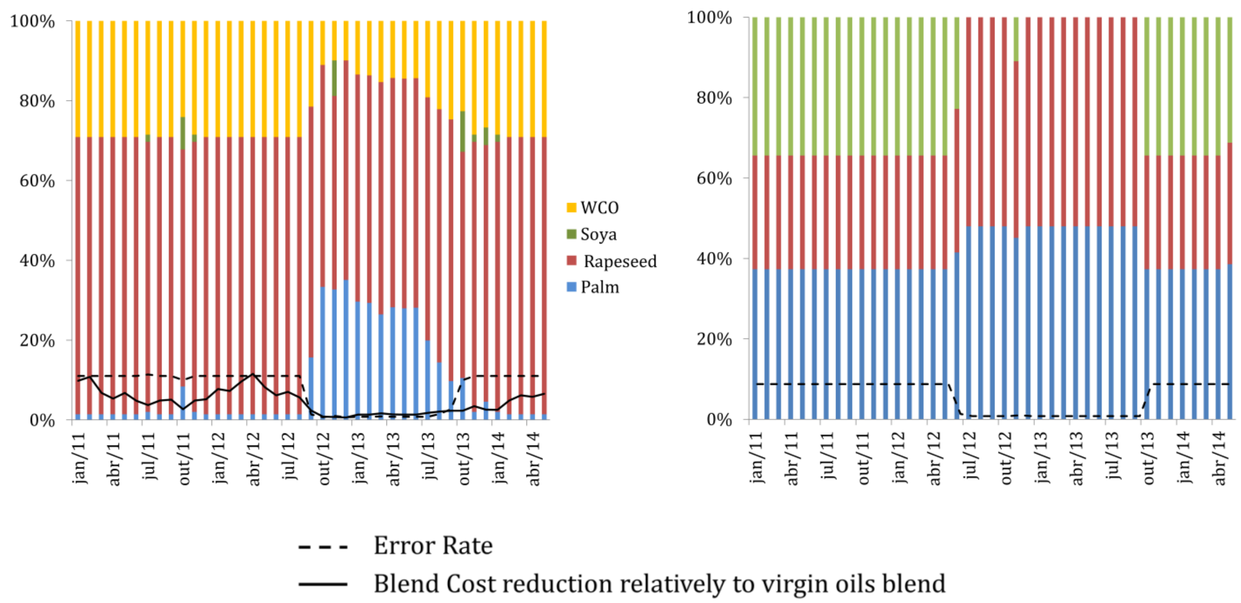

Figure 2.10 Blend composition for each month from January 2011 to May 2014 with WCO available (left-hand side) and without WCO available (right-hand side)

Using WCO in blends for biodiesel production allows a cost reduction relatively to blends without WCO that ranges from 1 to 10 %. This reduction is related to the WCO quantity in the blend and the relation among the feedstock prices. From January 11 to August 12, the virgin oils price is closer to each other relatively to the WCO price (**figure 2.7**) and in this period, the optimal blends are mainly composed of rapeseed and WCO. From September 12 to September 13, there is a reduction in the palm oil price relatively to soya and rapeseed oils price and the optimal blends of these months contain a higher quantity of palm and a lower quantity of WCO. Consequently, the cost reduction relatively to virgin oils blends in this period is lower. Then, from October 2013 to May 2014 the virgin oils prices are closer to each other again and the quantity of WCO in the blends increases and also, the cost reduction obtained.

2.3.2 SENSITIVITY ANALYSES ON THE DISTRIBUTION ASSUMPTION

The CCP formulation described previously is based on the assumption of a normal distribution of the uncertain parameter ($q_{i,j}$). However, this assumption may be questionable; the histograms of the compositional data and the results of the distribution fit test (performed using the statistic test goodness-of-fit Anderson-Darling, see section 2.2.2) presented in **Appendix IV** may raise doubts about the normality of the uncertain parameter. Nevertheless, the number of observations of the data collected is also a critical aspect that influences the results of the statistical analysis performed. Ideally, a data sample with a higher number of observations would be desirable. In any case, alternative CC formulations available in the literature that do not assume any type of distribution of the parameter were used to perform a sensitivity analysis.

2.3.2.1 Convex approximation

Nemirovski and Shapiro (2006) presented a formulation for CCP problems based on a convex approximation of the probabilistic constraints. This approximation is based on Bernstein inequality and it converts the probabilistic constraints to the convex deterministic ones making use of the theoretical bounds on the probability of violating the constraints. The authors extended the approach for the case of "ambiguous chance-constrained problems" where the uncertain parameters are not represented according to an existing probability distribution function. Using this approach, the equivalent deterministic constraints 2.19 and 2.20 can be expressed as **equation 2.27 and 2.28**, respectively. α_k^{max} and α_k^{min} control the confidence level for the Max. and Min. constraints and can be adjusted in order to obtain the required error rate. This formulation requires the knowledge of appropriate upper bound and lower bounds corresponding to the compositional specifications. In this work, the upper and lower bounds were set to be the upper (qup_{ij}) and the lower (qlw_{ij}) value found in the compositional data.

$$\sum_{j\in J}\left(PropCoef_{l,j}\sum_{i\in I}QU_i\,\overline{q_{i,j}}\right)+PropConst_l - \sqrt{2\log(1/\alpha_k^{min})}\left(\sqrt{\sum_{j\in J}PropCoef_{l,j}{}^2\sum_{i\in I}QU_i{}^2\left(\frac{qlw_{ij}-qup_{ij}}{2}\right)^2}\right) \geq PropGT_l, \qquad \forall_{l\in L} \qquad \text{Eq. 2.27}$$

$$\sum_{j \in J} \left(\mathrm{PropCoef}_{m,j} \sum_{i \in I} \mathrm{QU}_i \, \overline{q_{i,j}} \right) + \mathrm{PropConst}_m + \sqrt{2 \log(1/\alpha_k^{max})} \left(\sqrt{\sum_{j \in J} \mathrm{PropCoef}_{m,j}{}^2 \sum_{i \in I} \mathrm{QU}_i{}^2 \left(\frac{\mathrm{qlw}_{ij} - \mathrm{qup}_{ij}}{2} \right)^2} \right) \leq \mathrm{PropLT}_m , \quad \forall_{m \in M} \qquad \text{Eq. 2.28}$$

2.3.2.2 Linear approximation using fuzzy chance-constrained

Rong and Lahdelma (2008) suggested a CCP formulation where the uncertainty of the parameters is represented using fuzzy set theory and the constraints are based on a possibility measure. This approach represents the combination of adding safety margins and allowing some violations of the constraints. The conversion of the constraints with the fuzzy sets into their crisp equivalent is discussed by Liu and Iwamura (1998). Although the fuzzy constraints can be interpreted as soft constraints Prade and Dubois (1980), in this study the technique used by Rong and Lahdelma (2008) was applied. In their problem of scrap charge optimization in steel production, the ordinary fuzzy constraints are interpreted based on a likelihood measure using relaxed tolerance constraints. Tolerance constraints imply that the right hand side of the constraint is interpreted as a maximum tolerance for the left hand side. This approach extends significantly the feasible region and eliminates any conflict that may come from dropping or relaxing some of the constraints (Rong et al. 2008). In an application problem were constraints are addressing the compositional specification of the product, the crisp equivalent is expected to be less relaxed than the ones based on the concept of soft constraints (Rong et al. 2008).

Assuming parameter $q_{i,j}$ as a fuzzy number $\tilde{q}_{i,j}$, triangular fuzzy numbers was used to represent the statistical uncertainty as illustrated in **figure 2.11**. The representation for $\tilde{q}_{i,j}$ is the 3-tuple of parameters $\tilde{q}_{i,j} = (\mathrm{qlw}_{i,j}, \overline{q_{i,j}}, \mathrm{qup}_{i,j})$, where $\overline{q_{i,j}}$ is the mean and $\mathrm{qlw}_{i,j}$, and $\mathrm{qup}_{i,j}$ are the left and right spreads of the fuzzy number. Rong & Lahdelma (2008) used the shape for the probability density function of the parameter and fit it to the statistical data based on mean and standard deviation, assuming a normal distribution. The probability distribution was then transformed into a fuzzy set. In this work the left and right side spread of the fuzzy number are the minimum and maximum value in our data, respectively.

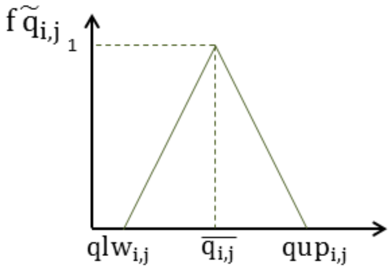

Figure 2.11. Representation of triangular fuzzy number and triangular possibilistic distribution

According to the implementation done by Rong & Lahdelma (2008), the crisp equivalent of the chance-constrained replaces the deterministic constraints 2.19 and 2.20 by **equations 2.29 and 2.30**, respectively. λ^{max} and λ^{min} control the confidence level for the maximum and minimum constraints and can be adjusted in order to obtain the required error rate.

$$\sum_{j\in J}\left(PropCoef_{l,j}\sum_{i\in I}QU_i\left(\overline{q_{i,j}}-\left(2\,\lambda^{min}-1\right)\left(\overline{q_{i,j}}-qlw_{i,j}\right)\right)\right)+PropConst_l \geq PropGT_l,\ \forall_{l\in L} \qquad \text{Eq. 2.29}$$

$$\sum_{j\in J}\left(PropCoef_{m,j}\sum_{i\in I}QU_i\left(\overline{q_{i,j}}+\left(2\,\lambda^{max}-1\right)\left(qup_{i,j}-\overline{q_{i,j}}\right)\right)\right)+PropConst_m \leq PropLT_m,\ \forall_{m\in M} \qquad \text{Eq. 2.30}$$

2.3.2.3 Hybrid approximation combining probabilistic and possibilistic chance-constrained programming

Sakallı & Baykoç (2013) suggested a hybrid technique, using probability and possibilistic distributions, applied to a scrap optimization problem in the brass casting process. The authors distinguish types of materials according to uncertainty associated with them, aleatory or epistemic, and use respectively, probabilistic and possibilistic distributions to model it. According to Sakallı & Baykoç (2013), when very few information is available about a parameter, a possibilistic approach should be followed. In their model, three types of materials with different uncertainty representation were considered: i) pure raw materials and some scrap of raw materials for which the composition is known and deterministic; ii) scrap products, for which the uncertainty of the composition is represented using probability distributions; and, iii) scrap raw materials which uncertainty is modelled using possibility distributions. In the biodiesel blending model, probabilistic distributions are used to represent the uncertainty associated with the virgin oils composition and possibilistic distributions to represent the WCO composition uncertainty.

As both types of possibilistic uncertainties are not equivalent, they cannot be added up and the transformation of one type of uncertainty in the other is necessary. However, this transformation presents some drawbacks independently of the direction taken. According to Sakallı & Baykoç (2013), "the probability/possibility transformation is a mapping from complete knowledge to incomplete knowledge. Therefore, it is unavoidable to lose knowledge during the transformation process. In contrast, possibility/probability transformation needs non-existent extra knowledge that transforms the incomplete information into complete information". To overcome this issue, Sakallı & Baykoç (2013) suggested a methodology that transforms each of the uncertainties into their deterministic counterparts avoiding to use probability/possibility or possibility/probability transformations. To each term is associated a confidence level: β, that represents the confidence level for the probabilistic term and γ, which represents the confidence level for the possibilistic term. Since a possibility measure is not likely to be as meaningful to the decision maker as a probability one, the authors developed a heuristic approach based on the consistency principle that computes a possibility level by using a probability measure. The heuristic approach consists in determining only a minimum probability level at the beginning of the solution process and then transforms it into a possibility degree according to $\gamma = 1 - \alpha$. γ will determine the γ-cut in the possibilistic distribution and determine the values of the parameter to use in the model. If for example, in the case of the biodiesel blending model, the decision maker wants to have $\alpha=0.75$ confidence level of compliance of the constraints, this will correspond to $\gamma=0.25$. Having a representation of the uncertain possibilistic parameter as a triangular distribution as presented in figure 2.11, the values of the possibilistic parameter that correspond to a possibilistic level of 0.25 are obtained performing a γ-cut in the distribution as exemplified in **figure 2.12**.

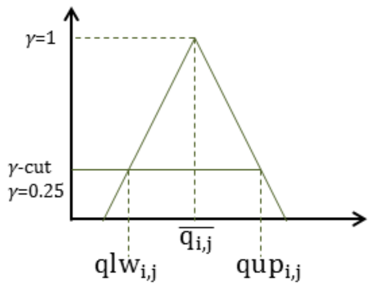

Figure 2.12 Representation of a γ-cut for γ=0.25 (75% confidence level, β=0.75)

According to this approach, the deterministic constraints 2.19 and 2.20 are replaced by **equations 2.31 and 2.32**, respectively.

$$\sum_{j\in J}\left(PropCoef_{l,j}\sum_{i\in I\setminus\{WCO\}} QU_i\,\overline{q_{i,j}}\right)+PropConst_l-\beta\left(\sqrt{\sum_{j\in J} PropCoef_{l,j}^{\,2}\sum_{i\in I\{WCO\}} QU_i^{\,2}\,\sigma_{i,j}^{\,2}}\right)$$
$$+\sum_{j\in J} PropCoef_{l,j}\,QU_{WCO}\,qlw_{WCO,j}\geq PropGT_l,\qquad \forall_{l\in L} \qquad \text{Eq. 2.31}$$

$$\sum_{j\in J}\left(PropCoef_{m,j}\sum_{i\in I\setminus\{WCO\}} QU_i\overline{q_{i,j}}\right)+PropConst_m+\beta\left(\sqrt{\sum_{j\in J} PropCoef_{m,j}^{\,2}\sum_{i\in I\setminus\{WCO\}} QU_i^{\,2}\,\sigma_{i,j}^{\,2}}\right)$$
$$+\sum_{j\in J} PropCoef_{m,j}\;QU_{WCO}\,qup_{WCO,j}\leq PropLT_m,\qquad \forall_{m\in M} \qquad \text{Eq. 2.32}$$

The different formulations were applied using the feedstock prices for July 2013 and the results are presented in **table 2.3**. The same reference blend (considering no WCO available, Blend A) is used as benchmark. The confidence level in each formulation was adjusted in order to obtain the same error rate.

Table 2.3 Optimal blends composition and cost obtained with different CCP formulations.

CCP formulation	**Blend**	**Blend Composition (%)**				**Cost**
		Palm	**Rapeseed**	**Soya**	**WCO**	**(€/ton)**
Normal	**A**	**50.5**	**49.5**	_	**n.a.**	666
Normal	D	21.1	60.4	_	18.5	654
Convex	E	13.1	67.1	_	19.8	667
Fuzzy	F	8.6	73.4	_	18.0	683
Hybrid	G	50.5	49.5	_	_	666

Comparing the results obtained with the different approaches (blends D to G) the normal provides the lowest cost blend. The optimal blend obtained with the convex approach (Blend E) has a higher WCO content but to comply with the technical constraints it needs to add more rapeseed that is more expensive, thus, the optimal blend cost is higher than the normal approach optimal solution. The optimal blend obtained using the fuzzy approach (Blend F) is the most expensive among all because it has a higher percentage of rapeseed. The hybrid approach provides the same optimal solution (Blend G) as the normal when WCO is not available (Blend A), meaning that considering the WCO a possibilistic parameter is too conservative and so, the use of this feedstock in the blend leads to problem unfeasibility. Based on these results, one can conclude that the use of the normal CCP formulation seems adequate to the biodiesel blending problem.

2.4 CONCLUDING REMARKS

A biodiesel blending model to optimize the blending of virgin oils and WCO addressing the oils compositional uncertainty (FA composition) using chance-constrained programing was developed and presented in this chapter. A review and assessment of biodiesel properties prediction models based on the FA composition was presented and selected models were integrated in the optimization model using CCP formulation. Results show that addressing the compositional uncertainty using the CCP formulation allows the use of feedstocks with high compositional uncertainty like WCO in biodiesel blends without compromising the biodiesel technical performance. Cost reduction is obtained for blends with WCO relatively to blends composed only of virgin oils. This cost reduction depends on the relation among the prices of the feedstocks. The use of low-cost feedstocks in a diversified portfolio of raw materials used in blending optimization models represents a cost reduction opportunity for the biodiesel producer without compromising the biodiesel quality.

3 BIODIESEL BLEND OPTIMIZATION ADDRESSING FEEDSTOCK PRICE UNCERTAINTY

The content of this chapter is presented in the following article:

Caldeira, C., Swei, O., Dias, L., Freire, F., Olivetti, E., Kirchain, R. **Planning strategies to manage production cost and cost variation of biodiesel production addressing operational and price uncertainty** (in final preparation)

3.1 INTRODUCTION

Biodiesel cost effectiveness is highly influenced by feedstock costs and feedstock price fluctuation. As outlined in Chapter 2, low cost waste-based feedstocks (such as WCO) can be used in biodiesel blends to reduce production costs without compromising biodiesel quality, as long as compositional uncertainty is managed. Additionally, blending WCO with conventional feedstocks may also be advantageous to manage biodiesel cost variation because this feedstock presents lower price volatility comparatively to conventional feedstocks. The complexity of the conventional oils market (because they are used in other food industries and their price is influenced by the crude oil price (Hasanov et al. 2016)) is the reason for the high volatility. The high uncertainty associated with feedstocks prices may compromise the biodiesel cost effectiveness, by threatening the long-term financial stability of producers. For this reason, robust production planning that accounts for feedstock price uncertainty is of utmost relevance for biodiesel producers.

This chapter presents an approach to address biodiesel feedstock price uncertainty. A stochastic dynamic programming model was developed to support production planning decisions to reduce cost and cost variation in biodiesel production. The model simultaneously addresses operational uncertainty (using the chance-constrained formulation described in chapter 2) and price uncertainty (using time series analysis to forecast feedstock price). Cost and cost variation performance metrics were used to investigate and interpret the behavior of the proposed approach.

3.2 ADDRESSING PRICE UNCERTAINTY USING TIME SERIES FORECAST MODELS

Several authors have addressed uncertainty in prices within an optimization framework. The most used approach to deal with price volatility is the two stage stochastic programming with recourse model. For example, Al-Othman et al. (2008) used two-stage stochastic linear program with fixed recourse to determine the optimum production plans for a petroleum supply chain that minimize the risks due to fluctuations in market conditions. Besides showing profitability levels comparable to those of the base case, the stochastic model provided information about the consequences of implementing the developed optimal production plan. Calfa & Grossmann (2015) proposed a multi-period two-stage stochastic programming model to explicitly account for uncertainty in spot market prices of raw materials and the predictability of demand response models (DRM) applied to a chemical production network. Lin & Wu (2014) formulated a two-stage stochastic programming model to determine product prices and design an integrated supply chain operations plan under demand uncertainty. Results showed that when there is an increase in the variance of the demand, the manufacturer should increase its inventory to prevent the potential loss of sales and will simultaneously raise product prices to obtain higher profit.

Other authors presented different approaches. Khor et al. (2008) applied Markowitz's Mean-Variance model to deal with price uncertainty, using a set of scenarios that best represents the trend of raw material prices and the sales values (based on available historical data), the model maximizes the expected profit while the magnitude of operational risk due to price volatility (measured by variance) is minimized. Chen et al (2015) used geometric Brownian motion (GMB) to model oil price behavior and built a multiperiod stochastic programming model to optimize refinery operation. Moradi & Eskandari (2014) addressed the uncertainty associated with electrical power price in energy management in microgrids using fuzzy set theory.

Another body of literature can be found that investigates price commodities fluctuation using time series analysis (TSA) in different case studies (Caporale et al. 2014; Apergis et al. 2016; Gil-Alana et al. 2016; Hasanov et al. 2016; Lee et al. 2016; Nicola et al. 2016). Within an optimization context, the model developed by Calfa and Grossmann (2015) accounts for uncertainty in spot market prices of raw materials where TSA was used to predict spot market prices scenarios. The objetive of the authors was to define optimal optimal procurement contract selection with selling price optimization under supply and demand uncertainty.

In this thesis, a stochastic dynamic model that addresses feedstocks price uncertainty using forecasted prices was developed. This model was built based on the model presented in chapter 2 but it was extended to accommodate a more realistic situation where the biodiesel producer has storage capacity. The model developed here determines the optimal planning that minimizes costs by identifying both 1) the quantities of each available feedstock to buy, store and use and 2) the specific combination of feedstocks to blend in a biodiesel production plant, in face of two types of uncertainty: (a) the feedstocks compositional uncertainty and (b) the feedstocks price uncertainty. The former type of uncertainty influences the constraints of the model and is addressed using chance-constrained programming. The later influences the coefficients of the objective function and is addressed by adding a term to the objective function that reflects the uncertainty of the forecasted future prices.

The model uses the feedstock prices forecast and information on current inventory to decide the quantities to blend, buy and store in each period (in our model one period represents one month).The decision in each period is made based on actual prices for that period and forecasted prices for the next 2 periods. For example, to decide what to buy (Quantity to buy - QB), store (Quantity to store - QS), and use (Quantity to use - QU), in period 1, the actual prices in 1 and forecasted prices for periods 2 and 3 are used. Then, to decide what to buy, store and use in period 2, the prices for period 2 are replaced by the actual prices and predicted prices for periods 3 and 4 are used. The optimization is repeated for W cycles (number of periods). The modelling approach is illustrated in **figure 3.1**.

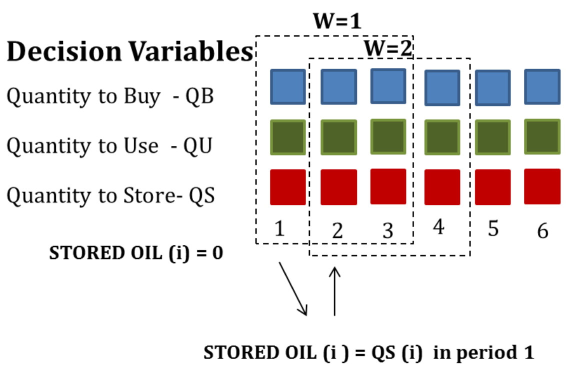

Figure 3.1 Schematic representation of the modelling approach

Feedstock prices are forecasted using the highly general Autoregressive Integrated Moving Average (ARIMA) framework. The ARIMA model is usually referred to as an ARIMA *(p,d,q)* since it is composed of p autoregressive terms, d non-seasonal differences (in order to transform a non-stationary stochastic process into a stationary one), and q lagged forecast errors in the prediction equation.

Prices for WCO were obtained from a European broker (Grennea 2014) and price information for palm, rapeseed and soya oils was taken from (IndexMundi 2014). The monthly prices for the four feedstocks (palm, rapeseed, soya and WCO) from January 2011 to May 2014 are depicted in **Figure 2.7** (chapter 2).

Some fundamental issues for time-series forecasting include (a) determining whether the dataset at hand is trend stationary (e.g., the statistical properties of a process once detrended are constant over time) or difference stationary and (b) incorporating the appropriate number of lags (Chatfield 2003). A typical approach to address the former is to use traditional unit-root tests, which evaluate the null hypothesis of a stochastic process having a unit-root and therefore being difference-stationary. The accuracy of these models, however, largely depends on having a significant sample size over a multi-decade period of time, both of which do not apply to this study. With that said, it is likely that sudden price shocks for this given system will have long-term effects on future prices, suggesting the presence of a unit-root and, therefore, that prices should be treated as difference stationary (e.g., d = 1) over time. Results from the Augmented Dickey Fuller (ADF) test, one typical unit-root test, further corroborated this assumption, though the robustness of these results is weak due to the sample size issues noted.

Three separate metrics were used to determine and appropriate lag order for the models. First, the overall fit of different lag orders was evaluated using two common goodness-of-fit metrics, the Bayesian Information Criterion (BIC) and the Akaike Information Criterion (AIC) (Liew 2004). Additionally, the partial autocorrelation function (PACF) of each dataset to confirm lag orders selected per the BIC and AIC was estimated. For each dataset, all three metrics suggested that only one lag order should be incorporated. Further inspection of the residuals suggested that the one lag model adequately removed serial correlation from the estimation, an initial concern given the possible presence of seasonality. The structural form of the model selected, ARIMA (1, 1, 0), for each dataset is described by **equation 3.1**:

$$P_{t+1} = (P_t - P_{t-1}) * \rho + P_t + C + \varepsilon \qquad \text{Eq. 3.1}$$

where, P_{t+1} is price the forecasted price, P_t and P_{t-1} are the prices in month t and t-1, ρ is the autoregressive parameter, C is a constant and ε is white noise that follows a normal distribution with mean 0 and standard deviation of σ.

The model adopted was validated using backcasting (McDowall 2004). In this technique, a known outcome is compared to the prediction, and the accuracy of the forecast is measured by the Mean Absolute Percent Error (MAPE) according to **equation 3.2** where *n* is the number of forecasts (Armstrong 2001).

$$\text{MAPE} = \frac{100\%}{n}\sum_{i=1}^{n}\left|\frac{\text{Actual} - \text{Predicted}}{\text{Actual}}\right| \qquad \text{Eq. 3.2}$$

Forecasts made from July 2013 to May 2014 were compared to the real prices and a MAPE ranging from 3.4 to 4.6% was obtained for the first month predicted and 4.6 to 6.1% for the second month predicted.

3.2.1 MODEL FORMULATION

The objective is to minimize the cost objective function Z (**equation 3.3**) that is composed by three terms: the first term is the cost of the feedstock, given by the quantity of each feedstock to buy ($QB_{i,p}$) multiplied by the feedstock price ($P_{i,p}$, actual price for p=1 and forecasted prices for p=2 and 3); the second term is the storage cost, given by the quantity stored ($QS_{i,p}$) multiplied by the storage cost (StCost); and the third term reflects the uncertainty associated with the price. Parameter α is the risk tradeoff parameter associated with price uncertainty. Specifically, α creates a penalty within the objective function for price risk (uncertainty); a higher α penalizes risk more. Theoretically, α can vary over the entire range of positive real numbers (0,∞) to generate a set of feasible decisions that have minimum cost for a given level of risk but in practice it was verified that after a certain value (α=10) no changes in the total cost and cost variation were observed.

The model is subject to demand and supply constraints (**equations 3.4 and 3.5**); since the goal is to analyze the proportions of each feedstock in the blend, the demand (D) was set equal to 1 and considered no supply limitations. The storage constraints are given by equations 3.6 to 3.9. A storage capacity of 20% of the production was considered. For each property (Den, CN, CFPP, IV and OS) the final blend must comply with the technical specifications (**equations 3.10 and 3.11**) as explained in chapter 2, section 2.3. The constraints confidence level was set to 95%. The mathematical formulation of the problem is presented below (nomenclature is described in **table 3.1**). The model was implemented in GAMS 24.4.2 (GAMS 2011) and the problems solved using the non-linear solver CONOPT (Arne 2014).

Table 3.1 Biodiesel blending optimization problem (considering feedstock price variation) nomenclature

Indices and sets	$i \in I$	I = {soya, rapeseed, palm, WCO}, feedstock oils
	$p \in P$	P = {1, 2, 3}, periods
	$j \in J$	J = {1, 2,..., 18}, Fatty Acids (FA) index
	$l \in L$	L = {DenLB, CN, OS}, set of properties with lower bound
	$m \in M$	M = {DenUB, IV, CFPP}, set of properties with upper bound
Parameters	$P_{i,p}$	Price of feedstock i in period p
	StCost	Storage cost
	$\sigma fc_{i,p}$	Standard deviation of the price of feedstock i in period p
	D	Demand
	$S_{i,p}$	Supply of feedstock i in period p
	$StCap_i$	Storage Capacity of feedstock i
	$\overline{q_{i,j}}$	Average quantity (%) of FA-j in feedstock i
	$\sigma_{i,j}$	Standard deviation of the quantity (%) of FA-j in feedstock i
	$PropCoef_{l,j}$	Coefficient of FA-j in the prediction model for property l
	$PropCoef_{m,j}$	Coefficient of FA-j in the prediction model for property m
	$PropConst_l$	Constant in the prediction model for property l
	$PropConst_m$	Constant in the prediction model for property m
	$PropGT_l$	Threshold for property l
	$PropLT_m$	Threshold for property m
	α	Risk tradeoff parameter
	β	Test coefficient for normal distribution, one tailed
Variables	$QB_{i,p}$	Quantity of feedstock i to buy in period p
	$QU_{i,p}$	Quantity of feedstock i to use in the blend in period p
	$QS_{i,p}$	Quantity of feedstock i to store in period p

Objective function

$$\text{Minimize:}\quad Z = \sum_{p\in P}\sum_{i\in I} P_{i,p}\, QB_{i,p} + \sum_{p\in P}\sum_{i\in I} StCost\, QS_{i,p} + \alpha \sqrt{\sum_{p\in P}\sum_{i\in I} \sigma\, fc_{i,p}^{\,2}\, QB_{i,p}^{\,2}} \qquad \text{Eq. 3.3}$$

Demand and Supply constraints

$$\sum_{i\in I} QU_{i,p} = D \quad \forall_{p\in P} \qquad \text{Eq. 3.4}$$

$$QB_{i,p} \le S_{i,p} \quad \forall_{p\in P}, \forall_{i\in I} \qquad \text{Eq. 3.5}$$

Storage constraints

$$QB_{i,1} = (QS_{i,1} - QS_{i,0}) + QU_{i,1} \quad \forall_{i\in I} \qquad \text{Eq. 3.6}$$

$$QB_{i,2} = (QS_{i,2} - QS_{i,1}) + QU_{i,2} \quad \forall_{i\in I} \qquad \text{Eq. 3.7}$$

$$QB_{i,3} = (QS_{i,3} - QS_{i,2}) + QU_{i,3} \quad \forall_{i\in I} \qquad \text{Eq. 3.8}$$

$$QS_{i,p} \le StCap_i \quad \forall_{p\in P}, \forall_{i\in I} \qquad \text{Eq. 3.9}$$

Technical Constraints

$$\sum_{j\in J}\left(PropCoef_{l,j}\sum_{i\in I} QU_{i,p}\overline{q_{i,j}}\right) + PropConst_l - \beta\sqrt{\sum_{j\in J} PropCoef_{l,j}^{\,2}\sum_{i\in I} QU_{i,p}^{\,2}\,\sigma_{i,j}^{2}} \ \ge PropGT_l \quad \forall_{p\in P}, \forall_{l\in L} \qquad \text{Eq. 3.10}$$

$$\sum_{j\in J}\left(PropCoef_{m,j}\sum_{i\in I} QU_{i,p}\overline{q_{i,j}}\right) + PropConst_m + \beta\sqrt{\sum_{j\in J} PropCoef_{m,j}^{\,2}\sum_{i\in I} QU_{i,p}^{\,2}\,\sigma_{i,j}^{2}} \ \le PropLT_m \quad \forall_{p\in P}, \forall_{m\in M} \qquad \text{Eq. 3.11}$$

$$QB_{i,p} \ge 0;\ QS_{i,p} \ge 0;\ QU_{i,p} \ge 0 \qquad \forall_{p\in P}, \forall_{i\in I} \qquad \text{Eq. 3.12}$$

3.2.2 Performance assessment

To investigate and interpret the behavior of the proposed approach to address feedstock price uncertainty, different variants of the model were defined: i) a no storage model (*No St*) obtained by setting the parameter StCap to zero where the producer can purchase all needed materials each period; ii) a storage model with no weight on the risk tradeoff parameter obtained setting the parameter α to zero (*St_α =0*); and, iii) a storage model with different weights for the risk tradeoff parameter setting the parameter α to 1, 3, 5 and 10 (*St_α=1*; *St_α=3*, *St_α=5* and *St_α=10*, respectively). These models assessed the influence of including storage capacity (comparing (i) and (ii)) and the influence of the weight given to the uncertainty term (comparing (ii) with (iii)).

Notably, the results obtained for the No storage model (*No St*) reflect a hypothetical situation where there is no uncertainty in the prices; the producers buy in each period knowing the exact feedstock price and the quantity necessary to use in that period. Although this situation does not reflect reality, it serves as a useful benchmark against which other model variants can be compared. This formulation also most closely resembles previous work that has examined the application of stochastic optimization to blending-related questions.

To test the robustness of the optimization results, we developed two sets of price series – uptrend and downtrend. Each set contains 40 price series each comprising four annual prices. To develop these sets, we first randomly generated 40 simulated historical price datasets for each commodity using the parameter estimates for the ARI (1, 1, 0) model from section 2.2. In other words, the parameter estimates for ρ and C for each ARI (1, 1, 0) model were preserved, but random price shocks were generated to allow the time-series to have behaved in a different stochastic manner over time. This collection of price series represents the downtrend set. Additionally, since all of the raw data from which the ARI(1,1,0) models were developed exhibited a downward stochastic trend over time (see Figure 2.7) we generated another 40 simulated historical price data series for each commodity, but now changing the sign of the drift term, C, such that it was positive. These price series are referred to as the uptrend set.

To analyze the cost performance of the models, average total cost of each model for the uptrend and downtrend sets and the relative difference (RD) of the total cost obtained by two different models were calculated. For example, the comparison between the results obtained for the storage model with no weight on the risk tradeoff parameter (St_α =0) relatively to the no storage (No St) model was calculated using **equation 3.13**.

$$\mathrm{RD}_{\mathrm{St}_{\alpha}=0\ \ \mathrm{No\ St}}\,(\%) = \frac{\text{Total cost}_{\mathrm{St}_{\alpha}=0} - \text{Total cost}_{\mathrm{No\ St}}}{\text{Total cost}_{\mathrm{No\ St}}} * 100 \qquad \text{Eq. 3.13}$$

The cost variation performance of the models was assessed through the Mean Absolute Deviation (MAD). This parameter was calculated as the average of the absolute differences obtained between period *p* and period *p-1* as given in **equation 3.14**.

$$\text{MAD} = \frac{1}{n}\sum_{i=1}^{n}|P_t - P_{t-1}| \qquad \text{Eq. 3.14}$$

3.3 Influence of the proposed approach on biodiesel cost and cost variation

The different models defined in section 3.2.2 were tested on each set of data (40 with a negative drift term and another 40 with a positive drift) and the average total cost was calculated. The results are presented in **figure 3.2**.

The results obtained with the different models present distinct profiles depending on the price trend. It is observed that when prices are generally increasing (uptrend – left-hand plot) average costs are lower when some amount of storage is available (St_α=0…St_α=10) compared to when no storage is available (No St). Furthermore, when more weight is given to price risk (increasing α) average inventory grows and average cost drops; in the uptrend, clever inventory purchases can lead to savings, avoiding a purchase later at higher cost.

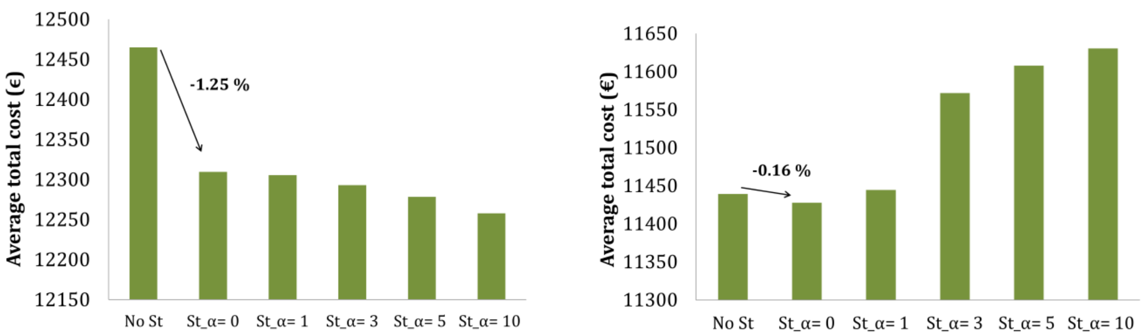

Figure 3.2 Total average cost obtained for the different models, for the uptrend (left-hand side) and downtrend (right-hand side) data sets. No St: No Storage; St_α: Storage available and risk tradeoff α=0, 1, 3, 5 and 10

Interestingly, in the downtrend case (right-hand plot) we also observe a small drop in average cost when comparing the model that has no storage capacity (*No*

St) to the model with storage capacity without considering the uncertainty (*St_α=0*). This savings declines as the alpha parameter rises. Increasing alpha places more emphasis on reducing cost risk. This, in turn, drives up average inventory. For the downtrend cases, purchases for inventory are on average more expensive than deferred purchases.

As noted, average cost reductions are observed when comparing the model that has no storage capacity (*No St*) to the model with storage capacity without considering the uncertainty (*St_α=0*) for both price trends: about 1.25% for the uptrend and 0.16 % for the downtrend. Despite the fact that these results were obtained for a storage cost of zero, the sensitivity analyses performed on the storage cost parameter considering it up to 3% of the feedstock portfolio price (15 €/ton), show the same type of behavior of the models. Nevertheless, the cost reductions obtained are lower: about 0.8% for the uptrend and about 0.07% for the downtrend.

To analyze the results in more detail (the results shown in **figure 3.2** are average results) the relative difference (RD) of the total cost obtained for each data set, by two different models, was calculated. Selected results are presented in **figure 3.3** for: Storage with α=0 relative to No storage (blue dots); Storage with α=5 relative to No storage (yellow dots); Storage with α=5 relative to Storage with α=0 (red dots); and, Storage with α=10 relative to Storage with α=0 (green dots). The cumulative distribution functions of the RD are presented in **figure 3.3**. The statistical significance of the relative differences was verified using a paired sample t-test (α=0.05).

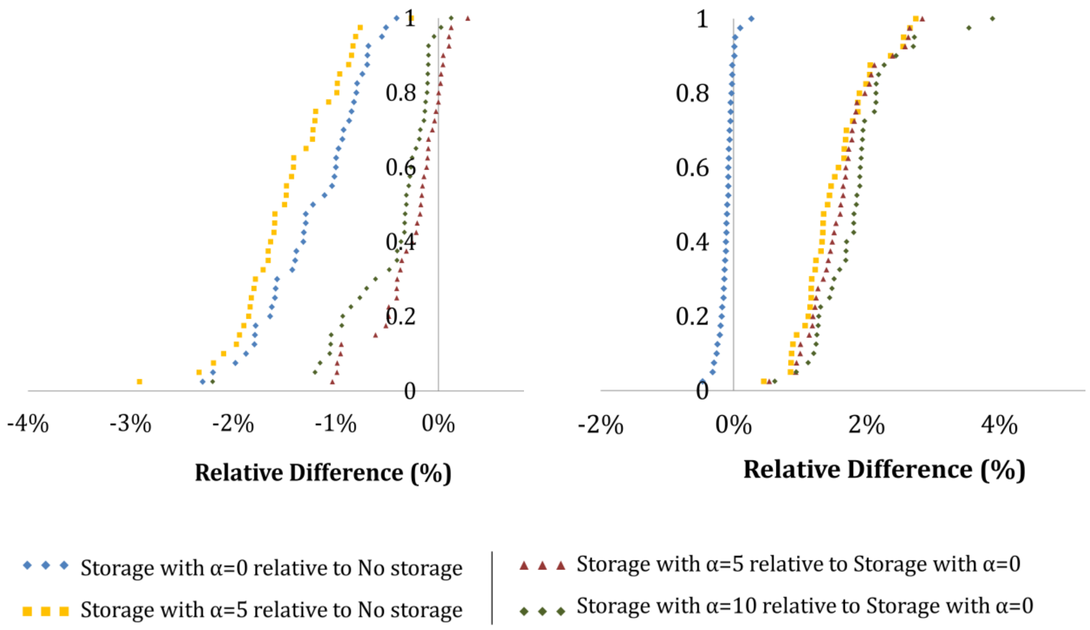

Figure 3.3 Cumulative Distribution Functions of the relative difference (RD) of the total cost obtained for each data set with uptrend (left-hand side) and with downtrend (right-hand side)

As shown in **figure 3.3**, for the uptrend (left-hand plot), in 100% of the cases storage capacity represents cost reduction and the reduction ranges from 0.5 to 2% (blue line); if uncertainty is considered (α=5) the probability of having cost reduction higher than 1% increases (yellow line). A cost reduction is also achieved for α=5 and or for α=10 (red and green curves) in the majority of cases when compared to the α=0 solutions. For the downtrend, in 95% of the cases, cost reduction is obtained if storage capacity exists (relatively no storage capacity, blue line) but there is an increase in the cost as we increase weight of the risk tradeoff parameter α. This is observed if we are comparing the results with a no-storage capacity model (yellow line) or with storage capacity and α=0 (red and green lines).

To assess the influence on the cost variation of the proposed approach, the Mean Absolute Deviation (MAD) between consecutive periods was calculated. **Figure 3.4** depicts the MAD distribution obtained for the different models.

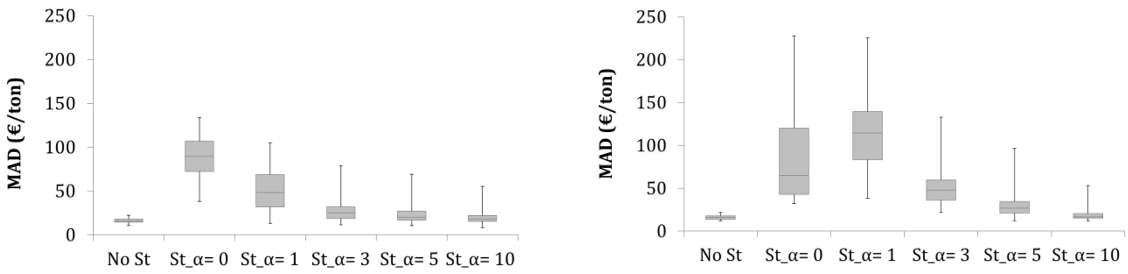

Figure 3.4 Box-and-Wiskers plots of the MAD between consecutive periods obtained for the different models for the uptrend (right-hand side) and downtrend (left-hand side). No St: No Storage; St_α: Storage available and risk tradeoff parameter α=0, 1, 3, 5 and 10

The results obtained for the No storage model (No St) reflect the situation where there is no uncertainty in the prices; the producers buy in each period knowing the exact feedstock price the quantity necessary to use in that period. Although this situation does not reflect the reality, it can be considered as an ideal situation towards which the model developed intends to approach. When storage capacity is added to the model (a more realistic situation) and if no weight is given to the risk tradeoff parameter (St_α=0) the cost variation results increase significantly for both trends. A reduction on the cost variation is observed with increasing weight given to the uncertainty term (increasing α) and for α=10, the cost variation is the closest one could obtain to the ideal situation of the No storage scenario. The results obtained for α higher than 10 show no reduction in the MAD average value or spread. The MAD average value and spread obtained for the models with storage available and risk tradeoff parameter α=0, 1 and 3 in the uptrend are lower than the values obtained in the downtrend.

Since the WCO price shows lower volatility than the conventional feedstocks, the influence on the cost variation of using WCO in the blends was analyzed. The MAD for the different models and data sets setting the WCO quantity in the blends to zero was calculated. The median value obtained for the MAD is about 1% higher for St_α=1, 4% for St_α=3, 26% for St_α=5 and 50% for St_α=10 in the uptrend and 1% higher for St_α=1, 5% for St_α=3, 33% for St_α=5 and 57% for St_α=10 in the downtrend.

3.4 CONCLUDING REMARKS

In this chapter, a cost optimization model was developed to support production planning decisions to reduce cost and cost variation in biodiesel production. The model simultaneously addresses operational (using the chance-constrained (CCP) formulation) and feedstock price uncertainty (using time series analysis (TSA) to forecast the feedstock price). Cost and cost variation performance metrics were used to investigate and interpret the behavior of the proposed approach. The model proved to be useful in determining optimum planning for feedstocks acquisition, blending and storage that minimize the risks associated with feedstock price fluctuations. If feedstock prices present an uptrend behavior, the suggested optimization approach also allows the biodiesel producer to obtain a cost reduction. Moreover, the use of WCO in blends showed to be advantageous to reduce biodiesel cost variation.

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4 ENVIRONMENTAL LIFE-CYCLE ASSESSMENT OF OILS USED IN BIODIESEL PRODUCTION

The content of this chapter is presented in the following articles:

Caldeira, C., Queirós, J., Freire, F. (2015) **Biodiesel from Waste Cooking Oils in Portugal: alternative collection systems**. Waste and Biomass Valorization, vol. 6 (5), pp. 771-779

Caldeira, C., Queirós, J., Noshadravan A., Freire, F. (2016) **Biodiesel from Waste Cooking Oils: Life-Cycle Assessment incorporating uncertainty**. Resources, Conservation and Recycling, vol. 112, pp. 83-92

Caldeira, C., Quinteiro, P., Castanheira, E., Boulay, AM., Dias, A.C., Arroja, L., Freire, F. **Water footprint profile of crop-based oils and waste cooking oil** (submitted)

4.1 INTRODUCTION

The focus of research and policies on environmental impacts of biodiesel has been on the reduction of GHG emissions (e.g. Camobreco et al. 2000; Bozbas 2008; Fargione et al. 2008; Atabani et al. 2012) but other impacts, particularly related to freshwater use, need to be considered. Freshwater is related to fresh surface and groundwater; i.e. the freshwater in lakes, rivers and aquifers. In the particular case of agricultural production, it refers to irrigation freshwater (Pfister et al. 2009). As the majority of biodiesel is produced from crop-based vegetable oils feedstocks (Eisentraut 2010; OECD-FAO 2013; Issariyakul and Dalai 2014) that can require large quantities of freshwater depending on the location where the crops are cultivated (Pfister and Bayer 2014), if those areas present high water scarcity, the freshwater consumption impacts can be significant. Additionally, freshwater quality can be worsened due to the use of fertilizers and pesticides in the crops cultivation (Emmenegger et al. 2011).

In this chapter, a life-cycle environmental assessment of palm, soya, rapeseed and waste cooking oils is presented. A freshwater footprint profile, including water scarcity footprint and freshwater degradation impacts, was calculated together with GHG emissions. A comparison of two water scarcity footprint methods, the water stress index (WSI) (Pfister et al. 2009; Ridoutt and Pfister 2013) and the available water remaining (AWARE) (Boulay et al. 2016; WULCA 2015) was performed. As the AWARE method is new and learnings are still expected from this initial phase of application, we performed a sensitivity analysis on the AWARE characterization factors (CFs) based on different modelling choices. Freshwater degradation was assessed for freshwater and marine eutrophication using the ReCiPe, aquatic acidification using the IMPACT, and, human toxicity and freshwater ecotoxicity using the USETox model.

4.2 IMPACT ASSESSMENT: WATER FOOTPRINT PROFILE AND CLIMATE CHANGE

In the past years, WF based on LCA methodology has progressed rapidly, and several models for addressing freshwater impacts have been developed. An extensive and comprehensive review of existing models can be found in Kounina et al. (2013) and Boulay et al. (2014). Studies have been carried out on water scarcity at midpoint level (e.g. Milà i Canals et al. 2009; Pfister et al. 2009; Ridoutt et al. 2010; Boulay et al. 2011; Núñez et al. 2012; Quinteiro et al. 2014; Quinteiro et al. 2015; Boulay et al. 2016) freshwater stress at endpoint level (e.g. Pfister et al. 2009; Hanafiah et al. 2011; Van Zelm et al. 2011; Verones et al. 2013; Tendall et al. 2014) and on freshwater degradation related to the discharge of eutrophying, acidifying and ecotoxic compounds into freshwater systems (e.g. (Knuuttila 2004; Struijs et al. 2011; Helmes et al. 2012; Azevedo et al. 2013; Goedkoop et al. 2013)

The need to ensure consistency in addressing freshwater use impacts led to the formation in 2007 of the Water Use in LCA (WULCA) working group. The group was formed under the auspices of the Life-cycle Initiative of the United Nations Environment Programme (UNEP)/Society of Environmental Toxicology and Chemistry (SETAC) (WULCA 2014) and is focused on assessment of use and depletion of water resources within LCA framework. In 2014, the international standard ISO 14046 (ISO 2014) was published providing guidelines on how to perform an assessment of freshwater related environmental impacts. According to ISO 14046 (ISO 2014), the water footprint profile should consider a range of potential environmental impacts associated with water, encompassing the consumption of freshwater (water scarcity assessment) and impact categories related to water pollution.

Regarding the water scarcity assessment, in the last years, the development of LCA-oriented impact assessment methods for addressing the potential environmental impacts related to the freshwater consumption has been significant and different methods are available. Kounina et al. (2013) and Boulay et al. (2014) contributed to understanding the different scopes, strengths and weaknesses of the existing scarcity LCA-oriented impact assessment methods, showing that at the midpoint level, most of the freshwater scarcity methods use different hydrological data sources and a scarcity model algorithm, mainly developing the characterization factors (CFs) based on a withdrawal-to-availability (WTA) ratio.

In this thesis, two LCA-oriented impact assessment methods were compared: the WSI method (Pfister et al. 2009; Ridoutt and Pfister 2013) and the AWARE method (Boulay et al. 2016) In the former, midpoint CFs are water stress indexes (WSIs) estimated at country level and in the later, the CFs are based on the demand-to-availability ratio (DTA) at the country level. The WSIs represent the portion of the freshwater consumption that deprives other users of freshwater. The AWARE method builds on the assumption that the potential to deprive another user of water (resulting from the multiplication of the inventory with the CF) is directly proportional to the amount of freshwater consumed (inventory) and inversely proportional to the available water remaining per unit of surface and time in a region (watershed). The AWARE CFs represent the relative available water remaining per area in a watershed, after the demand of humans and aquatic ecosystems has been met, answering, therefore, to the following question: "what is the potential to deprive another freshwater user (human or ecosystem) by consuming freshwater in this region?" (Boulay et al. 2016).

The WSIs range from 0.01 to 1.00 following a logistic function and it is a modified WTA ratio that accounts monthly and annual variability in precipitation influence. It can be interpreted as the water deprivation proportion caused by freshwater consumption, that is, how much of the freshwater consumed is considered to be taken away from downstream users (Pfister and Bayer 2014). The AWARE CF ranges from 0.1 and 100 and are based on the inverse of the difference between freshwater availability and demand, in which demand is related to the human freshwater consumption and environmental water requirements (EWR). The value is normalized using the world average, hence it represents whether a region has more or less remaining water in comparison to the world average.

The WSIs do not explicitly account for groundwater stocks and surface infrastructures within the sub-watershed, while the AWARE indicators take into account surface infrastructures such as dams.

Because of the difference in the structure of the CFs for both methods, the scale and the interpretation are different and WF results are in different units (cubic meter equivalent referring to different equivalencies). To allow an adequate comparison between the water scarcity footprint results of the vegetable oils under analysis, the WSIs from the Pfister et al. (2009) are normalized by the world average global average consumption weighted value (0.602) derived by Ridoutt and Pfister (2013). This value is compatible with the WSIs calculated by Pfister et al. (2009). Therefore, the normalized water scarcity footprint results from both impact assessment methods correspond to equivalent units of "world-m^3 equivalent" for both applied methods, even though the interpretation remains different.

As the AWARE method is new and learnings are still expected from this initial phase of application, a sensitivity analysis on the AWARE CFs based on different modelling choices was performed. Three sets of CF (WULCA 2015) obtained according to different assumptions were tested: i) AWARE100 EWR 50% (that was defined to test the sensitivity of the results to the choice of EWR), was defined following the EWR method author's recommendation of applying an upper value of EWR by taking 150 % of the value provided by the original method (VMF); ii) AWARE10; and, iii) AWARE1000, that have a max cut-off of 10 and 1000, respectively, instead of 100. A cut-off limits the span of the indicator to a maximal range (the minimum cut off is set to 0.1) that sets the difference between the lowest and the highest value, eliminating the tailing values where the meaning of the indicator would be lost (Boulay et al. 2016). **Table 4.1** presents the different CFs used.

Table 4.1 Characterization factors used in the sensitivity analysis of AWARE method for agricultural (Agri.) and non-agricultural (Non-Agri.) uses

	AWARE100		AWARE100 ERW 50 %		AWARE10		AWARE1000	
	Agri.	Non- Agri.	Agri.	Non-Agri.	Agri.	Non-Agri.	Agri.	Non-Agri.
Colombia	0.56	0.77	0.56	0.79	0.54	0.49	0.59	1.15
Malaysia	2.23	0.58	4.76	0.62	1.33	0.55	2.20	0.58
Argentina	54.38	6.81	60.88	7.61	7.29	2.42	334.77	31.19
Brazil	2.42	1.86	9.75	4.57	2.04	1.60	2.54	2.07
US	36.52	9.51	42.72	10.65	5.70	2.31	316.11	66.63
Germany	1.63	1.24	1.73	1.16	1.61	1.11	1.61	1.25
France	8.29	2.31	34.10	5.88	4.44	1.69	32.92	6.98
Spain	77.51	30.93	89.15	37.88	9.41	5.14	711.71	263.44
Canada	9.65	2.62	9.80	4.21	5.12	2.02	22.01	3.57
Portugal	51.03	15.33	75.97	23.33	8.66	3.85	389.39	101.70
ROW	45.88	22.19	58.18	31.89	6.43	6.27	361.22	299.92

ROW: Rest of the world
ERW: Environmental water requirements

Regarding the midpoint impacts from water pollution, and in agreement with the approach followed by Boulay et al. (2015), impact categories from different LC impact assessment methods were chosen to assess the potential environmental impacts due to pollutant substances released into water. Following Boulay et al. (2015), freshwater and marine eutrophication were addressed using the ReCiPe model (Goedkoop et al. 2009), aquatic acidification using the Impact 2002+ model (Jolliet et al. 2003), and human toxicity (cancer and non-cancer) and ecotoxicity were addressed using the Usetox model (Rosenbaum et al. 2008). GHG emissions were also assessed using the ReCiPe model (Goedkoop et al. 2009).

4.3 LIFE-CYCLE MODEL AND INVENTORY

A life-cycle (LC) model was implemented to assess the WF profile (freshwater consumption and water degradation impacts) of different vegetable oils used for biodiesel production: virgin oil (palm, soya and rapeseed) and WCO. The functional unit is defined as one kilogram of vegetable oil. It is assumed that after the refining step, the virgin oils and the WCO have the required characteristics for the transesterification reaction (biodiesel production). Technically, the production of biodiesel from WCO is similar to conventional transesterification processes of the virgin oils (Knothe et al. 1997). The variation on the energy content (low heating value) of biodiesel produced from palm, soya, rapeseed and WCO is below 1% (Hoekman et al. 2012).

The system boundary is schematically presented in **figure 4.1**. The virgin oils systems (palm, soya and rapeseed) include cultivation, oil extraction, feedstocks transportation and oil refining. Different cultivation locations for the feedstocks were considered: Colombia (CO) and Malaysia (MY) for palm fruit; Argentina (AR), Brazil (BR) and United States (US) for soybean; and, Germany (DE), France (FR), Spain (ES), Canada (CA) and US for rapeseed. However, it should be noted that the results cannot be extrapolated to the country level since the data regarding crop cultivation is, in some cases, not representative of the country. The palm oil was extracted near the cultivation site while soya and rapeseed oils were extracted in Portugal (PT). The refining of all virgin oils is performed in Portugal. The transportation of palm oil, soybean and rapeseed to Portugal was considered within the system boundaries. For the WCO, the stages are the WCO collection and refining in Portugal. The system reflects the reality of biodiesel production in Portugal. A short description of each stage considered is presented in the following sections.

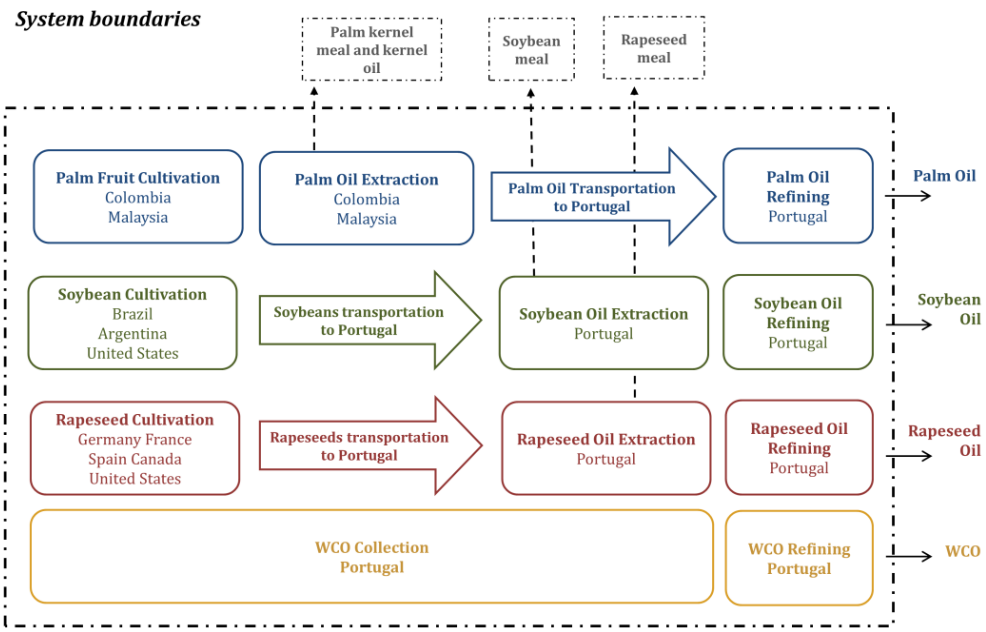

Figure 4.1 System boundaries of the vegetable oils for biodiesel production

The background system includes production of fuels, electricity, chemicals and other ancillary materials, i.e. all other processes which interact directly with the foreground system, usually by supplying material or energy to the foreground or receiving material or energy from it. Data on freshwater for the background were obtained from the Ecoinvent 3.1 database. The infrastructures and the materials and chemicals transportation were not considered in this study. The inputs for each one of the systems including fertilizers, fuels, ancillary materials and transportation are presented in **Appendix VII**.

The freshwater balance was calculated for each process. The difference between the water inputs and water outputs is calculated as the freshwater consumption (Pfister et al. 2015). The green water - rainfall water on land that does not run off or recharge the groundwater but is stored in the soil or temporarily stays on the top of the soil or vegetation (Hoekstra et al. 2011) - was not considered in the scope of this study as data for assessing the potential impacts of palm fruit, soybeans and rapeseed production resulting from changes in green water flows due to land use changes were not available. The inventory results of freshwater consumption (m^3 per kg of palm oil, soybean oil, and rapeseed oil) for each one of the production systems included in the system boundaries are presented in **table 4.2**.

Table 4.2 Inventory results of consumptive freshwater for the cultivation (expressed in m³ per kg of palm fruit, soybeans and rapeseeds); transportation, extraction and refining (expressed in m³ per kg of palm oil, soybean oil, rapeseed oil and WCO)

Feedstock	Cultivation			Transport /collection	Extraction			Refining		
	Location	Foreground	Background		Location	Foreground	Background	Location	Foreground	Background
Palm	Colombia	0	0.00070	0.0010	Colombia	0.0055	0.00090	Portugal	0.075	0.00057
	Malaysia	0.0064	0.00063	0.0013	Malaysia	0.0034	0.00025			
Soya	Argentina	0.17	0.0023	0.0031	Portugal	0.00070	0.00076	Portugal	0.075	0.00057
	Brazil	0.14	0.0027	0.0078						
	US	0.0076	0.0013	0.0048						
Rapeseed	Germany	0.086	0.0060	0.0040	Portugal	0.000020	0.00042	Portugal	0.075	0.00057
	France	0.21	0.0060	0.0023						
	Spain	1.11	0.0077	0.0017						
	Canada	0.013	0.010	0.0048						
	US	0.060	0.014	0.0021						
WCO	Portugal	n.ap.		0.0014		n.ap.		Portugal	0.000035*	0.00053*
									n.ap.	0.000015**

n.ap. – not applicable
*data for refining of high quality WCO
**data for refining of low quality WCO

4.3.1.1 Cultivation

The data (freshwater consumption and emissions) for palm fruit cultivation in Colombia were adapted from Castanheira et al. (2014). These authors presented a detailed LC inventory for a specific plantation equipped with its own mill, in the Orinoquía Region. Although the authors assessed five fertilization schemes we selected the one using urea for this study. According to Castanheira and Freire (2016a) urea is among the preferred nitrogen sources and the main N-fertilizers used in Colombia. The data (consumption and degradation) for palm fruit cultivation in Malaysia was adapted from the Ecoinvent 3.1 database (Jungbluth et al. 2007).

The irrigation water data for each of the spatially explicit feed of soya and rapeseed was obtained from Pfister and Bayer (2014). The freshwater degradation data for the soya and Rapeseed feedstocks were collected from different sources: for soybean cultivation in Argentina were obtained from Castanheira and Freire (2013) (considering the reduced tillage cultivation system); for soybeans cultivation in Brazil, data were collected from Castanheira et al. (2015) (although the authors assessed the cultivation of soybean in four Brazilian states, this study considers the inventory for the cultivation in Mato Grosso because it is the state with the highest production share); for cultivation of soybeans in the US data were taken from the Ecoinvent 3.1 database (Jungbluth et al. 2007); for Rapeseed cultivation in Spain, Germany, France, Canada data were retrieved from Malça et al. (2014); and, for Rapeseed cultivation in the US data was obtained from the Ecoinvent 3.1 database.

Land Use Change (LUC)

GHG emissions due to direct LUC were considered in this study. For each of the feedstock and cultivation location two scenarios, a pessimistic and an optimistic, were considered. The carbon stock changes were calculated based on the difference between the carbon stock associated with reference (previous) and actual land use. Data was obtained from different studies available in the literature. The reference and actual land use of the pessimistic and optimistic scenarios considered as well as the respective GHG emissions for the different feedstocks and locations are presented in **table 4.3**. A short description of the selected scenarios follows.

For palm cultivation in Colombia, the reference land use for the pessimistic scenario was forest and for the optimistic scenario, shrubland. According to Castanheira et al., (2014) the palm fruit cultivation area in Colombia expanded by 84% from 1990 to 2010, mainly from shrubland (51%) and savanna (42%). A small share of arable land (7%) and forest (less than 1%) was used for palm cultivation. The authors analyzed 13 LUC scenarios having values ranging from -3.4 to 4.3 g CO_2 eq kg^{-1} oil palm oil. Although forest has low use for palm cultivation (only 1%) this scenario was considered as it was the scenario with higher emissions value. Hassan et al., (2011) modelled five different types of land use: peat forest, primary forest, secondary forest, grassland and degraded land based on the current land use by Malaysian oil-palm plantation. The authors obtained values ranging from -1.19 to 11.2 g CO_2 eq kg^{-1} oil. The secondary forest and the grassland were the pessimistic and optimist scenarios selected for this work.

Castanheira and Freire (2013) considered alternative previous land uses for the cultivation of soya in Argentina and in Brazil: tropical forest land, forest plantations, perennial crop plantations, savannah and grasslands. The values obtained for soybean cultivation in Argentina range from -0.17 to 6.79 g CO_2 eq kg^{-1} oil while for Brazil from 0 to 26.26 kg CO_2 eq kg^{-1} oil. The reference land use scenarios selected for Argentina were the perennial crop and grassland severely degraded and for soybean in Brazil the savanna with improved management and grassland severely degraded for the pessimistic and optimistic scenarios, respectively.

For Rapeseed in Spain, Germany, France and Canada, grassland severely degraded and grassland improved were the selected reference land use for the optimistic and pessimistic scenarios, respectively (Castanheira and Freire 2016b). The reference land use for the optimistic scenario for soybean and rapeseed cultivated in the US was arable land and the pessimistic scenario value was obtained from an IPCC report (Edenhofer et al. 2012) but no detailed information about the reference land was available.

Table 4.3 Reference land use and GHG emissions of the optimistic and pessimistic scenario defined to address LUC

Feedstock_Location	Data source	Optimistic Scenario		Pessimistic Scenario	
		Ref Land Use	**LUC min ($g\ CO_2\ eq\ kg^{-1}$ oil)**	**Ref Land Use**	**LUC max ($g\ CO_2\ eq\ kg^{-1}$ oil)**
Palm_CO	Castanheira et al., (2014)	Shrubland	-0.11	Forest	3.75
Palm_MY	Hassan et al., (2011)	Grassland	1.50	Secondary forest	4.52
Soya_AR	(Castanheira and Freire, 2013)	Grassland severely degraded	-0.17	Perennial crop	6.79
Soya_BR	(Castanheira and Freire, 2013)	Grassland severely degraded	0.48	Savanna improved management	10.98
Soya_US	Ecoinvent	Arable land	0	Not specified (Edenhofer et al. 2012)	2.17
Rapeseed_DE	(Castanheira and Freire, 2016)	Grassland, Severely degraded	0.13	Grassland, Improved	2.95
Rapeseed_FR			0.15		2.87
Rapeseed_SP			-0.10		1.57
Rapeseed_CN			0.14		4.59
Rapeseed_US	Ecoinvent	Arable Land	0	Not specified (Edenhofer et al. 2012)	1.51

4.3.1.2 Extraction and transportation

Palm oil is extracted in the cultivation location. The palm fruits harvested are transferred to the mill located close to the cultivation site to be sterilized, stripped, digested into a homogeneous oily mash and pressed to extract most of the crude palm oil. In addition, there are other outputs of the extraction system, such as kernels, fibers, shells, empty fruit bunches and palm oil mill effluent. Kernels are cracked and milled to produce palm kernel oil and palm kernel meal. These latter are the co-products of the extraction system. Fibers and shells are used as a fuel in the boiler of the cogeneration plant to produce both electricity and steam. The empty fruit bunches and the treated palm oil mill effluent are used as a fertiliser in the palm fruit cultivation. Freshwater consumption and degradation data for the palm oil extraction in Colombia and Malaysia was obtained from Castanheira et al. (2014) and Jungbluth et al. (2007), respectively.

The soybean and rapeseed oils are extracted in Portugal. Due to the lack of complete primary data for the extraction stage, the foreground freshwater consumption of soybean and rapeseed oil extraction was obtained from the Ecoinvent 3.1 database. The soybeans are dehulled, cracked, heated, rolled into flakes and solvent-extracted with hexane. Soybean meal is obtained as co-product. Freshwater emissions for soybean extraction was obtained from Castanheira et al. (2015). The rapeseeds are grinded and cooked to facilitate the oil extraction process. After that, the seeds are pressed mechanically to extract the oil. During this process a rapeseed meal is also produced. Since this cake has high oil content, a chemical extraction step using hexane is performed to extract the remaining oil. The rapeseed meal is obtained as a co-product of this process. Freshwater emissions for extraction of rapeseed oil were obtained from (Castanheira and Freire 2016b).

The distances travelled and the type of transportation used to transport the palm oil, soybean and rapeseeds from the cultivation sites to the biodiesel plant in Portugal are presented in **Appendix VII**.

4.3.1.3 WCO collection

The inventory data for WCO collection were obtained from (Caldeira et al. 2015; Caldeira et al. 2016). A comprehensive inventory for three alternative WCO collection systems was implemented, which included two types for the domestic sector and one for the food service industry. A description follows. The domestic sector included:

i) Street *Drop-off containers*: Plastic containers placed in specific points within the collection area where citizens can dispose the recipients with WCO. The collection (frequency and routes) is planned by each collector according to the specificity of each location. Six collection locations (A to F) were considered. The location and population density are presented in **table 4.4**.

ii) *Door-to-door* (DtD)*:* The citizens store the WCO at home using 5 L plastic containers and, once a month, a special collection service collected the containers. This system has been implemented in locations where the placement of street containers is not practical (e.g. historical neighborhoods, areas of difficult access). **Table 4.4** shows data for one collection system implemented in the Azores - Angra do Heroismo.

For the food service industry sector, WCO collection from restaurants in a Portuguese midsize municipality (Coimbra) was selected as case study (HRC) (**table 4.4**). The oil is stored in 30 or 50 L plastic containers and once a month the container is collected and replaced by an empty one. **Figure 4.2** shows the location and areas covered by each system analyzed.

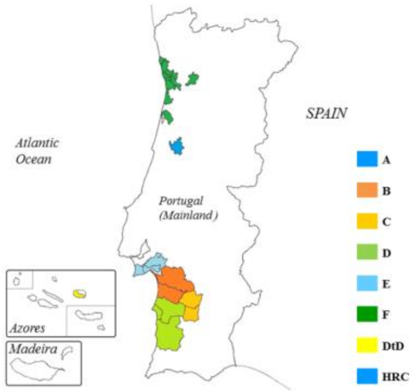

Figure 4.2. Map of Portugal, showing the WCO collection areas covered by each collection system

The distance travelled and quantity of WCO collected in each route were provided by the collection companies. The temporal horizon of the data is from 2008 to 2013, as detailed in **table 4.4**. The quantity of WCO collected and the distance travelled in each route were different within each system (the collection routes do not cover always the same collection points).

A performance indicator (PI) for WCO collection, defined as the average volume of WCO collected per kilometer travelled, was calculated (Table 4.4). The highest PI (18.4 L WCO km^{-1}) was calculated for the system implemented in Coimbra to collect WCO from restaurants (HRC) and the lowest (1.5 L WCO km^{-1}) for the system *Door-to-Door* implemented in Angra do Heroísmo. Within the same type of collection system (Drop-off containers, A to F), the PI ranged significantly: from 9.1 (A) to 2 (C) L WCO km^{-1}. Low values were calculated for low population density areas (B to E). Despite covering the highest population area analyzed, system F did not have the highest PI (5.2 L WCO km^{-1}).

The type of fuel and average fuel consumption for WCO collection were provided by the WCO collectors and are presented in **table 4.4**. Systems E and F used biodiesel from WCO as fuel in the collection fleet. All the other systems used diesel. The higher fuel consumption registered for systems B, C and D (0.14 L km^{-1}) is related to the size of the vehicle (3.5 to 7.7 tons capacity). In the other systems, although smaller vehicles were used (maximum capacity of 3.5 tons), some differences in the consumption were observed. The higher consumption observed for the system E (0.10 L km^{-1}) and F (0.11 L km^{-1}) is due the use of biodiesel in the vehicle (increases the consumption comparatively to diesel) (Dermibas 2003). Emission factors for diesel and biodiesel from Jungbluth et al. (2007) were considered.

Table 4.4. Collection systems (areas and population density), performance indicator (PI), vehicle fuel consumption and temporal horizon of the data

Sector	Collection system		Location	Population density (inhabitants km^{-2})	Temporal horizon	Vehicle Fuel Consumption (L km^{-1})	PI (L WCO km^{-1})
Households	Drop-off Containers	A	Coimbra	450	2009-2012	0.09[a]	9.1
		B	Grândola-Alcácer do Sal	12	2011-2012	0.14[a]	4
		C	Ferreira do Alentejo-Aljustrel	16	2011-2012	0.14[a]	2
		D	Odemira-Santiago do Cacém-Sines	23	2011-2012	0.14[a]	3.2
		E	Sesimbra-Setúbal-Palmela	281	Jul-Aug 2013	0.10[b]	3.5
		F	Espinho, Gondomar Maia, Matosinhos Porto, Póvoa de Varzim, Valongo Vila do Conde	959	Jan-Mar 2013	0.11[b]	5.2
	Door-to-door	DtD	Angra do Heroísmo	148	2008-2013	0.09[a]	1.5
HRC	Containers	HRC	Coimbra	–	2011	0.09[a]	18.4

[a] diesel / [b] biodiesel

For the household systems, a recovery ratio between the WCO actually collected and the WCO generated as waste was estimated between 4% and 6%. The WCO generated was calculated based on the virgin oil consumption in Portugal (22.1 kg per inhabitant per year), number of inhabitants and considering that 45% of the virgin oil becomes residue (IPA 2004). According to Math et al. (2010), if adequate collection incentives are applied, a recovery ratio of about 70% would be possible. However, the inexistence of standardized collection schemes can lead to very low recovery ratios (Peiró et al. 2008).

To assess the CC impacts, the best and worst case in terms of PI observed in the collection systems analyzed was selected: WCO collected from restaurants with a PI of 18.4 L WCO km^{-1} and oils collected from a door-to-door system with a PI of 1.5 L WCO km^{-1}. For the remaining impact categories assessed, an average value was considered.

4.3.1.4 Refining

The main processes for crude virgin oil refining for biodiesel production are neutralisation (to neutralise the free fatty acids (FFA)) and degumming (to remove phosphatides). The refining process is the same for the three virgin oils and the freshwater emissions were obtained from Castanheira et al. (2015). The freshwater consumption data was adapted from the Ecoinvent 3.1 database.

For the WCO, the quality of the oil has major influence on the refining process. The quality is mainly related to the quantity of FFA in the oil. FFA cause saponification problems during the biodiesel production process (transesterification) and depending on the WCO quality different refining (pre-treatment) procedures can be used (Araújo et al. 2013). Two alternative WCO refining processes were considered in this study: if the WCO has high quantity of FFA (low quality WCO) the refining consists of an acid-catalysed process to perform the esterification FFA (Jungbluth et al, 2007); if the WCO presents low quantity FFA (high quality WCO) the refining consists in filtering to remove impurities and heating the WCO (above 100º during approximately two hours) to remove water (evaporated to the atmosphere) (Caldeira et al. 2015).

Multifunctionality

The palm, soybean and rapeseed oils production are multifunctional systems; the co-products of palm oil production are palm kernel oil and palm kernel mill; of soybean oil is soybean meal; and, of rapeseed oil is rapeseed meal. The allocation of water consumption and degradability impacts between the oils and the co-products was based on energy content (lower heating value) following the European Directive 2009/28/EC on the promotion of the use of energy from renewable sources (European Commission 2009). **Table 4.5** presents the allocation factors used in the study for the different feedstock systems.

Table 4.5 Allocation factors based on energy content

Feedstock system	Co-Product	Energy Allocation Factor (%)
Palm (Castanheira et al. 2014)	Crude Palm oil	81
	Palm Kernel oil	10
	Palm kernel mill	9
Soybean (Castanheira et al. 2015)	Crude Soybean oil	36
	Soybean Meal	64
Rapeseed (Castanheira and Freire 2016b)	Crude Rapeseed oil	59
	Rape seed Meal	41

4.4 ENVIRONMENTAL IMPACTS

4.4.1 WATER SCARCITY FOOTPRINT

Figure 4.3 compares the water scarcity footprint calculated for the WSI and AWARE methods. The results are normalized in order to bring all units to a common unit cubic meter world equivalent. The water scarcity profile calculated following the WSI method range from 0.002 to 2.11 world m^3eq kg^{-1} oil, while the water scarcity profile vary from 0.008 to 133.57 world m^3eq kg^{-1} oil following the AWARE method. Although the range of values are different in magnitude, both methods lead to same conclusions about which is the most freshwater consuming system and which is the stage contributing the most to the overall water scarcity impacts.

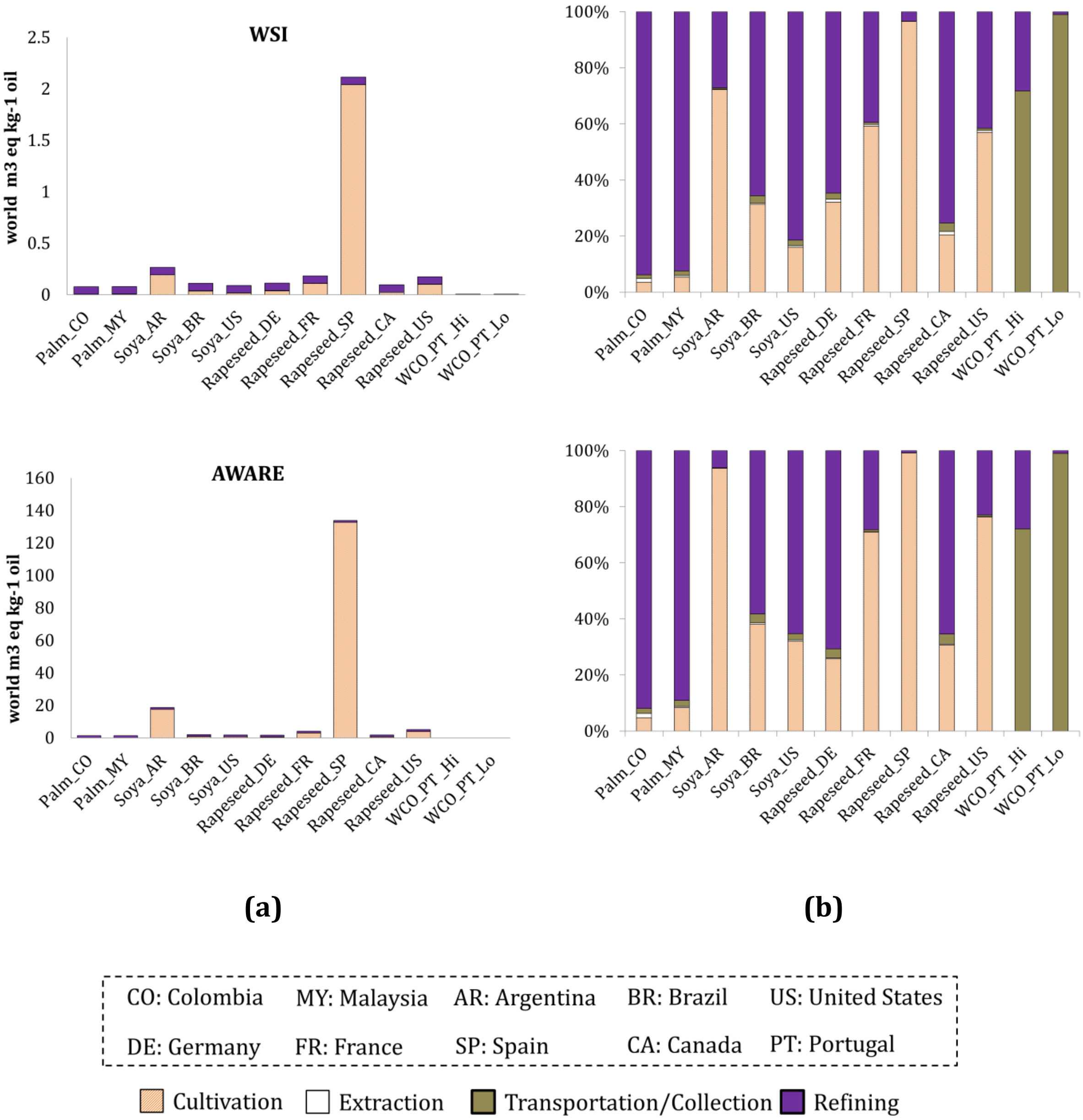

Figure 4.3 a) Water scarcity footprint calculated using WSI and AWARE CFs. b) Relative contribution of each stage to the water scarcity footprint

Within the oils analyzed, rapeseed_SP presents the highest impact due to the cultivation stage. This is because the data adopted for rapeseed cultivation in Spain presents higher water consumption than the remaining systems. In addition, Spain is the country that presents the highest water scarcity among the ones analyzed. The water scarcity footprint of the oil Rapeseed_SP is about eightfold the impact of the oil Soya_AR (data adopted for rapeseed cultivation in Argentina), which is the second oil with higher impact. Also for this oil, the stage that contributes the most to the overall impacts is cultivation. Although the cultivation of rapeseed in France (Rapeseed_FR) presents a higher water consumption than the cultivation of soya in Argentina (**table 4.2**), the latter presents higher water scarcity footprint impacts because Argentina has a higher water scarcity than France.

Table 4.6 presents the water scarcity footprint (in descending order) obtained with the WSI and AWARE CFs. For the four oils with higher impacts - Rapeseed_SP, Soya_AR, Rapeseed_FR and Rapeseed_US - the stage that contributes the most is cultivation and the majority of the freshwater is consumed by the foreground system, more specifically the water used for irrigation. As was also pointed out by Emmenegger et al. (2011), agricultural water consumption for irrigation dominates the overall freshwater consumption of biofuels produced from irrigated crops.

Table 4.6 Water scarcity footprint (from higher to lower value) obtained with the Pfister et al. (2009) – WSI – and Boulay et al. (2016) – AWARE – methods and the life-cycle stage that contributes de most to overall impacts for the virgin and WCO

Oil System	**WSI (world m^3eq kg^{-1}oil)**	**Oil System**	**AWARE (world m^3eq kg^{-1}oil)**	**Higher contribution stage**
Rapeseed_SP	2.11	Rapeseed_SP	133.57	Cultivation (irrigation water)
Soya_AR	0.26	Soya_AR	18.54	
Rapeseed_FR	0.18	Rapeseed_US	4.64	
Rapeseed_US	0.17	Rapeseed_FR	3.92	
Rapeseed_DE	0.11	Soya_BR	1.84	Refining
Soya_BR	0.11	Soya_US	1.69	
Rapeseed_CN	0.10	Rapeseed_CN	1.45	
Soya_US	0.088	Rapeseed_DE	1.44	
Palm_MY	0.078	Palm_MY	1.23	
Palm_CO	0.076	Palm_CO	1.18	
WCO_PT _Hi*	0.002	WCO_PT _Hi	0.011	WCO collection
WCO_PT_Lo**	0.001	WCO_PT Lo	0.008	

CO: Colombia MY: Malaysia AR: Argentina BR: Brazil US: United States
DE: Germany FR: France SP: Spain CA: Canada PT: Portugal

*High quality WCO; **Low quality WCO

For virgin oils produced from crops or locations that require less irrigation water (**table 4.6**) - with water scarcity footprints lower than 0.11 world m^3eq kg^{-1} oil using WSI and 1.84 world m^3eq kg^{-1} oil using the AWARE - the stage contributing the most is the refining stage. In this stage, the majority of the freshwater is consumed by the foreground system (around 99 %) and corresponds to tap water consumed in the process. Among the virgin oils, the lower impacts are obtained for palm oil production. This is because the data adopted for cultivation of palm fruits show that it requires little (Malaysia) or no irrigation (Colombia) at all. The lowest water scarcity footprint is obtained for the WCO systems. In this case, the main contribution (70% in the WCO_PT_Hi and 99% in the WCO_PT_Lo systems) arises from the collection (background system).

The oils with data adopted for rapeseed cultivated in France (Rapeseed_FR), Germany (Rapeseed_DE) and in the US (Rapeseed_US) and for soya cultivated in Brazil (Soya_BR) and in the US (Soya_US) are ranked in different positions in each method. These differences are related to the CF of each method. For example, there is an inversion of the impacts order for oils Rapeseed_FR and Rapeseed_US when using WSI or the AWARE CFs. Looking at the foreground level, although the cultivation of rapeseed in France presents higher freshwater consumption (0.22 m^3 kg^{-1} seed) than in the US (0.060m^3 kg^{-1} seed) the multiplication of these values by the CFs of each method (WSI: 0.18 for France and 0.50 for the US; AWARE: 8.29 for France and 36.52 for the US) different orders are obtained. The results for the Pfister et al. (2009) method are 0.038 world m^3 eq kg^{-1} for rapeseed cultivation in France and 0.030 world m^3 eq kg^{-1} in the US while for the Boulay et al. (2016) are 1.76 world m^3 eq kg^{-1} for rapeseed in France and 2.18 world m^3 eq kg^{-1} for rapeseed cultivated in the US. This highlights the high variation of water scarcity CFs. AWARE indicators range by a higher factor than WSI as explained in section 2.2. Therefore, although the cultivation of rapeseed in France presents higher freshwater consumption than in the US, it is expected that when applying a higher CF, this has influence on the water scarcity footprint relative to the inventory.

Both the CF and the inventory play a role in the resulting water scarcity footprint, meaning that for an effective reduction of freshwater consumption impacts, beside the reduction of the amount of water consumed also the choice of location is very important. The latter will be even more important for technologies where the range of inventory variation for water consumption is small (e.g. less than one order of magnitude). Notwithstanding, the differences between both CFs considered should be taken into account. WSIs are calculated based on WTA ratios, rather than on DTA ratios of freshwater at the sub-watershed level. This overestimates water scarcity footprint results (Berger and Finkbeiner 2012). In addition, the AWARE CFs also comprises the ecosystem and human water demands, representing the potential environmental impacts due to freshwater consumption more comprehensively than WSIs.

4.4.1.1 AWARE CFs sensitivity analysis

Table 4.7 presents the water scarcity footprint (from lower to higher value) obtained with different AWARE CFs. We considered the AWARE results as a baseline and the shaded area in the table shows those feedstocks that are not in the same rank order as the AWARE results. The results obtained with the AWARE100 EWR 50% present an inverted order for the oils Soya_US/Rapeseed_CN and Rapeseed_US/Rapeseed_FR. The latter situation is also verified in the results of the AWARE10. The AWARE10 also shows an inversion of the order for Soya_US/Rapeseed_US. The AWARE1000 results are the ones showing less agreement with the order obtained with the AWARE CFs.

Table 4.7 Water scarcity footprint (from higher to lower value) obtained with the AWARE method using different characterization factors for the virgin oils and WCO

Water scarcity footprint world m^3 eq kg^{-1} oil							
Oil system	**AWARE**	**Oil system**	**AWARE 100 EWR 50%**	**Oil system**	**AWARE 10**	**Oil system**	**AWARE 1000**
WCO_PT_Lo	0.03	WCO_PT_Lo	0.03	WCO_PT_Lo	0.03	WCO_PT_Lo	0.04
WCO_PT _Hi	0.04	WCO_PT _Hi	0.05	WCO_PT _Hi	0.04	WCO_PT _Hi	0.19
Palm_CO	1.26	Palm_CO	1.91	Palm_CO	0.32	Palm_MY	8.98
Palm_MY	1.30	Palm_MY	2.00	Palm_MY	0.35	Palm_CO	9.10
Rapeseed_DE	1.64	Rapeseed_DE	2.37	Soya_US	0.40	Soya_BR	10.89
Rapeseed_CA	1.77	Soya_US	2.51	Rapeseed_CA	0.51	Rapeseed_DE	11.54
Soya_US	1.77	Rapeseed_CA	2.56	Rapeseed_DE	0.58	Soya_US	13.55
Soya_BR	1.99	Soya_BR	4.63	Soya_BR	0.89	Rapeseed_CA	13.93
Rapeseed_FR	4.10	Rapeseed_US	6.43	Rapeseed_US	0.96	Rapeseed_FR	21.76
Rapeseed_US	5.03	Rapeseed_FR	13.23	Rapeseed_FR	1.81	Rapeseed_US	43.84
Soya_AR	18.64	Soya_AR	21.37	Soya_AR	2.65	Soya_AR	116.30
Rapeseed_SP	133.79	Rapeseed_SP	154.39	Rapeseed_SP	16.45	Rapeseed_SP	1226.90

CO: Colombia	MY: Malaysia	AR: Argentina	BR: Brazil	US: United States
DE: Germany	FR: France	SP: Spain	CA: Canada	PT: Portugal

The differences observed in the order are mainly related to the magnitude of the CFs and the relation among the CFs of the different cultivation locations. For example, if one compares the water consumption of rapeseed cultivation in the US and in France, the value is respectively, 0.060 m^3 per kg oil and 0.21 m^3 per kg oil (**table 4.2**). Although the cultivation of rapeseed in France presents higher consumption, since the AWARE CF is lower for France (8.29) than for the US (36.52) (**table 4.3**), the results for AWARE show that the water scarcity footprint for feedstock Rapeseed_US is higher. This does not happen with the AWARE100 EWR 50% or AWARE10, because the CF values are closer (e.g. for the AWARE10 the CF for France is 4.44 and for the US 5.70) and so, the impacts order is the same as the water consumption, meaning that the feedstock Rapeseed_FR has higher impacts than Rapeseed_US.

Besides obtaining different results, the use of alternative CFs also influences the contribution of each stage and consequently the identification of “hotspots” as shown in **figure 4.4** that displays the contribution of each stage in each feedstock system for each group of CFs. An example to illustrate this influence of the different CFs is the oil produced from soya cultivated in Brazil (Soya_BR). According to the results obtained with the AWARE and AWARE1000, the stage contributing the most is refining (about 60% for the AWARE and about 70% for the AWARE1000) but according to AWARE100 EWR 50% and AWARE10, the contribution of this stage diminishes to about 40%.

In the cultivation and refining stages, the foreground has the largest water consumption share and the relation between the CF for Brazil (cultivation location) and Portugal (refining location) dictate the contribution of each stage. According to **table 4.7**, the relation Brazil CF/Portugal CF varies for the different CF group: for AWARE Portugal´s CF is 6 times higher than Brazil´s CF; for AWARE100 EWR 50% and AWARE10, about 2 times higher; and, for AWARE1000, about 39 times higher. For this reason, the refining stage has more weight in the results obtained with the AWARE1000 CFs, followed by the results obtained with the AWARE and less contribution in the results obtained with AWARE100 EWR 50% and AWARE10 CFs. The large difference seen when using AWARE1000 illustrates the fact that too much weight is given to the geographical location (scarcity) which masks the effect of differences in inventory.

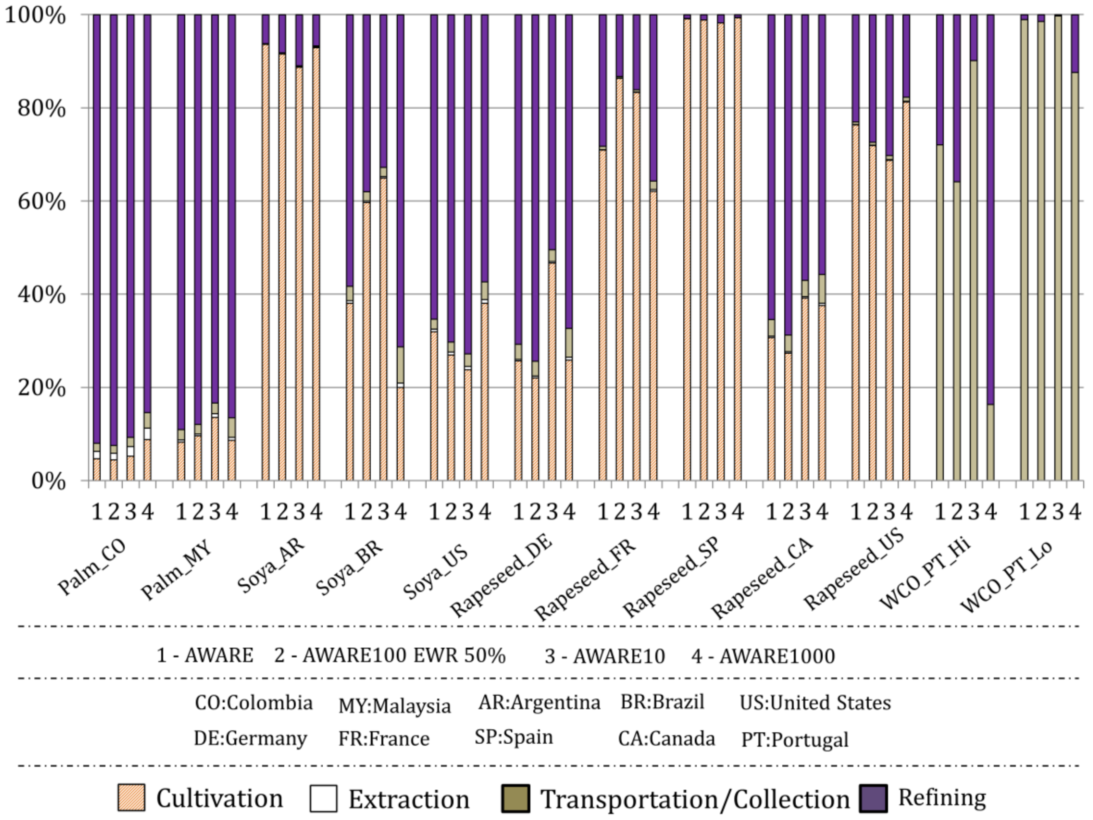

Figure 4.4 Contribution of each stage to the overall water scarcity impacts calculated with different AWARE CFs.

4.4.2 WATER DEGRADATION IMPACTS

Figure 4.5 depicts the contributions to the freshwater degradation impacts, including freshwater eutrophication (FE), marine eutrophication (ME) and aquatic acidification (AA). Virgin oils production has higher impacts than WCO, due to the cultivation stage.

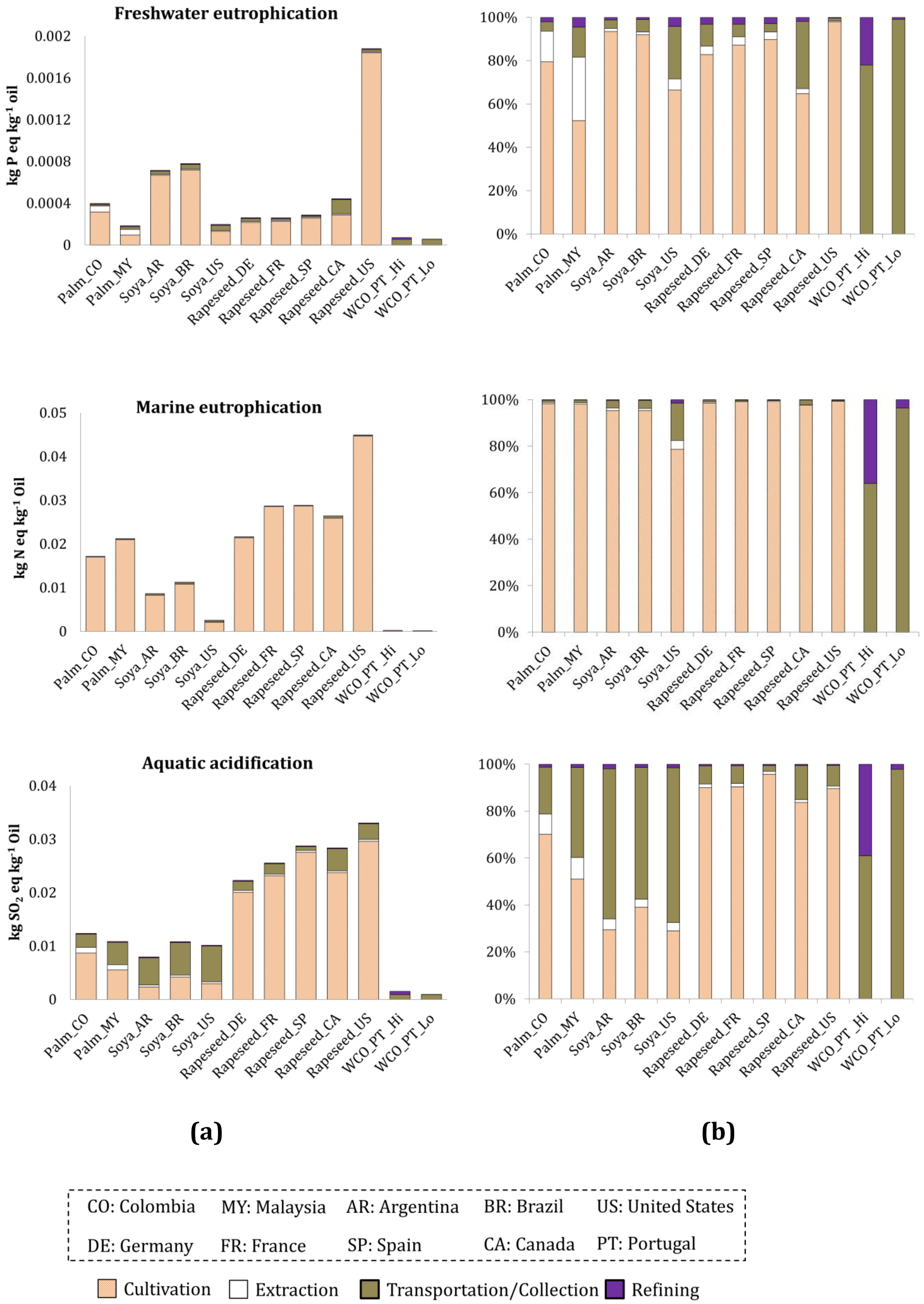

Figure 4.5 Freshwater eutrophication, marine eutrophication, and aquatic acidification of 1 kg of oil (a) and the relative contribution of each stage to the overall impacts (b)

Rapeseed_US oil has the highest impacts for FE, ME and AA. The phosphate and phosphorus emissions due to P-fertilizers are the explain the higher FE impacts observed for Rapeseed_US, Soya_Ar and Soya_Br oils. ME and AA are mainly due to ammonia, nitrates and nitrogen oxides released due to the use of N-fertilizers. Since the fertilization scheme of Rapeseed cultivation uses higher quantities of N-fertilizers (comparatively to soya and palm cultivation, see table 1 in Appendix VII), the rapeseed oils present higher impacts in these categories. The fertilization scheme strongly influences the impacts in acidification and eutrophication. The higher contribution of the transportation to AA observed for the oils Palm_MY, Palm_CO, Soya_Ar, Soya_Br, Soya_US, and Rapeseed_US are due to the heavy fuel oil used in the transoceanic ship. Oil produced from Rapeseed cultivated in Europe and WCO domestically collected (in Portugal) present lower AA impacts associated with the transportation stage.

Figure 4.6 shows the environmental impacts for human toxicity-cancer (HTc), human toxicity-non cancer (HTnc), and freshwater ecotoxicity (FT) and the contribution of each stage to the overall water pollution impacts. In general, the Rapeseed systems present higher impacts for HTc, HTnc and FT due to the use of higher quantities of pesticides. The exception is the oil Rapeseed_DE because the quantity of pesticide used in the cultivation is lower. HTc and HTnc impacts are mainly caused by the emissions of trifluralin. For FT, the impacts are due the emissions of carbendazim and iprodione (for Rapeseed_SP and Rapeseed_FR) and due to ethalfluralin and parethion (for Rapeseed_CA). The differences observed in the toxicity results are mainly related to the different types and quantity of pesticides used in the crops cultivation.

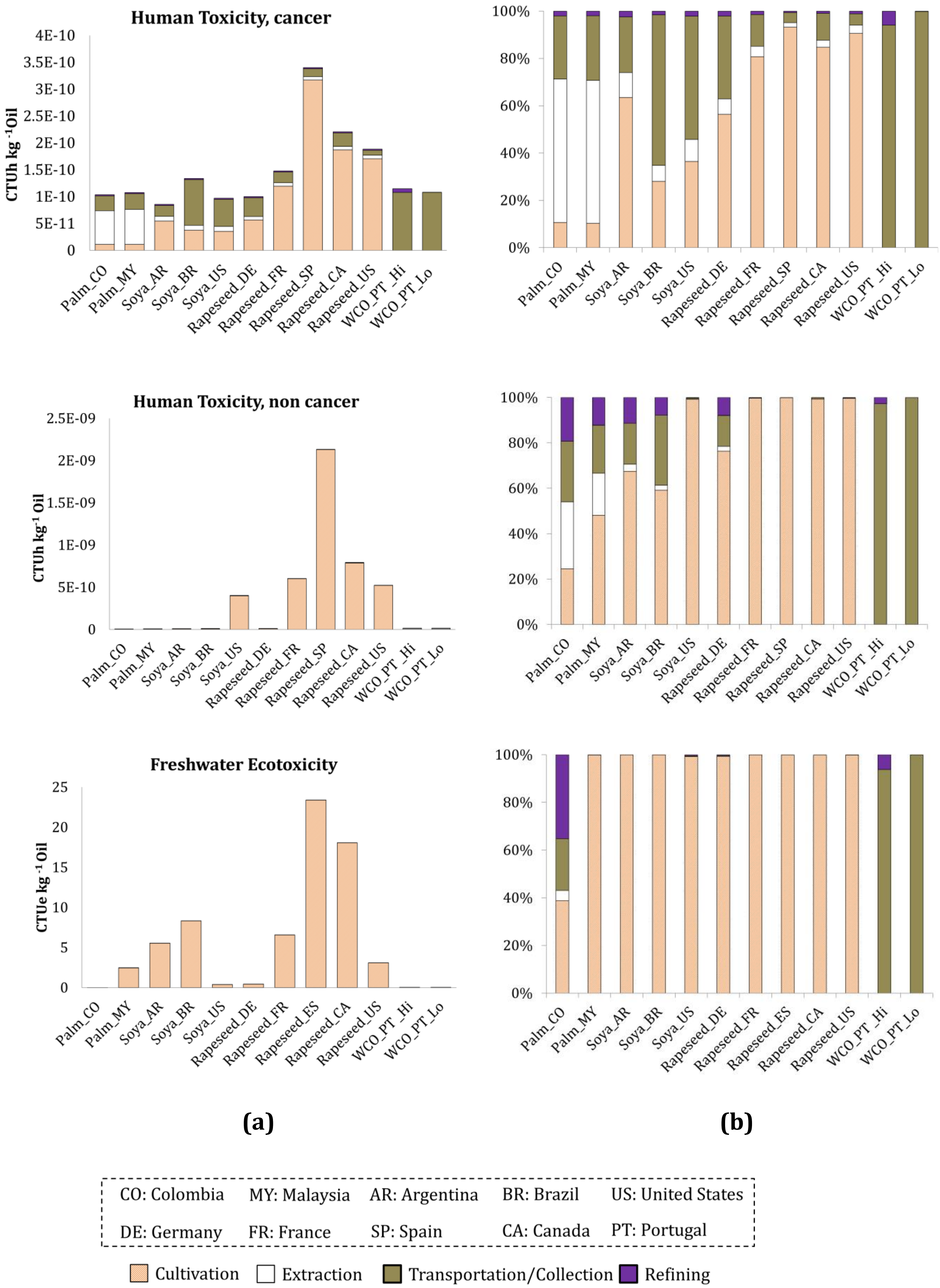

Figure 4.6 Human toxicity-cancer, human toxicity-non cancer, and freshwater ecotoxicity of 1 kg of oil (a) and the relative contribution of each stage to the overall impacts (b)

Formaldehyde emissions due to diesel combustion in the transportation/collection stage contributed the most for HTc of oil produced from WCO (almost 100%), Soya_BR (65%) and Soya_US (55%,). The higher contribution of the refining stage (about 60%) in the oils Palm_CO and Palm_MY is due to the dioxins and formaldehyde released in the cogeneration plant on the extraction mill.

4.4.3 CLIMATE CHANGE

The CC results of the various oil systems are presented in **figure 4.7** for each life-cycle stage and for the optimistic and pessimistic scenarios considered for LUC and the collection scenarios. **Figure 4.7** also shows the contribution of each stage (excluding Land Use Change) to the overall impacts.

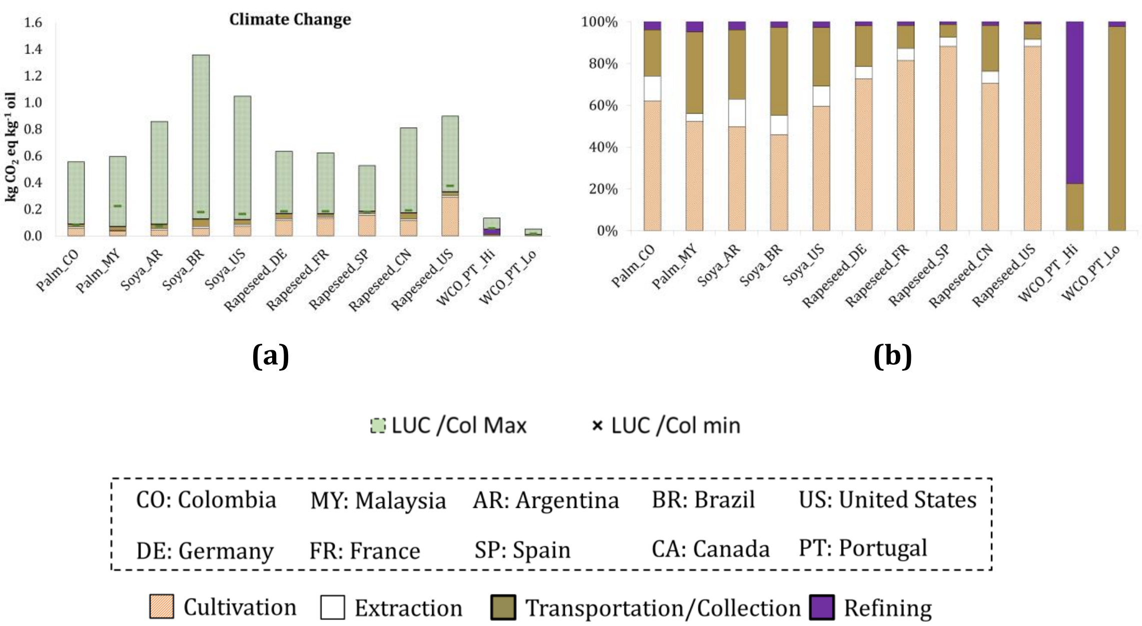

Figure 4.7 Impacts for Climate Change of the production of 1 kg of oil for biodiesel production (a) and the contribution of each stage to the overall impacts (b)

The soil carbon change associated with different LUC scenarios can have a significant influence in the results obtained for CC. Oils that present lower impacts when the LUC are disregarded such as Palm_MY or Soya_Br or Soya _US, can have high impacts if the cultivation site was previously forest or savanna. Higher variations between the pessimistic and optimistic scenarios are obtained for rapeseed cultivation in the US and soybean in Brazil, the US and Argentina.

Carbon exchange credits are obtained for the optimistic scenario for palm cultivation in Colombia, soya in Argentina and rapeseed in Spain. In these cases, the reference land are shrubland and grassland severly degraded. When soil carbon change is excluded, the cultivation stage is the one contributing the most to the overall impacts. These impacts are mainly related to N_2O emissions from soils due to the application of nitrogen fertilizers. The extraction and refining steps have low contribution to the overall GHG emissions.

The lower impacts are obtained for the WCO systems. The impacts are mainly attributed to the collection stage and are related to the diesel use in the collection vehicles.

4.5 CONCLUDING REMARKS

This chapter presents the environmental assessment of vegetable oils made from palm, soya, rapeseed and waste cooking oil used for biodiesel production. A water footprint profile, including the water scarcity footprint and impacts due to the freshwater degradation, and impacts due to GHG emissions were calculated. Two methods were used to assess water scarcity: the WSI and AWARE.

The water scarcity impacts obtained using the WSI and AWARE methods lead to similar conclusions in what concerns the highest and lowest water scarcity impacts but, for the oils systems with close results, the rank order given by each method is different. Nevertheless, the AWARE method seems more adequate to support decision making since the AWARE CFs were developed taking into account the water demand for both ecosystems and humans, thus addressing more comprehensively the impacts due to freshwater consumption.

The differences observed in the assessment of the various virgin oils are mainly related to water scarcity of the cultivation location and the fertilization and pesticides schemes used. The choice of the locations with lower water scarcity to produce oil crops can be determinant for obtaining lower impacts. Additionally, optimizing fertilization schemes or choosing climatic conditions that require less fertilizers and pesticides will contribute to reduce the water footprint profile of vegetable oils.

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5 A LIFE-CYCLE MULTI-OBJECTIVE DECISION AIDING TOOL TO ASSESS THE USE WASTE COOKING OIL IN BIODIESEL PRODUCTION

The content of this chapter is presented in the following article:

Caldeira, C., Olivetti, E., Kirchain, R. Freire, F., Dias, L. **A life-cycle multi-objective decision aiding tool to assess the use of waste cooking oil in biodiesel production** (in final preparation)

5.1 INTRODUCTION

The controversy around biodiesel sustainability has pushed policy makers and biodiesel producers to assess biodiesel systems in a more comprehensive manner, including economic and environmental performance. The life-cycle multi-objective (LCMO) framework has been widely used to analyze tradeoffs between environmental and economic aspects (Pieragostini et al. 2012; Jacquemin et al. 2012). Among the LCMO studies of biofuel systems found in the literature (presented in chapter 1), environmental performance is mainly addressed through impacts caused by GHG emissions. However, as already highlighted in this thesis, other environmental impact categories should also be considered when assessing biodiesel systems.

The main problem in including more impact categories as objective functions in a LCMO model is related to the complexity of tradeoffs analysis due to antagonistic behavior of the objectives. For this reason, the development of tools that facilitate the tradeoff analysis and the decision process is very important within the LCMO framework.

In this chapter, a LCMO decision aiding tool to assess the use WCO in blends for biodiesel production is presented. The tool has the particularity of facilitating the decision process by allowing the decision-maker to decide based on an explicit overall environmental performance. The environmental objectives include GHG emissions and water use impacts. The latter, measured in terms of scarcity and degradability (acidification, eutrophication, human toxicity and freshwater toxicity).

5.2 LIFE-CYCLE MULTI-OBJECTIVE CHANCE-CONSTRAINED MODEL

The LCMO model developed integrates the LCA results presented in chapter 4 within the stochastic blending model developed in chapter 2 (pp 35-36). For sake of simplicity, it is assumed that there is no uncertainty associated with the feedstock price. The model determines the Pareto optimal blends that minimizes costs and environmental impacts by deciding the quantity of each feedstock to use in the blend. The mathematical formulation is similar to the one presented in

Chapter 2 except the objective function that is replaced by **equation 5.1**, where $C_{k,i}$ is the coefficient of objective function k for feedstock i. The chance-constrained technical constraints confidence level was set to 95%. The model is illustrated for a single price period (month). The month July 2013 was selected because it is the month when the price of WCO is closer to the virgin oils price that represents a more conservative situation to evaluate the benefits of WCO. The prices were 559 €, 767 €, 765 € and 400 € per ton of palm, rapeseed, soya and WCO, respectively. The price information for palm, rapeseed and soya oils was taken from IndexMundi (2014) and prices for WCO were obtained from a European broker (Grennea 2014). The environmental impacts include: Climate Change (CC), Water Stress Index (WSI), Freshwater Eutrophication (EU), Aquatic Acidification (AC), Human toxicity (HT) and Freshwater toxicity (FT). The impact inputs used in the model were calculated in the previous chapter and are presented in **table 5.1**.

$$\min z_k = \sum_{i \in I} \left(C_{k,i} \ QU_i \right) \ , \ \ k \in K = \{Cost, CC, WSI, FE, AA, HT, FT\} \qquad \text{Eq. 5.1}$$

Table 5.1 Climate Change (CC), Water footprint (WSI), Eutrophication (EU), Acidification (AC), Human Toxicity (HT) and Freshwater toxicity (ET) for the different feedstocks

	Climate Change (CC)	WSI	Eutrophication (FE)	Acidification (AA)	Human Toxicity (HT)	Ecotoxicity (FT)
Feedstock_origin	kg CO_2 eq kg^{-1} oil	m^3 eq Kg^{-1} oil	kg P eq kg^{-1} oil (*10^{-4})	kg SO_2 eq kg $^{-1}$oil (*10^{-2})	CTUh kg oil $^{-1}$ (*10^{-11})	CTUhe kg-1 oil
Palm_CO	0.90	0.076	3.98	1.24	0.44	0.004
Palm_MY	0.72	0.078	1.83	1.09	0.69	2.47
Soya_AR	0.90	0.264	7.15	0.80	0.74	5.54
Soya_BR	1.29	0.109	7.81	1.08	1.08	8.32
Soya_US	1.23	0.088	1.97	1.02	40.1	0.39
Rapeseed_DE	1.69	0.111	2.62	2.23	1.1	0.45
Rapeseed_FR	1.68	0.182	2.6	2.56	60.2	6.57
Rapeseed_SP	1.85	2.113	2.87	2.88	213.0	23.38
Rapeseed_CN	1.75	0.095	4.42	2.84	79.2	18.06
Rapeseed_US	3.32	0.172	18.8	3.30	52.2	3.09
WCO_PT _Hi*	0.41	0.0020	0.71	0.15	1.37	0.03
WCO_PT_Lo**	0.29	0.0015	0.56	0.10	1.33	0.03

*High quality WCO; **Low quality WCO

In multi-objective models, since more than one objective function exists to optimize, there is no single optimal solution. Instead, the decision-makers are looking for a “best compromise” solution. Therefore, the concept of optimality is replaced with that of Pareto optimality or efficiency (Mavrotas 2009). The Pareto optimal (or efficient, non-dominated, non-inferior) solutions are the solutions that cannot be improved in one objective function without worsening one of the others (Mavrotas 2009; Antunes et al. 2016).

To determine the Pareto optimal solutions the ε-constraint method was used. According with this method, one of the objective functions is optimized while using the other objective functions as constraints. The constraint level ranges from the ideal to the anti-ideal values of each objective. The ideal and anti-ideal values are calculated from the payoff table, which is the table with the results from the individual optimization of the k objective functions. The anti-ideal value is the maximum of the corresponding column.

The ε-constraint method was applied to optimize costs, CC and WSI but when more objectives were included, a different approach was followed. The approach was developed to facilitate the decision process by enabling the decision-maker to decide based on an explicit overall environmental performance. Moreover, it allows visualizing in a simpler manner the tradeoff between cost and environmental impacts. According to it, only the cost objective is minimized and the other objectives are considered to be constraints as described by **equation 5.2**:

$$\sum_{i \in I} \left(C_{k,i} QU_i \right) \leq \mathrm{Ideal}_k + \theta \left(\mathrm{Anti\ ideal}_k - \mathrm{Ideal}_k \right), \quad \forall_{k \in K \backslash \{cost\}}, \theta \in [0,1] \qquad \text{Eq. 5.2}$$

Θ is a parameter that reflects the constraint level of the environmental impacts and ranges from 0 to 1. When Θ=1, the environmental impacts are allowed to be as high as the anti-ideal value and the solution with the minimum cost can be obtained. As Θ decreases, the upper limit for all environmental impacts also contracts, departing from the anti-ideal values and getting closer to the ideal values (e.g., Θ=0.5 means that the upper limit on each environmental indicator will be halfway between the ideal and anti-ideal values). Thus, the feasible region decreases leading to more expensive solutions, up to a minimum value (Θ_{Lim}) such that for $\Theta < \Theta_{Lim}$ the problem becomes unfeasible.

The model was implemented in GAMS 24.4.2 (GAMS 2011) and the problem solved using the non-linear solver CONOPT (Arne 2014).

To assess the use of WCO in the blends, results were obtained for two scenarios: (a) WCO is available to blend with the virgin oils; and, (b) only virgin oils are available. The solutions obtained in (b) are used as reference to assess the advantages of using WCO in the blends.

5.3 TRADEOFFS ANALYSIS

5.3.1 COST, CLIMATE CHANGE AND WATER SCARCITY

Table 5.2 presents the pay-off tables obtained for both scenarios considering three objectives: Cost, Climate Change (CC) and Water Stress index (WSI). The diagonal of each table (green shaded cells) presents the ideal value of each objective (column), i.e., the value obtained when minimizing each objective on its own. The red shaded area indicates the anti-ideal value of each objective: the worst value found when minimizing the other objectives. The ideal and anti-ideal values provide an indication of the range of impacts obtained by Pareto optimal solutions.

When WCO are available to blend with the virgin oils, the blends incorporate 34% of WCO when the cost objective is minimized, 10% when CC is minimized and 32% when WSI is minimized. The incorporation of WCO allows a reduction of the minimum value obtained for each objective (ideal values) comparatively to the ideal values obtained with blends composed only of virgin oils (**table 5.2**). The ideal value for cost, CC and WSI obtained with WCO available are (respectively) 3%, 2% and 32% lower than the ideal values obtained when only virgin feedstocks are available. Also the anti-ideal value for cost is lower (2%) when WCO are included in the blend. Nevertheless, for the anti-ideal values for CC and WSI there is an increase of 3% and 14%, respectively.

Table 5.2 Pay-off tables obtained by minimizing cost, CC and WSI in two scenarios: a) WCO is available to blend with the virgin oils and, b) only virgin feedstocks are available.

Objective minimized	a) With WCO Cost (€/ton)	CC (kg CO_2 eq kg^{-1} oil)	WSI (m^3 eq kg^{-1} oil)	b) Without WCO Cost (€/ton)	CC (kg CO_2 eq kg^{-1} oil)	WSI (m^3 eq kg^{-1} oil)
Cost	**642.7**	**1.48**	**0.354**	**662.4**	**1.43**	**0.304**
Climate Change	**677.9**	**1.07**	0.149	**692.1**	**1.09**	0.159
WSI	650.1	1.31	**0.065**	**689.6**	1.26	**0.086**

The diagonal contains ideal values of the objective (column)
The red shaded values are anti-ideal values of the objective (column)

The Pareto optimal solutions were obtained using the Ɛ-constraint method miminizing costs and using CC and WSI as constraints, incorporating them in the constraint part of the model. The contraint level ranges, interactively, from the anti-ideal to the ideal values presented in **Table 5.2.** The iteration step for each objective is one tenth of the difference between the anti-ideal and ideal value. **Figure 5.1** shows the Pareto surface obtained minimizing cost, CC and WSI for the two scenarios considered: (a) having WCO available in the model (left-hand side) and, (b) without WCO available (right-hand side). The Pareto surface is displaced to lower costs when WCO is included in the blends. The quantity of WCO incorporated in the blends ranges from 10 to 34%. Lower CC and WSI solutions can be obtained at a lower cost if WCO is included in the blends.

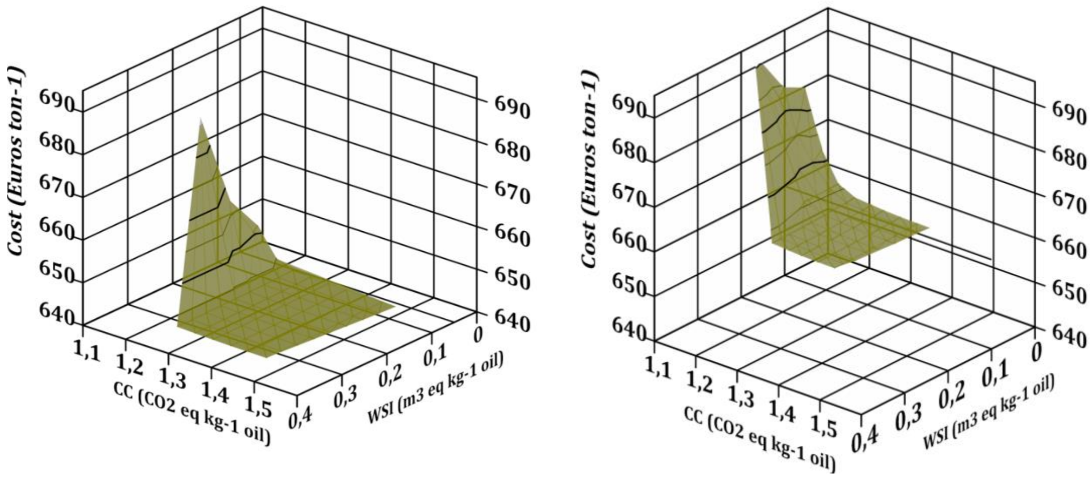

Figure 5.1 Pareto surface obtained minimizing cost, climate change (CC) and water stress index (WSI) having WCO available in the model (left-hand side) and without WCO available (right-hand side).

5.3.2 GLOBAL ASSESSMENT

In this section, the analysis was extended to include the other environmental impacts: eutrophication (EU), acidification (AA), human toxicity (HT) and ecotoxicity (FT). The payoff tables obtained for the two scenarios, with and without WCO available, are presented in **table 5.3** and **table 5.4**, respectively. Similarly to what was observed for the ideal values obtained for cost, CC and WSI, the use of WCO also reduces the ideal values in 9% for EU, 3% for AA and 4% for FT relatively to the situation when only virgin oils are available to blend. For HT, the ideal value is the same in both situations. The quantity of WCO incorporated in the blend when minimizing EU is 33% and 11% when minimizing AA or FT. The blend obtained when minimizing HT has no WCO in its composition.

Table 5.3 Pay-off table for Cost, Climate Change (CC), Water footprint (WSI), Eutrophication (EU), Acidification (AA), Human Toxicity (HT) and Freshwater Toxicity (FT) when WCO is available

Objective minimize	**Cost** €/ton	**CC** kg CO_2 eq kg^{-1} oil	**WSI** m^3 eq kg^{-1} oil	**EU** kg P eq kg^{-1} oil (*10^{-4})	**AA** kg SO_2 eq kg^{-1} oil (*10^{-2})	**HT** CTUh kg^{-1} oil (*10^{-11})	**FT** CTUhe kg^{-1} oil
Cost	**642.7**	**1.48**	**0.354**	4.36	1.87	54.03	6.82
CC	677.9	**1.07**	0.149	3.62	1.39	13.10	4.09
WSI	650.1	1.31	**0.065**	**3.22**	**1.98**	**54.32**	**12.30**
EU	647	1.24	0.101	**1.95**	1.64	23.62	2.55
AA	676.9	1.11	0.127	3.60	**1.34**	2.79	2.36
HT	**693.7**	1.17	0.146	**4.49**	1.44	**0.74**	1.86
FT	668	1.32	0.091	3.07	1.74	0.83	**0.25**

The diagonal contains ideal values of the objective (column)
The red shaded values are anti-ideal values of the objective (column)

Table 5.4 Pay-off table for Cost, Climate Change (CC), Water footprint (WSI), Eutrophication (EU), Acidification (AA), Human Toxicity (HT) and Freshwater Toxicity (FT) when WCO is not available

Objective minimized	**Cost** €/ton	**CC** kg CO_2 eq kg^{-1} oil	**WSI** m^3 eq kg^{-1} oil	**EU** kg P eq kg^{-1} oil (*10^{-4})	**AA** kg SO_2 eq kg^{-1} oil (*10^{-2})	**HT** CTUh kg^{-1} oil (*10^{-11})	**FT** CTUhe Kg^{-1} oil
Cost	**662.4**	**1.43**	**0.304**	**4.57**	1.96	**40.60**	5.74
CC	692.1	**1.09**	0.159	3.87	1.43	12.37	4.24
WSI	689.6	1.26	**0.086**	**3.27**	**1.70**	**38.73**	**6.54**
EU	693.4	1.20	0.105	**2.13**	1.50	24.36	2.28
AA	689.7	1.13	0.132	3.85	**1.38**	3.35	2.57
HT	**693.7**	1.17	0.146	4.49	1.44	**0.74**	1.86
FT	676.9	1.35	0.096	3.21	1.80	0.79	**0.26**

The diagonal contains ideal values of the objective (column)
The red shaded values are anti-ideal values of the objective (column)

As typically occurs in multi-objective problems, the antagonistic behavior of the objectives makes it difficult for decision-makers to decide about the "best" solution. For example, minimizing cost leads to solutions (blends) that correspond to the anti-ideal solution for CC and WSI. On the other hand, minimizing WSI leads to the anti-ideal solution for AA, FT and AA (**Table 5.3**).

As the number of objectives increased to seven, it would be impossible to visualize the Pareto solutions as it was shown for Cost, CC and WSI. In this case, the approach described in section 5.2 (equation 5.2) was applied. Results obtained for different Θ for the two scenarios, with and without WCO available, are depicted in **figure 5.2.**

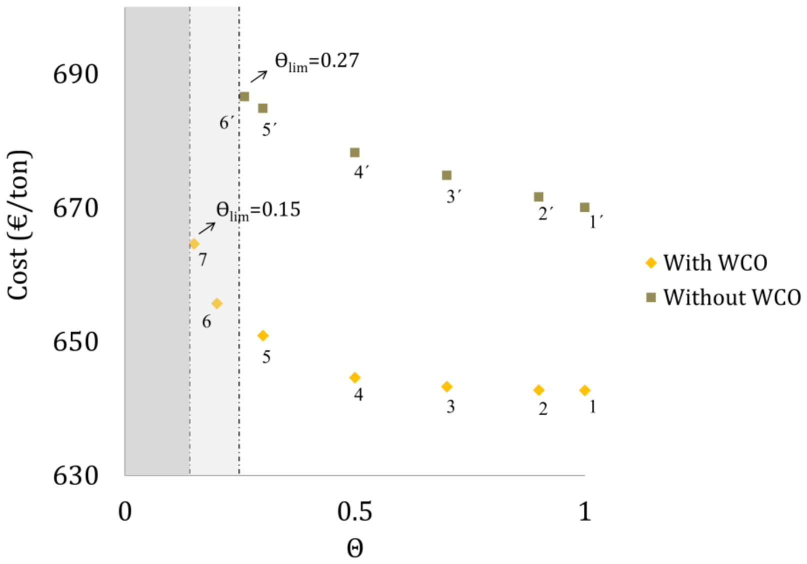

Figure 5.2 Blends cost obtained for different Θ. For Θ lower than 0.15 and 0.27 the problem is unfeasible (shaded area) for the situation with and without WCO, respectively.

Lower cost blends are obtained if WCO is available (yellow dots). Blend 1 was obtained setting Θ=1 and corresponds to the lowest cost solution (642.7 € /ton). Decreasing the value of Θ increases the cost and for Θ values lower than 0.15 the problem becomes unfeasible. For Θ_{Lim}= 0.15 the solution corresponds to blend 7 which has a cost of 665.1 €/ton. In the scenario were WCO is not available (green dots), the cost of blend obtained with Θ=1 (Blend 1') is 670 €/ton, 4% higher than blend 1. The Θ_{Lim} for this scenario is 0.27 and corresponds to blend 6' that has a cost of 686.6 €/ton, 2.3% higher than Blend 7'. The cost and environmental impacts obtained with Θ=1 (Blends 1, 1') and Θ= Θ_{Lim} (7, 6') in both scenarios (with and without WCO) are presented in **table 5.5.**

Table 5.5 Results for Cost, Climate Change (CC), Water footprint (WSI), Eutrophication (EU), Acidification (AA), Human Toxicity (HT) and Ecotoxicity (FT) obtained for Θ=1 and Θ= Θ $_{lim}$ when WCO is available (a) and when it is not (b)

Objective	**Θ=1 (a) (Blend 1)**	**Θ=1 (b) (Blend 1´)**	**Θ=0.15 (a) (Blend 7)**	**Θ=0.27 (b) (Blend 6´)**
Cost (€//ton)	642.7	670.0	665.1	686.6
CC (kg CO_2 eq kg^{-1} oil)	1.48	1.22	1.17	1.18
WF (m^3 eq kg^{-1} oil)	0.354	0.304	0.120	0.145
EU (kg P eq kg^{-1} oil *10^{-4})	4.35	3.13	2.41	2.79
AA (kg SO_2 eq kg^{-1} oil *10^{-2})	1.87	1.7	1.44	1.47
HT (CTUh kg^{-1} oil *10^{-11})	54.08	27.83	8.07	11.5
FT (CTUhe kg^{-1} oil)	6.82	4.25	1.52	1.94
Quantity of WCO (%)	34	—	18	—

The environmental impacts of Blend 1 are higher than Blend 1' because for Blend 1 to comply with the technical constraints, the use of WCO in the blend is compensated with the use of rapeseed feedstocks while in Blend 1' there is a high quantity of palm feedstocks (20% Palm_CO + 26% Palm_MY). Since the rapeseed feedstocks have higher impacts than the palm ones (see Table 5.1), the environmental impacts of Blend 1 are higher than Blend 1'. Nevertheless, with decreasing Θ, the environmental impacts decrease and for Θ=0.15 (Blend 7) the environmental impacts are lower than the ones of Blend 6' (blend with the lowest environmental impacts in the no WCO available scenario). This means that lower environmental impacts at a lower cost are obtained when WCO is available.

This approach allows the decision-maker to decide based on an overall performance without needing to attribute weights to each of the environmental impacts. For example, if the decision-maker wants to be sure that the blend is in the 50% best solutions of the efficient solutions in terms of environmental performance, one can set Θ=0.5 and the optimal solution is Blend 4. The choice of Blend 4 represents an increase in the cost of 0.3% relatively to blend 1 (lower cost blend) but a reduction of 11% in AA, 13% in CC, 40% in WSI, 45% in EU, 50% in HT and 72% in FT. **Figure 5.3** shows the relative position of this solution to the ideal and anti-ideal values.

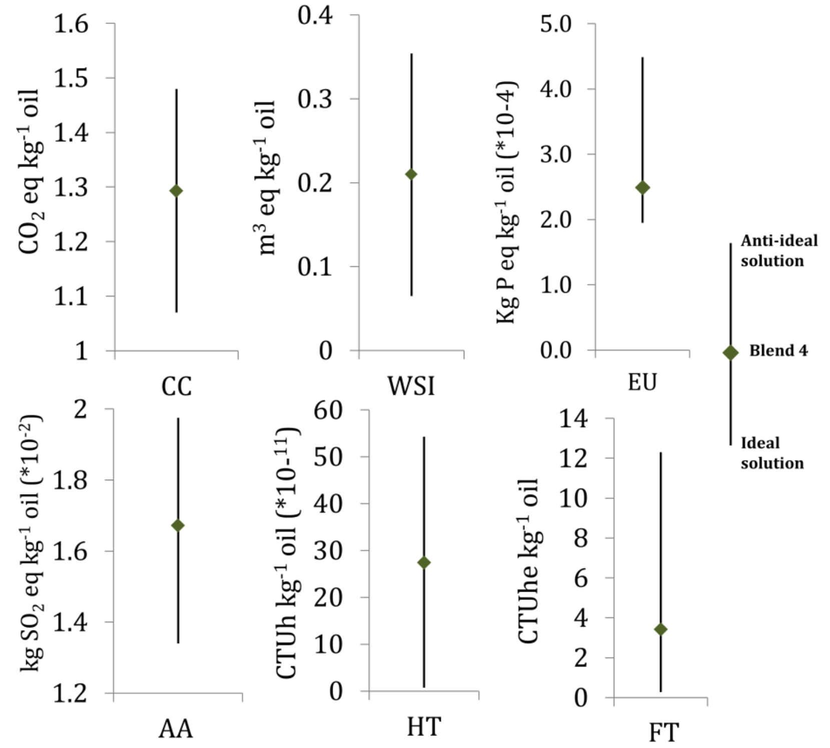

Figure 5.3 Relative position to the ideal and anti-ideal values of blend 4 (obtained with Θ = 0.5)

The composition of Blends 1, 4 and 7 are presented in **Figure 5.4**. Blend 1, the lowest cost blend (obtained with Θ=1), is composed of WCO and rapeseed. Since the goal is to minimize cost and this blend is obtained for the less stringent constraint level for the environmental impacts, the model distributes the quantity of WCO and rapeseed equitably for the different “types” of those feedstocks that only differ in the environmental impacts value. Blend 1 is the blend that incorporates the highest quantity of WCO, 34% (adding the low and high quality WCO).

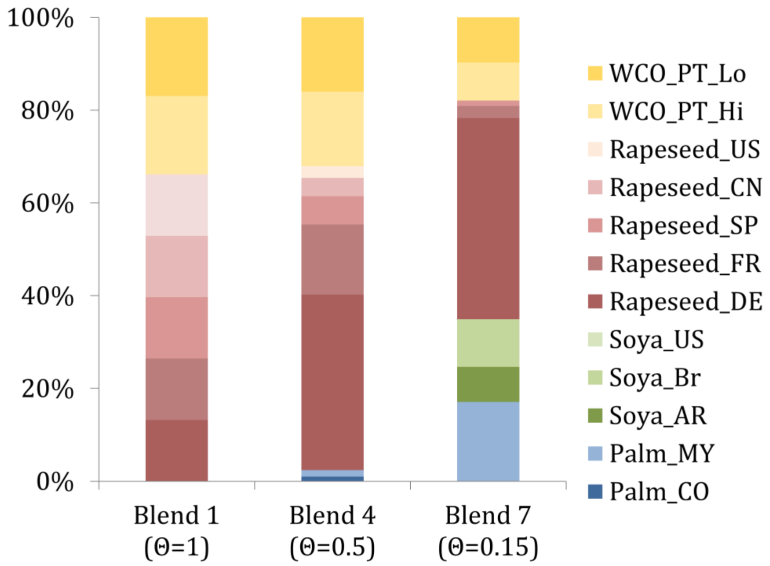

Figure 5.4 Blends composition obtained for Θ=1, Θ=0.5 and Θ=0.15 (Θ_{Lim})

When the feasible region contracts by decreasing Θ, the quantity of WCO diminishes and palm is added to the blend. The quantity of WCO incorporated in Blend 4 is 32%. For Θ_{Lim} =0.15, Blend 7 is the optimal blend obtained and the four types of feedstock compose it: palm, soya, rapeseed and WCO. The quantity of WCO in this blend is 18%. The quantity of WCO in the blend diminishes with decreasing Θ because WCO have higher impacts for HT (**Table 5.6**) and to reduce this category, this feedstock is replaced by others that have lower impacts such as Palm_MY, Soya_US or Rapeseed_DE. This latter presents higher percentage in the blends when the environmental impacts are reduced because among the available rapeseed feedstocks is the one with lower impacts for all the categories with exception of EU and WSI.

It should be noted that the results obtained correspond to a single period price – July 2013. As mentioned in the beginning of this chapter, this period was selected to illustrate the model because it is the month when the price of WCO is closer to the virgin oils price, representing a more conservative situation to evaluate the cost benefits of WCO. Nevertheless, although in the other periods the use of WCO is expected to be beneficial, the type and quantity of each feedstock used in the blend may change and consequently, the environmental impacts of the blends may also be different.

Table 5.6 Ranking from lower to higher impact value of each feedstock for CC, WSI, EU, AA, HT and FT

CC	WSI	EU	AA	HT	FT
WCO_PT Lo	WCO_PT_Lo	WCO_PT Lo	WCO_PT Lo	Palm_CO	Palm_CO
WCO_PT _Hi	WCO_PT _Hi	WCO_PT _Hi	WCO_PT _Hi	Palm_MY	WCO_PT Lo
Palm_MY	Palm_CO	Palm_MY	Soya_AR	Soya_AR	WCO_PT _Hi
Soya_AR	Palm_MY	Soya_US	Soya_US	Rapeseed_DE	Soya_US
Palm_CO	Soya_US	Rapeseed_FR	Soya_BR	Soya_BR	Rapeseed_DE
Soya_US	Rapeseed_CN	Rapeseed_DE	Palm_MY	WCO_PT Lo	Palm_MY
Soya_BR	Soya_BR	Rapeseed_SP	Palm_CO	WCO_PT _Hi	Rapeseed_US
Rapeseed_DE	Rapeseed_DE	Palm_CO	Rapeseed_DE	Soya_US	Soya_AR
Rapeseed_FR	Rapeseed_US	Rapeseed_CN	Rapeseed_FR	Rapeseed_US	Rapeseed_FR
Rapeseed_CN	Rapeseed_FR	Soya_AR	Rapeseed_CN	Rapeseed_FR	Soya_BR
Rapeseed_SP	Soya_AR	Soya_BR	Rapeseed_SP	Rapeseed_CN	Rapeseed_CN
Rapeseed_US	Rapeseed_SP	Rapeseed_US	Rapeseed_US	Rapeseed_SP	Rapeseed_SP

Lowest impact

Highest impact

5.3.3 ADDRESSING UNCERTAINTY ASSOCIATED WITH LUC AND WCO COLLECTION

Up to this point, Climate Chance (CC) values used in the model for crop-based feedstocks did not include LUC and for WCO an average value for the collection was used. Nevertheless, as presented in section 4.4.3, CC for crop-based feedstocks and for WCO can vary depending on the LUC scenario associated with the crop cultivation and the type of WCO collection system implemented. In this section, we explore an approach to deal with the variation observed in LUC and the WCO collection.

The suggested approach to deal with the uncertainty associated with the lack of information about the LUC and the WCO collection system is to reformulate the CC objective as a chance-constrained constraint according to **equation 5.3**

$$\sum_{i\in I}(\overline{CC_i}\,QU_i) + \beta\sqrt{\sum_{i\in I} {QU_i}^2\sigma_{CCi}^2} \le \text{CC Limit value} \qquad \text{Eq. 5.3}$$

where $\overline{CC_i}$ is the average value of the CC impact and, σ_{CCi} is the standard deviation of the CC impact . $\overline{CC_i}$ is the average value of LUC between the pessimistic and optimistic scenario for each "feedstock_location" that was presented in Chapter 4 (table 4.3) and the best and worst case in terms of PI observed in the WCO collection systems. σ_{CCi} was calculated assuming a normal distribution and that the range of values between the optimistic/best and pessimistic/worst scenarios are located at 2*σ_{CCi} of the average value. The average and standard deviation values are presented in **Table 5.7,** as well as the savings relatively to the fossil fuel of each of the feedstocks. Analyzing each feedstock individually, considering the average value for CC, only the WCO systems comply with reduction targets (relatively to fossil fuel) defined in regulatory documents. In the EU, the RED establishes this reduction target to 50% for biofuels produced after 2016 (European Comission 2009) and in the US, the GHG threshold varies from 20% to 50% depending on the type of feedstock (Olivetti et al. 2014).

Table 5.7 Average value for CC and standard deviation of each oil system

Feedstock_origin	$\overline{CC_i}$ kg CO_2 eq /kg oil	σ_{CCi}	Savings relatively to fossil fuel (83.8 g CO_2 eq/MJ)
Palm_CO	2.72	0.96	13%
Palm_MY	3.56	0.76	-14%
Soya_AR	4.20	1.74	-35%
Soya_BR	7.02	2.63	-125%
Soya_US	2.32	0.55	25%
Rapeseed_DE	3.23	0.71	-4%
Rapeseed_FR	3.19	0.68	-2%
Rapeseed_SP	2.59	0.42	17%
Rapeseed_CN	4.12	1.11	-32%
Rapeseed_US	4.08	0.38	-31%
WCO_PT _Hi*	0.56	0.07	82%
WCO_PT_Lo**	0.16	0.07	95%

*High Quality Waste cooking oil

**Low Quality Waste cooking oil

To analyze which would be the blend that would comply with the regulatory targets, the constraint level of **equation 5.3** can be defined according to those targets. A 50% reduction target relatively to fossil fuel means that the oil blend must have at the most 1.395 g CO_2 eq kg^{-1} oil blend. This value was calculated based on the following data: fossil fuel comparator emissions 83.8 g CO_2 eq MJ^{-1} (European Comission 2009); biodiesel production (transesterification): 4.4 g CO_2 eq MJ^{-1} (Castanheira et al. 2015); biodiesel lower heating value: 37.2 MJ kg^{-1}.

Using 1.395 g CO_2 eq kg^{-1} oil blend as a threshold and setting the constraint confidence level to 95%, the problem is unfeasible. The maximum GHG reduction level possible (obtaining a feasible solution) is 33%. The blend obtained at this constraint level (Blend 8) is mainly composed of WCO (32%) and oil produced from rapeseed cultivated in Spain (49%) (Blend 8 in **figure 5.5**).

If only virgin oils are available, the maximum GHG reduction drops to 13%. As shown in **table 5.7,** the average value of the crop-based oils CC is higher than the required value to achieve a 50% reduction. Only WCO presents CC values that correspond to savings above the required. Although using WCO in the blends would allow higher GHG savings relatively to crop-based oils blends, the LUC associated with the virgin oils does not allow a blend that complies with the 50% GHG reduction thresholds.

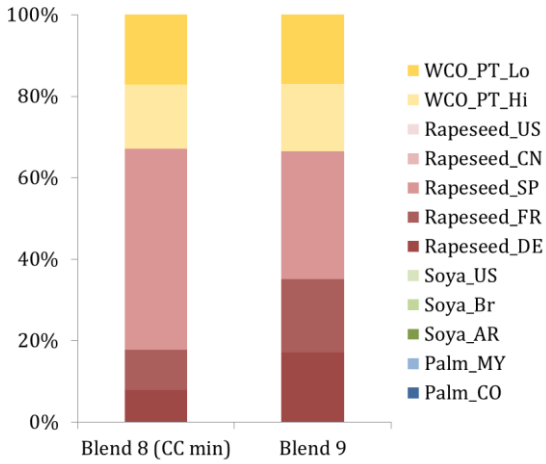

Figure 5.5 Blend 8 and blend 9 obtained using the CC objective as a chance-constrained using a confidence level of 95% and ignoring uncertainty.

Considering uncertainty associated with the LUC value comes at the cost of increasing all the other objectives. This can be observed by comparing blend 8, that was obtained with a confidence level set to 95%, with a blend obtained with without considering uncertainty (Blend 9). The composition of Blends 8 and 9 are presented in **figure 5.5** and their impact values in **table 5.8.** This table also shows the variation in the values of Blend 8 relatively to Blend 9. For all the impact categories, there is an increase in its value when LUC uncertainty is considered. This means that, considering uncertainty associated LUC using CPP, has resulted in a burdens shift. Blend 8 includes a higher quantity of feedstock with lower $\overline{CC_i}$ and standard deviation $\sigma_{CC\,i}$: oil produced from rapeseed in Spain

(Rapeseed_Sp). Since this feedstock has higher impacts for the other environmental impact categories, blend 8 has an increase of about 49% in the WSI, 3% for EU, 6% for AA and about 42% for HT and ET comparatively to the blend determined without taking into account the LUC uncertainty.

Table 5.8 Impact values for Blend 8 and Blend 9 and the relative variation for cost, CC, WSI, EU, AC, HT and ET

Objective	Blend 8 (CC min 95% conf level)	Blend 9 No uncertainty	Relative variation (%)
Cost (€/ton)	646.2	644.1	0.3
CC (kg CO_2 eq kg^{-1} oil)	2.1	2.1	0
WSI (m^3 eq kg^{-1} oil)	1.07	0.72	48.6
EU (kg P eq kg^{-1} oil $*10^{-4}$)	2.09	2.03	2.8
AA (kg SO_2 eq kg^{-1} oil$*10^{-2}$)	1.89	1.79	5.5
HT (CTUh kg^{-1} oil$*10^{-11}$)	111.57	78.36	42.4
FT (CTUhe kg^{-1} oil)	12.23	8.61	42
Quantity of WCO (%)	33	34	

Addressing LUC becomes even more complex if the indirect LUC are to be considered due to the lack of agreement on a methodology to use to quantify this value. Recently, the European Commission published Directive 2015/1513 recommending the use of values for indirect LUC for oil crops feedstocks (European Comission 2015): 55 g CO_2 eq MJ^{-1} representing 1.882 g CO_2 eq kg^{-1} oil blend. This value is above the 50% reduction threshold (1.395 g CO_2 eq kg^{-1} oil blend) limiting the use of this type of feedstocks individually or even in blends with WCO, that present very low CC impacts. **Figure 5.6** depicts the CC values for the crop-based feedstocks considering the average value for direct LUC and the indirect LUC value suggested by the RED. As one can see, the overall CC value is significantly above the 50% reduction threshold required.

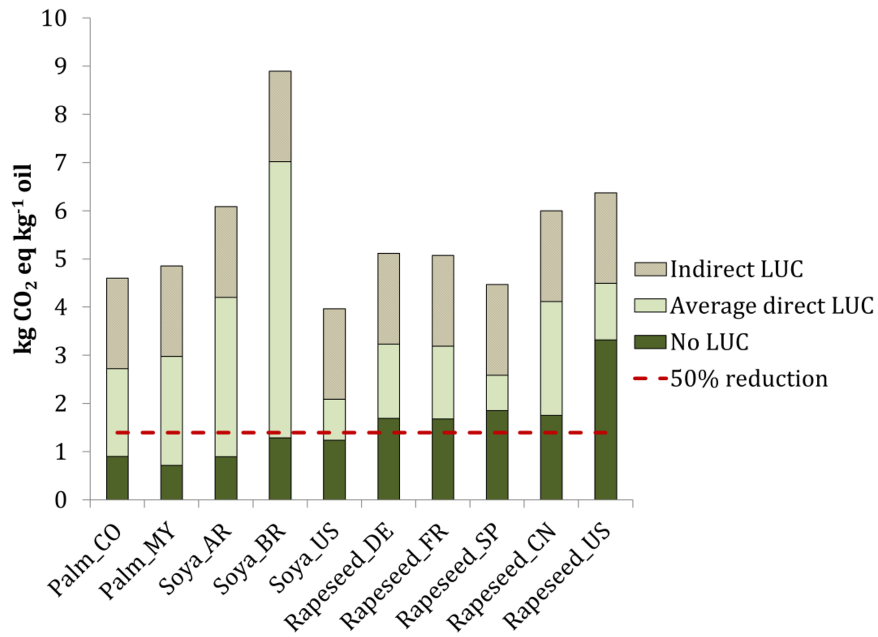

Figure 5.6 CC values without LUC, direct and indirect LUC for the different crop-based feedstocks

5.4 CONCLUDING REMARKS

In this chapter, a life-cycle multi-objective (LCMO) decision-aiding tool to assess the use of WCO in blends for biodiesel production and the tradeoffs between economic and environmental objectives was presented. The tool has the particularity to facilitate the decision process by allowing the decision-maker to decide based on an explicit overall environmental performance. Moreover, an approach to deal with uncertainty in the CC due to the lack of information about LUC was presented.

The decision-aiding tool developed showed to be useful to support decision-making by allowing visualization in a simpler manner of the tradeoff between cost and environmental impacts. Results show that the use of WCO in the blends can reduce both costs and environmental impacts relatively to blends composed only of crop-based oils. If uncertainty in CC due to the lack of information about LUC is considered may lead to decisions that result in a burdens shift, increasing other environmental impacts.

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6 CONCLUSIONS

6.1 MAJOR CONTRIBUTIONS AND KEY RESEARCH FINDINGS

This thesis explores opportunities to improve biodiesel cost effectiveness by assessing the use of waste-based feedstocks in biodiesel blends and hedging feedstock purchase, whilst managing environmental impacts. A Life-Cycle Multi-Objective (LCMO) model was developed to assess economic and environmental tradeoffs of feedstock blending decisions, addressing feedstock composition and price uncertainty. This model was built based on the following steps:

- Review and assessment of biodiesel properties prediction models based on the oils composition addressing compositional uncertainty;
- Integration of prediction models into an optimization blending model of conventional oils (palm, rapeseed and soya) and WCO, addressing the oils compositional uncertainty using chance-constrained programing;
- Development of a cost optimization model to minimize production cost variation by planned prices hedging informed by forecasted feedstock prices;
- Life-Cycle Assessment (LCA) of palm, soya, rapeseed and waste cooking oils addressing water use and GHG emissions impacts;
- Integration of the LCA results in the blending optimization model through the development of a stochastic LCMO model.

A major contribution of this thesis is the development of an uncertainty-aware decision aiding tool to assess economic and environmental tradeoffs of decisions at the operational level in biodiesel production, addressing feedstock compositional and price uncertainty. The tool was developed combining environmental LCA with blending models using multi-objective optimization towards novel engineering systems methodologies that allow the decision maker to decide based on an overall environmental performance. Although the tool was designed specifically for biodiesel systems, it can be adapted to other industries, particularly recycling industries and be used to support production planning at the operational level to enhance the technical, economic and environmental performance of these industries.

This tool was built using different models that can be used to improve biodiesel cost effectiveness. The chance-constrained blending model presented in chapter 2 showed that addressing feedstocks compositional uncertainty, secondary material such as WCO can be used in blends for biodiesel production without compromising technical performance and, consequently reduce production costs. This model can be further used to optimize the blending of alternative fatty-acid based feedstocks and to assess the viability of other waste-based feedstock (e.g. animal fat) or emerging feedstocks such as algae.

The cost optimization model presented in chapter 3 showed that managing feedstock price uncertainty using forecasted feedstock price information can reduce biodiesel production cost variation. The model can be used to manage cost variation in biodiesel production by supporting production planning decisions relatively to feedstock purchase, storage and use.

Both models (presented in chapter 2 and 3) were built upon a composition-based prediction model for biodiesel properties that was developed based on a review and assessment of existing models, incorporating compositional uncertainty. This review provided a quantified range of the variation of the results of existing models when considering the feedstocks compositional uncertainty and showed how the different models available in the literature reflect compositional uncertainty and, raised awareness on the importance of reporting the uncertainty associated with the prediction models.

This research also provides in chapter 4 an environmental life-cycle assessment of conventional and waste-based feedstocks used in biodiesel production, including GHG emissions and freshwater use impacts. Freshwater use impacts were assessed according to the ISO 14046 standard encompassing the consumption of freshwater (water scarcity footprint) and impact categories related to water pollution. The water scarcity footprint was calculated using the impact assessment method AWARE, recently developed by the WULCA working group. This group was formed under the auspices of the Life-cycle Initiative of the UNEP/SETAC and the AWARE method intends to be a consensus on water scarcity assessment. This study provided to the method developers feedback on their model, specifically on modelling options that define the characterization factors.

The key findings from this thesis are presented in the following paragraphs with respect to the research questions formulated in Chapter 1 (Table 1.1).

1. Can biodiesel production cost be reduced by the incorporation of WCO in blends for biodiesel production without compromising the biodiesel technical performance?

To assess the use of WCO in blends for biodiesel production a cost optimization blending model was developed based on a composition-based model to predict specific biodiesel properties. The following properties were considered: density, cetane number (CN), iodine value (IV), cold filter plugging point (CFPP) and Oxidative stability (OS). Existing prediction models exploring the underlying variability associated with the oils composition were assessed. The potential range given by the models was compared with values for the properties reported in the literature for the feedstocks considered: palm, rapeseed, soya and WCO.

The range of results obtained by the models was generally lower than the reference values because the results provided by the models do not reflect other sources of variability (impurities, the chemical process used, the clean-up process, the storage time and conditions prior to analysis) that may originate higher variation in the results obtained in real production. Another source of uncertainty that is not reflected in the models results is the model uncertainty. The studies reporting the models are lacking information about the uncertainty related to the model coefficients that would be useful for a more comprehensive analysis. Among the feedstocks analyzed, the highest variation was observed for the WCO results. This difference can be attributed to the high FA compositional variability of the WCO due to the diversity of oil type and origin. Nevertheless, the comparison of the results of the prediction models incorporating composition uncertainty with reference values allowed the selection of prediction models to be used in the blending optimization model.

The blending optimization model was developed to optimize (minimizing cost) blends of virgin and waste oils, addressing feedstocks compositional uncertainty using chance-constrained optimization. It was found that addressing compositional uncertainty allows the use of WCO in blends with conventional feedstocks without compromising the biodiesel technical performance. Total feedstock cost reduction was obtained for blends with WCO relatively to equivalent (with the same technical performance) blends composed only of virgin oils. This cost reduction depends on the relation among the prices of the feedstocks. In this study the cost reduction ranged from 1 to 10%. The use of low-cost feedstocks in a diversified portfolio of raw materials used in blending optimization models represents a cost reduction opportunity for the biodiesel producer without compromising the biodiesel quality.

2. Can production cost variation be reduced by planned prices hedging informed by forecasted feedstock prices?

To address feedstock price uncertainty a cost optimization model using forecasted prices information was developed. This model also considers the feedstock composition uncertainty. The model determines the optimal planning that minimizes total feedstock costs and cost variation, deciding the quantity to buy, store and use in a biodiesel production plant. Total cost and cost variation performance metrics were used to investigate and interpret the behavior of the model using different price trends (up and down). A reference model corresponding to a "no uncertainty" scenario is used as benchmark.

The proposed formulation proved to be useful in determining optimum planning for feedstocks acquisition, blending and storage that minimize the risks associated with feedstock price fluctuations. Results show that increasing the risk tradeoff parameter (α) leads to a reduction in the cost variation for both trends. For $\alpha=10$, the cost variation is the closest one could obtain to the no uncertainty scenario used as benchmark. It was also found that the use of WCO in the blends allows a reduction of cost variation reduction relatively to virgin oils blends. This was because, according to WCO price information provided by an European broker, this feedstock presents lower price volatility comparatively to conventional feedstocks like palm, rapeseed and soya oils.

Average cost reductions are observed when comparing the model that has no storage capacity with the model with storage capacity (without considering price uncertainty) for both price trends: about 1.25% for the uptrend and 0.16 % for the downtrend. When more weight is given to price risk (increasing α) different results are obtained for each price trend. In the uptrend, average inventory grows and average cost drops; clever inventory purchases can lead to savings, avoiding a purchase later at higher cost. Interestingly, in the downtrend case the savings decline as the α parameter rises. Increasing α places more emphasis on reducing cost risk. This, in turn, drives up average inventory. For the downtrend cases, purchases for inventory are on average more expensive than deferred purchases.

3. What are the life-cycle GHG emissions and water use impacts associated with different feedstocks?

A LCA of palm, soya, rapeseed and waste cooking oils including water use (water scarcity and degradability) and GHG emissions impacts was performed. Virgin oils systems include the cultivation, oil extraction, feedstock transportation and oil refining whereas for WCO, collection and refining. Data from crop cultivation in different locations were considered: Colombia and Malaysia for palm; Argentina, Brazil and United States for soybean; and, Germany, France, Spain, Canada and US for rapeseed. Water scarcity was assessed using two methods, considering midpoint characterization factors (CFs): one based on water stress indexes (WSIs) and the other on the AWARE indicator. Freshwater degradation was assessed for eutrophication (ReCiPe), aquatic acidification (IMPACT), and human toxicity and freshwater ecotoxicity (USETox).

The results obtained with the two methods used to assess the water scarcity footprint (WSI and AWARE) lead to similar conclusions in what concerns the highest and lowest water scarcity impacts; Rapeseed_SP presents the highest water scarcity footprint due to high water consumption and water scarcity of the country and WCO have the lower water scarcity impacts. Nevertheless, for oils systems with close results, the rank order given by each method is different. These differences are due to the characterization factor of each method as they were developed following different assumptions. WSI indicator is based on withdraw-to-availability ratio while the AWARE indicator is based on demand-to-availability ratio comprising ecosystems and human water demands. The AWARE method seems more adequate to support decision making since the

AWARE CFs were developed taking into account the water demand for both ecosystems and humans, thus addressing more comprehensively freshwater consumption impacts.

In terms of water degradability, Rapeseed_SP also presents the highest impacts for human and ecosystems toxicity due to a higher quantity of pesticide used in the cultivation. The highest acidification and eutrophication impacts were calculated for Rapeseed_US. This is due to the high use of fertilizers comparatively to other cultivation systems. WCO systems present the lowest impacts for freshwater degradation impacts with the exception of human toxicity-cancer.

CC results are highly influenced by the soil carbon change associated with different LUC scenarios. Higher variations between the pessimistic and optimistic LUC scenarios are obtained for rapeseed cultivation in the US and soybean in Brazil, US and Argentina. When soil carbon change is excluded, Rapeseed_US presents the highest impacts. For the virgin oils, cultivation is the stage contributing the most to the overall impacts due mainly to N_2O emissions from the application of nitrogen fertilizers. Extraction and refining steps have low contribution to the overall GHG emissions. The lower CC are obtained for the WCO systems.

The differences observed in the environmental assessment of the various virgin oils systems are mainly related to water scarcity of the location and the fertilization and pesticides schemes used in each crop/location. The choice of the locations with lower water scarcity to produce oil crops can be determinant for obtaining lower impacts. Additionally, optimizing fertilization schemes or choosing climatic conditions that require less fertilizers and pesticides will contribute to reduce the impacts profile of vegetable oils.

4. What are the environmental benefits of using WCO in biodiesel blends and the tradeoffs between costs and environmental impacts?

To assess the economic and environmental benefits of using of WCO in blends for biodiesel a Life-Cycle Multi-Objective (LCMO) was developed. Pareto optimal solutions (blends) that minimize total feedstock cost, Climate Change (CC) and Water Stress Index (WSI) were determined. An approach to visualize in a simpler manner the tradeoff between cost and environmental impacts when more environmental impacts are considered was developed. Uncertainty in the CC parameters due to LUC was also addressed.

The use of WCO in the blends reduces the ideal value of all the objectives except for human toxicity (HT) comparatively to the scenario were only virgin oils are available. The ideal values are 3% lower for cost and acidification (AA), 2% for climate change (CC), 32% for water stress index (WSI), 9% for eutrophication (EU) and 4% for ecotoxicity (FT). The quantity of WCO incorporated in the blends ranges from 10% to 34% depending on the objective being minimized. For human toxicity, since WCO is not the feedstock with lowest impact, the optimal blend obtained minimizing it does not include WCO in its composition.

The Pareto surface obtained minimizing costs, CC and WSI is displaced to lower costs when WCO is included in the blends meaning that lower CC and WSI solutions (located in the lower edge of the Pareto surface) can be obtained at a lower cost if WCO is included in the blends. When AA, EU, HT and FT are included the suggested approach was used and results show that lower environmental impacts at a lower cost are obtained when WCO is available.

The suggested approach facilitates the visualization of the tradeoffs between the economic and environmental performance and allows the decision-maker to decide based on an overall environmental performance when more than three objectives are considered. For example, if the decision-maker wants to have a performance that is half way between the anti-ideal and ideal value, the optimal blend obtained would have a cost increase of 0.3% relatively to the lower cost blend (higher environmental impacts) but a reduction of 15% in AC, 13% on CC, 40% on WSI, 45% on EU, 50% on HT and 72% on FT relatively to the anti-ideal value. The best environmental performance blend would correspond to a cost increase of 3.5% relatively to the lowest cost blend.

It should be noted that the results obtained correspond to a single period price – July 2013. This period was selected to illustrate the model because it is the month when the price of WCO is closer to the virgin oils price, representing a more conservative situation to evaluate the cost benefits of WCO. Nevertheless, although in the other periods the use of WCO is excepted to be beneficial, the type and quantity of each feedstock used in the blend may change and consequently, the environmental impacts of the blends may also be different.

Another aspect addressed in this work was the uncertainty associated with the CC due to LUC scenarios and the WCO collection. The suggested approach reformulates the CC objective as a chance-constrained constraint. It was found that the maximum GHG reduction relatively to fossil fuel would be 33% using a blend mainly composed of WCO (32%) and Rapeseed_SP (49%). This value would drop to 13% if only virgin oils are available. Nevertheless, although using WCO in the blends would allow higher GHG savings relatively to crop-based oils blends, the LUC associated with the virgin oils does not allow a blend that complies with GHG thresholds required by the EU or the US (50%).

Advantages of collection and use of WCO for biodiesel production such as the fact that it avoids its disposal through sewage systems, reducing economic and environmental burdens by hindering sewage treatment at wastewater treatment plants had already been identified by some authors (Ortner et al. 2016). In this research it is shown that blending WCO with crop-based oils is an attractive approach to improve biodiesel cost effectiveness and simultaneously manage environmental performance. The different models developed tackled several issues that can be restraining of improving the biodiesel cost effectiveness and, as illustrated along the thesis, they can be used to support production planning decisions towards a more sustainable production.

6.2 LIMITATIONS AND FUTURE RESEARCH

The work developed in this thesis presents some limitations from which a number of topics can be developed in future research:

The technical constraints considered were defined based on composition-based models but some properties, specifically OS and CFPP, can be highly influenced by minor components. Consequently, their prediction just based on the composition may not be accurate. The calibration of the models with real production data would be useful to increase the accuracy and precision of the models. This would also allow the identification of differences in the composition of the same crop species but originated in different regions and build a regional composition profile.

A regional composition profile could then be mapped to regional/country requirements. The results were obtained using technical constraints thresholds based on European regulation but they can be adapted to other worldwide standards. For example in the US regulation there is no threshold for IV and for OS the limit is lower. Also, the CFPP limit value can be defined according to the type of climate. Moreover, OS and CFPP (that are biding properties in the model) can be enhanced using additives and so, explore the model developed in this work together with these techniques would provide a more complete framework to optimize the blends or assess the viability of other waste-based feedstock (e.g. animal fat) or emerging feedstocks such as algae.

The regional compositional profile could also be mapped to regionalized impacts. This is particularly relevant for water scarcity assessment. In this thesis, the characterization factors used were at the country level but CFs more spatially and temporally differentiated should be used for a more accurate assessment. This would also imply to gather regionalized data for the cultivation of the different feedstocks and regions. It was also assumed that the feedstocks would be used for biodiesel production in Portugal but other production sites can be assessed.

Since different cultivation locations were analyzed, but without this being reflected in the feedstock price, a point to explore in future research is to expand the model to a supply chain perspective. Additionally, a study that models future feedstock prices based on their environmental performance could provide useful information to design policies to financially support biodiesel production in a more cost-effective way.

The multi-objective analysis was performed for only one price period. The month selected represents a more conservative situation to analyze the benefits of WCO because it was when lower differences between the WCO and virgin oils prices was observed. Nevertheless, a more comprehensive analysis can be made considering all the months available and alternative price trajectories (e.g. if the WCO price is not always lower than all the virgin oils).

To increase robustness of results it could be considered the incorporation of parameter uncertainty in the LCA. This could be done by attributing adequate probability distributions to the input parameters either by data collection or expert judgment and conduct uncertainty propagation using for example, Monte Carlo simulation. Probabilistic triage can then use simulation results to assess the contribution of each input to the variance of the calculated impact. Stochastic optimization techniques should then be explored to incorporate this uncertainty in the optimization model. These techniques could be approaches used in this thesis (e.g. chance-constrained) or others like the two-stage resource programming.

Finally, although this thesis provides contribution towards improving insights into economic and environmental realms of biodiesel production, social aspects should also be investigated. The increasing consumption of biodiesel creates extra demand for new farmland, which leads to deforestation and land seizing, causing vulnerable communities to be displaced from their homes, and, an increase in the price of food crops, exacerbating food price volatility and hunger.

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APPENDIX I: CORE ARTICLES FOR PHD THESIS (ABSTRACTS)

A Multiobjective Model for Biodiesel Blends Minimizing Cost and Greenhouse Gas Emissions

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Abstract

The goal of this paper is to present a multiobjective model to optimize the blend of virgin oils for biodiesel production, minimizing costs and life-cycle Greenhouse Gas (GHG) emissions. Prediction models for biodiesel properties based on the chemical composition of the oils were used to establish technical constraints of the model. Biodiesel produced in Portugal from palm, Rapeseed and/or soya was used as a case study. The model was solved using the Ɛ-constraint method and the resulting Pareto curve reveals the tradeoff between costs and GHG emissions, from which it was possible to calculate GHG abatement costs. Illustrative results are presented: GHG emissions (not accounting for direct and indirect Land Use Change -LUC) and biodiesel production costs (focused on oil feedstock). Analyzing the blends along the Pareto curve, a reduction in GHG emissions is obtained by progressively replacing Rapeseed by soya and reducing the palm share in the blend used for biodiesel production.

Keywords: Biodiesel, blend, Life-Cycle, Greenhouse Gas (GHG), Multiobjective model.

Biodiesel from Waste Cooking Oils in Portugal: alternative collection systems

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Abstract

Waste Cooking Oils (WCO) have been gaining prominence as an alternative feedstock for biodiesel production due to is potential to reduce the economic and environmental costs of biodiesel produced with biomass. However, there are various types of WCO collection with different collection efficiency and environmental impacts. The aim of this paper is to present an environmental assessment of biodiesel from WCO addressing different collection schemes in Portugal. The implications of alternative allocation approaches (no allocation, mass allocation, energy allocation and economic allocation) in the final results are also assessed. Life-cycle Impact Assessment was calculated (ReCiPe method) for: Climate Change (CC); Terrestrial Acidification (TA); Marine Eutrophication (ME) and Freshwater Eutrophication (FE). WCO collection contribution for the overall impacts ranged significantly for the various collection system and impact categories. The application of different allocation approaches led to differences in the results up to 11%. A comparison between the GHG emissions calculated for biodiesel from WCO and the typical and default values presented in the Renewable Energy Directive (RED) was performed. The GHG emission saving for biodiesel from WCO collected in Portugal ranged from 81 to 89%.

Keywords: waste collection; Life-cycle Assessment (LCA); Waste Cooking Oil (WCO); allocation

Incorporating uncertainty in the Life-cycle Assessment of biodiesel from Waste Cooking Oil addressing different collection systems

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Abstract

Waste Cooking Oil (WCO) is increasing prominence as a feedstock for biodiesel production due to its potential in reducing costs and environmental impacts of biodiesel when compared with virgin oils. However, several life-cycle studies have reported a wide range of WCO biodiesel impacts, mainly due to the WCO collection stage, which has not been discussed in the literature. The lack of a comprehensive assessment of the collection stage influence on biodiesel overall impacts motivates this article, in which a detailed Life-Cycle Assessment (LCA) of biodiesel produced from WCO addressing different collection systems is presented. An inventory for WCO collection was implemented for different systems in the domestic and the food service industry sectors in Portugal as well as for biodiesel companies. The characterization and incorporation of the variation associated with WCO collection systems, parameter uncertainty and variability, as well as modelling options was performed. A wide range of impacts was calculated. Two factors contribute the most to the variation observed: the WCO collection efficiency and the characteristics of the collection system (e.g. sector, type of collection and population density). Results show that WCO collection cannot be neglected or simplified when assessing the overall environmental performance of biodiesel produced from WCO.

Keywords: Waste collection; Biodiesel production, Waste Cooking Oil, Multifuncionality, Domestic sector; Food service

Blends for biodiesel production: influence of technical constraints in GHG reduction and Cost effectiveness

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Abstract

Many vegetal oil feedstocks can be used for biodiesel production. The choice of the actual blend (mix of oils) has an important impact on the cost and environmental performance of the biodiesel produced. This paper aims at determining the optimal blend by means of mathematical programming that allows assessing the influence of technical constraints allocated to decision objectives: GHG emissions and production costs. The technical constraints control biodiesel properties based on the feedstocks chemical composition, taking into account inherent compositional uncertainty (using chance-constrained programming). For this purpose, an algorithm for the allocation of shadow prices to the constituent parts of the composite objective function is implemented. The information obtained from the shadow prices allowed the identification of the limiting technical properties for GHG reduction and cost effectiveness. Moreover, it can be used as a guideline for evaluating the efficiency of technical progress or policy mandatory measures relatively to the cost and GHG emissions of the biodiesel production process.

Keywords: Biodiesel blends, Uncertainty, Chance-constrained programming, Shadow prices, Multiobjective programming

Fatty Acid based prediction models for biodiesel properties incorporating compositional uncertainty

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Abstract

Biodiesel is globally produced by transesterification of vegetable oils. Each vegetable oil possesses a typical fatty acid (FA) profile that will influence the final properties of the biodiesel. Models have been developed to express the relation between the FA composition and the fuel properties. However, as the FA sources are variable and because the attributes of a FA source are not always fully characterized, this variability translates into uncertainty for the production planner. This paper explores the underlying variability associated with the FA composition and assesses the results of these models incorporating FA compositional uncertainty. Models for viscosity, density, cetane number, iodine value, cold filter plugging point and oxidative stability were considered. The potential range of properties given by the models was compared with values reported in the literature. The main goal is to assess the influence of compositional uncertainty and the potential existence of systematic deviations in the results provided by these models. This assessment can be used to improve production plans with tools that account for compositional uncertainty and variability, allowing the biodiesel producer planner to determine blends that minimize the risk of noncompliance with the technical requirements.

Keywords: Biodiesel properties, compositional uncertainty, prediction models

Planning strategies to address operational and price uncertainty in biodiesel production

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Abstract

The use of low-cost feedstocks such as waste cooking oil (WCO) has been gaining prominence in biodiesel production due to their potential to improve the economic and environmental performance of biodiesel compared with conventional feedstocks. However, the low available quantity and the high compositional variability of WCO (due to high diversity of sources) hinders guaranteeing biodiesel quality and may result in significant market limitations. A potential strategy to address these limitations and that is presented and discussed in this paper is to use stochastic blending models to optimize the blend of secondary (WCO) and primary material (virgin oils like palm, rapeseed and soya), managing the compositional variation. Another source of uncertainty considered in this research was the uncertainty associated with the feedstocks price, which may compromise the biodiesel cost effectiveness, by threatening the long term financial stability of the producers. A cost optimization model that incorporates chance-constrained (CC) formulation to account for compositional variability and uses forecasted prices information to address feedstock price uncertainty was implemented. The model was developed to support production planning decisions to minimize cost and cost variation in biodiesel production. The proposed approach proved to be useful in determining optimum planning for feedstocks acquisition, blending and storage that minimize the risks associated with feedstock price fluctuations. Results show that addressing the compositional uncertainty using the CC formulation allows the use of WCO in biodiesel blends without compromising the technical performance.

Keywords: waste cooking oil, feedstock blending, forecast models, time series analysis, compositional uncertainty, optimization

Water footprint profile of crop-based vegetable oils and waste cooking oil

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Abstract

Purpose

The main goal of this paper is to perform a comparative water footprint (WF) profile of vegetable oils used for biodiesel production. The profile includes the water scarcity footprint related to freshwater consumption and the environmental impacts due to freshwater degradation. Two methods to assess the water scarcity footprint are adopted to determine whether the methods lead to the same conclusions.

Methods

The WF profile of four feedstocks used for biodiesel production (palm, soya, rapeseed and waste cooking oil (WCO)) was performed following ISO 14046 guidelines. Virgin oils systems include the cultivation, oil extraction, feedstock transportation and oil refining whereas for WCO, collection and refining. Data from crop cultivation in different locations were considered: Colombia and Malaysia for palm; Argentina, Brazil and United States for soybean; and, Germany, France, Spain, Canada and US for rapeseed. The water scarcity footprint was assessed using two methods, considering midpoint characterisation factors (CFs): one based on water stress indexes (WSIs) and the other on the AWARE indicator. A sensitivity analysis on the influence of using different AWARE CFs was performed. Freshwater degradation was assessed for eutrophication (ReCiPe), aquatic acidification (IMPACT), and human toxicity and freshwater ecotoxicity (USETox).

Results and discussion

Both WSI and AWARE methods used to assess the water scarcity footprint lead to similar conclusions regarding the system with higher freshwater consumption impact and the stage contributing the most to this impact: cultivation. However, for the oils systems whit closer results, the rank order given by each method is different due to the

CFs of each method; WSIs are calculated based on withdrawal-to-availability ratios, rather than on demand-to-availability ratios (using human consumption instead of withdrawals) of freshwater. In addition, the AWARE CFs also comprise ecosystem and human water demands, representing the environmental impacts due to freshwater consumption more comprehensively than WSIs. The freshwater degradation impacts of virgin oils are mainly caused by fertilizers and pesticides used in cultivation. WCO systems present the lower impacts for all categories with exception of human toxicity-cancer.

Conclusions

The water footprint profile of the various oils systems shows that freshwater scarcity and degradation impacts are strongly related to the crop cultivation location and the fertilisation and pesticides schemes used. The water footprint scarcity rank order obtained with the WSI and AWARE methods present some differences. Nevertheless, the AWARE method seems more adequate to support decision making since the AWARE CFs were developed taking into account water demand.

Keywords: biodiesel, life-cycle assessment, water footprint, water scarcity, vegetable oils

A life-cycle multi-objective decision aiding tool to assess the use of waste cooking oil in biodiesel production

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Abstract

The controversy raised around biofuels sustainability increased the pressure on biodiesel producers to be as cost-efficient as possible and, simultaneously, ensure the sustainability of the biodiesel. As about 85% of biodiesel production costs are attributed to feedstock cost and each feedstock has a different environmental profile, operational level decision making about feedstock selection is crucial to reduce production costs and manage biodiesel environmental performance. This paper explores opportunities to reduce production costs at the operational level, particularly at the feedstock selection process, by assessing the use of waste cooking oil in blends with conventional feedstocks, whilst managing environmental impacts. A life-cycle multi-objective model was developed combining environmental life-cycle assessment with blending models using multi-objective optimization. Moreover, an approach to facilitate the decision process by enabling the decision-maker to decide based on an explicit overall environmental performance is presented. Results show that the use of WCO in the blends can benefit both costs and environmental impacts relatively to blends composed by conventional oils. The decision-aiding tool developed showed to be useful to support decision-making by allowing visualization in a simpler manner of the tradeoff between cost and environmental impacts.

Keywords: biodiesel, environmental impacts, feedstock selection, optimization

APPENDIX II: FULL LIST OF PUBLICATIONS

1. Articles in internationally reviewed scientific journals

1.1. Published

1. Caldeira, C., Gülsen, E., Olivetti, E. A., Kirchain, R., Dias, L., Freire, F. (2014). "A Multiobjective model for biodiesel blends minimizing cost and Greenhouse Gas emissions". Computational Science and Its Applications. Lecture Notes in Computer Science. Vol. 8581, pp 653-666. http://dx.doi.org/10.1007/978-3-319-09150-1_48

2. Caldeira, C., Queirós, J., Freire, F. (2015). "Biodiesel from Waste Cooking Oils in Portugal: alternative collection systems". Waste and Biomass Valorization, vol. 6 (5), pp. 771-779. http://dx.doi.org/10.1007/s12649-015-9386-z

3. Caldeira, C., Queirós, J., Noshadravan, A., Freire, F. "Incorporating uncertainty in the Life-cycle Assessment of biodiesel from Waste Cooking Oil addressing different collection systems". Resources, Conservation and Recycling vol. 112, pp. 83-92 http://dx.doi.org/10.1016/j.resconrec.2016.05.005

4. Caldeira, C., Freire, F., Olivetti, E., Kirchain, R. (2017) "Fatty Acid based prediction models for biodiesel properties incorporating compositional uncertainty". Fuel 196C pp. 13-20 http://dx.doi.org/10.1016/j.fuel.2017.01.074

1.2. Submitted or in final preparation for submission to ISI Journals

5. Caldeira, C., Freire, F., Kremmydas D., Rozakis, S. "Blends for biodiesel production: influence of technical constraints in GHG reduction and Cost effectiveness" (submitted)

6. Caldeira, C., Swei, O., Dias, L., Freire, F., Olivetti, E., Kirchain, R. "Planning strategies to manage production cost and cost variation of biodiesel production addressing operational and price uncertainty" (in final preparation)

7. Caldeira, C., Quinteiro, P., Castanheira, E.G., Boulay, A-M., Dias, A.C, Arroja, L., Freire, F. "Waterfootprint profile of vegetable oils for biodiesel production" (submitted)

8. Caldeira, C., Olivetti, E., Kirchain, R., Freire, F., Dias, L., "A life-cycle multi objective decision tool to incorporate waste cooking oil in biodiesel production" (in final preparation)

2. Refereed conferences and proceedings

1. Caldeira, C., Quinteiro, P., Castanheira, E.G., Boulay, A-M., Dias, A.C, Arroja, L., Freire, F. (2016) "Water footprint profile of virgin and waste cooking oils: assessing freshwater degradation and comparing the WSI and the AWARE methods to address scarcity impacts" SETAC Europe 22nd LCA Case Study Symposium, September 20-22 Montpellier, France (Oral Presentation)

2. Caldeira, C., Olivetti, E., Kirchain, R., Dias, L., Freire, F. (2016) A Life-cycle Multi-objective Decision Tool to Incorporate Waste Cooking Oil in Biodiesel Production." Gordon Research Conference on Industrial Ecology June 19 - 24, Stowe, United States (Poster presentation)

3. Caldeira, C., Olivetti, E., Kirchain, R., Dias, L., Freire, F. (2016) "A life-cycle multi-objective model to assess the use of secondary material in biodiesel production." Gordon Research Seminar on Industrial Ecology June 18 - 19, Stowe, United States (Oral Presentation)

4. Caldeira, C., Olivetti, E., Kirchain, R., Dias, L., Freire, F. (2015) "Stochastic multiobjective optimization for biodiesel blends using waste cooking oil." LCM 2015 - 7th International Conference on Life-cycle Management, August 30–September 2, Bordeaux, France (Poster presentation)

5. Caldeira, C., Dias, L., Freire, F., Olivetti, E., Kirchain, R. (2015) "Stochastic optimization for biodiesel blends using waste cooking oil." ISIE 2015 – 8th Conference of the International Society for Industrial Ecology, July 7 - 10, University of Surrey, Guildford, UK (Oral Presentation)

6. Caldeira, C., Dias, L., Freire, F., Kremmydas, K., Rozakis, S. (2015)"Allocating shadow prices in a multi objective chance-constrained model for biodiesel blending." Energy for Sustainability 2015 – Designing for People and the Planet, May 14-15, Coimbra, Portugal. (Oral Presentation)

7. Caldeira, C., Dias, L., Freire, F., Olivetti, E., Kirchain, R. (2015). "Cost optimization of biodiesel blends of waste and virgin oil addressing feedstock

compositional variability and life cycle impacts". 2nd Discussion Forum on Industrial Ecology and Life-Cycle Management, 5-6 March, Coimbra, Portugal.

8. Caldeira, C., Gülsen E., Olivetti E. A., Kirchain R., Dias L., Freire F. (2014) "A Multiobjective model for biodiesel blends minimizing cost and Greenhouse Gas emissions." International Conference on Computer Science and Applications, June 30 – July 3, Guimarães, Portugal (Oral presentation)

9. Caldeira, C., Gülsen, E., Olivetti, E., Kirchain, R., Dias, L., Freire, F. (2014). "A multiobjective model for biodiesel blends minimizing cost and greenhouse gas emissions". Discussion Forum on Industrial Ecology and Life-Cycle Management. 7-8 April. Coimbra. Portugal (Oral presentation)

10. Caldeira, C., Queirós, J., Castanheira, É., Freire, F. (2013)"GHG emissions analysis of biodiesel from waste cooking oil in Portugal." Energy for Sustainability 2013, Sustainable Cities: Designing for People and the Planet, September 8-10, Coimbra, Portugal. (Oral presentation)

11. Queirós, J., Caldeira, C., Castanheira, É. Freire, F. (2013) "Life-cycle energy and GHG assessment of biodiesel from waste cooking oil, addressing alternative collection scenarios." CILCA 2013, V Conferência Internacional sobre ACV na América Latina , March 24 - 27, Mendoza, Argentina (Oral presentation)

12. Caldeira, C., Gülsen, E., Olivetti, E.Castanheira, É., Figueiredo, F., Malça, J., Dias, L., Kirchain, R., Freire, F. (2012) "Capturing Uncertainty in Biofuels for Transportation. Resolving Environmental Performance and Enabling Improved Use." Gordon Research Conference on Industrial Ecology, Les Diablerets, Switerzland, June 18 – 22 (Poster presentation)

APPENDIX III: FATTY ACID COMPOSITION PROFILE

Table A.III.1 Fatty Acid (FA) composition profile (average-μ and standard deviation-σ) of biodiesel (FAME) produced from Palm, Rapeseed, Soya, and WCO (adapted from Hoekman et al. 2012).

Fatty Acid			Palm		Rapeseed		Soya		WCO	
Common Name	**Nomenclature (CX:Y)***	**j-index**	**μ**	**σ**	**μ**	**σ**	**μ**	**σ**	**μ**	**σ**
Caprylic	C8:0	1	0.1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Capric	C10:0	2	0.1	n.a.	0.6	n.a.	n.a.	n.a.	n.a.	n.a.
Lauric	C12:0	3	0.3	0.1	0.1	0.1	0.1	0.2	0.2	0.6
Myristic	C14:0	4	1.1	0.5	n.a.	n.a.	0.1	0.2	0.8	0.6
Palmitic	C16:0	5	42.5	3.2	4.2	1.1	11.6	2.0	16.5	5.6
Palmitoleic	C16:1	6	0.2	0.1	0.1	0.1	0.2	0.3	0.9	1.1
Heptadecenoic	C17:0	7	0.1	n.a.	0.1	n.a.	0.1	0.1	0.1	0.1
Stearic	C18:0	8	4.2	1.1	1.6	0.7	3.9	0.8	7.1	3.9
Oleic	C18:1	9	41.3	2.9	59.5	7.8	23.7	2.4	44.6	9.3
Linoleic	C18:2	10	9.5	1.8	21.5	2.8	53.8	3.5	25.1	10.3
Linolenic	C18:3	11	0.3	0.1	8.4	1.3	5.9	2.6	1.1	1.1
Arachidic	C20:0	12	0.3	0.1	0.4	0.5	0.3	0.3	0.3	0.1
Gondoic	C20:1	13	0.1	0.1	2.1	3.0	0.3	0.1	0.5	0.1
Eicosatrienoic	C20:2	14	n.a.	n.a.	0.1	n.a.	n.a.	n.a.	n.a.	n.a.
Behenic	C22:0	15	0.1	n.a.	0.3	0.3	0.3	0.2	0.4	0.2
Erucic	C22:1	16	n.a.	n.a.	0.5	0.5	0.1	0.1	0.1	0.1
Lignocric	C24:0	17	0.1	n.a.	0.1	n.a.	0.1	0.1	0.2	0.2
Nervonic	C24:1	18	n.a.	n.a.	0.1	0.1	0.3	0.6	4.4	n.a.
No of References			**27**		**20**		**39**		**19**	

* CX:Y is associated with each FA, where X is the number of carbon atoms and Y the number of carbon–carbon double bonds in the FA chain
n.a.- not applicable

APPENDIX IV: DISTRIBUTIONS AND HISTOGRAMS

Table A.IV.1 FAs distribution, number of observations used establish the distribution, value of the statistic test of goodness-of-fit Anderson-Darling and parameters of the distribution.

Fatty Acid		Feedstock	No observations	Distribution	Goodness of fit statics Anderson-Darling	Distribution parameters
Lauric	12:0	Palm	18	Lognormal	0.5452	Mean=0.34516, Std. Dev.=0.29315, Location=-0.1001
Myristic	14:0	Palm	21	Logistic	1.3540	Mean=1.05151, Scale=0.22284
		Soya	21	Max Extreme	1.5384	Likeliest=0.05887, Scale=0.09737
		WCO	18	Lognormal	0.4058	Mean=0.87396, Std. Dev.=1.05963, Location=0
Palmitic	16:0	Palm	26	Logistic	0.3400	Mean=42.46969, Scale=1.70526
		Rapeseed	20	Weibull	0.2661	Location=0.95421, Scale=3.65102, Shape=3.40059
		Soya	37	Max Extreme	1.1615	Likeliest=10.69528, Scale=1.76399
		WCO	21	Lognormal	0.2911	Mean=16.5691, Std. Dev.=6.15231, Location=4.35352
Palmitoleic	16:1	Soya	18	Max Extreme	1.0584	Likeliest=0.11543, Scale=0.15096
		WCO	17	Max Extreme	0.6318	Likeliest=0.51259, Scale=0.60306
Stearic	18:0	Palm	27	Logistic	0.6347	Mean=4.18125, Scale=0.58985
		Rapeseed	20	Logistic	0.4878	Mean=1.57923, Scale=0.39065
		Soya	38	Logistic	0.3405	Mean=3.95807, Scale=0.44824
		WCO	20	Lognormal	0.3136	Mean=7.36076, Std. Dev.=5.35326, Location=2.53383
Oleic	18:1	Palm	27	Logistic	0.3161	Mean=41.38462, Scale=1.537
		Rapeseed	19	Min Extreme	0.7722	Likeliest=62.31661, Scale=3.99486
		Soya	38	Logistic	0.5419	Mean=23.57532, Scale=1.11588
		WCO	21	Weibull	0.3418	Location=10.2472, Scale=37.85542, Shape=4.17407

Table A.IV.1 (cont) -FAs distribution, number of observations used establish the distribution, value of the statistic test of goodness-of-fit Anderson-Darling and parameters of the distribution.

Fatty Acid		Feedstock	No observations	Distribution	Goodness of fit statics Anderson-Darling	Distribution parameters
Linoleic	18:2	Palm	27	Logistic	0.3653	Mean=9.581, Scale=0.97866
		Rapeseed	20	Logistic	0.3620	Mean=21.52184, Scale=1.47283
		Soya	37	Logistic	0.8908	Mean=53.78714, Scale=1.70086
		WCO	21	Logistic	0.3099	Mean=26.37044, Scale=6.54395
Linolenic	18:3	Palm	21	Lognormal	0.7921	Mean=0.27909, Std. Dev.=0.14936, Location=0
		Rapeseed	17	Logistic	0.5667	Mean=8.36295, Scale=0.72507
		Soya	36	Min Extreme	1.3257	Likeliest=6.95598, Scale=1.65131
		WCO	19	Weibull	0.8485	Location=-0.00523, Scale=1.19962, Shape=1.06667
Arachidic	20:0	Soya	17	Logistic	0.8406	Mean=0.3234, Scale=0.13539

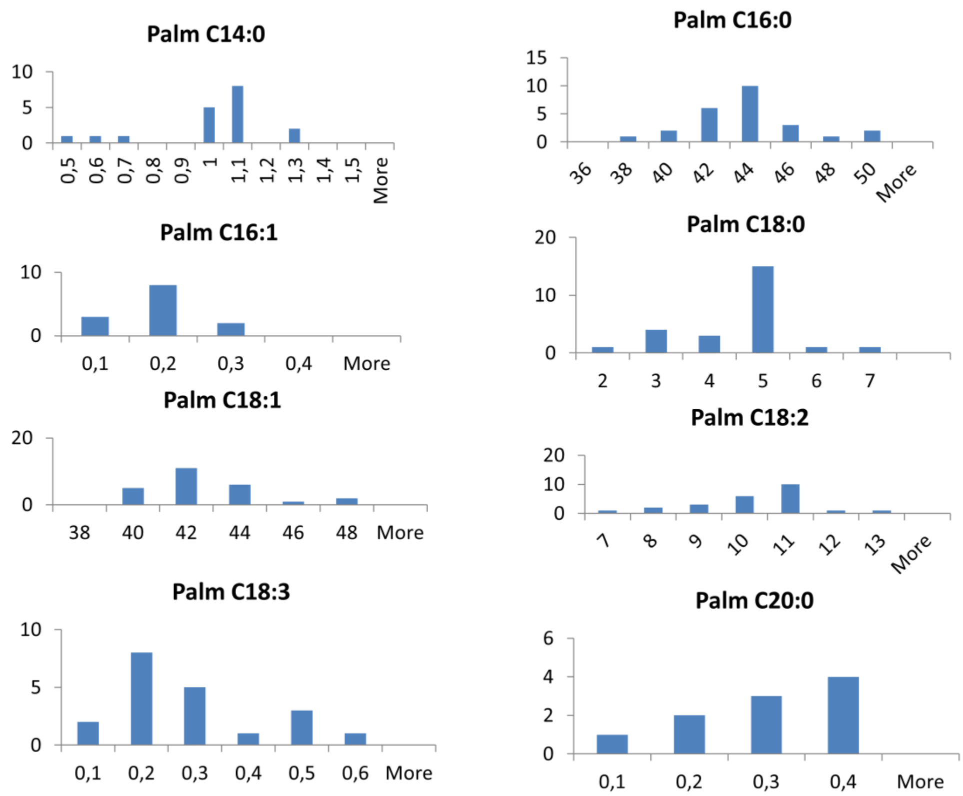

Figure A.IV.1 Histograms of the compositional data for palm

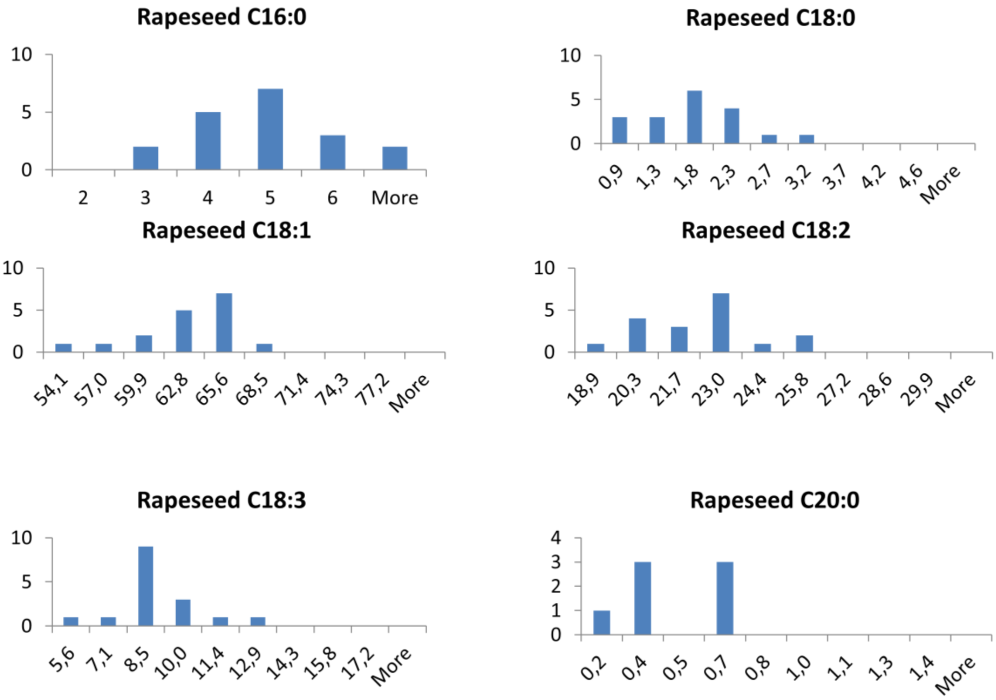

Figure A.IV.2 Histograms of the compositional data for Rapeseed

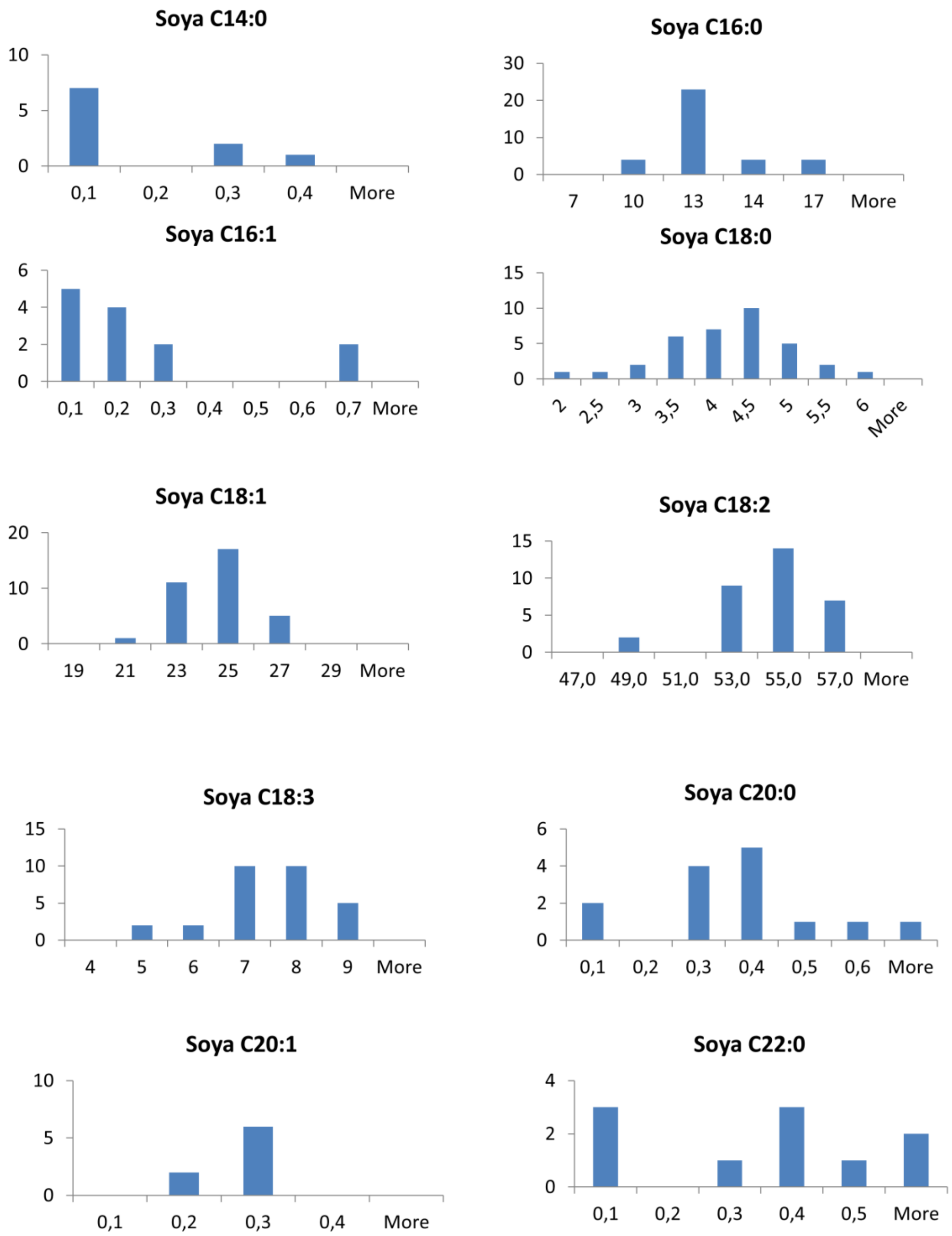

Figure A.IV.3 Histograms of the compositional data for soya

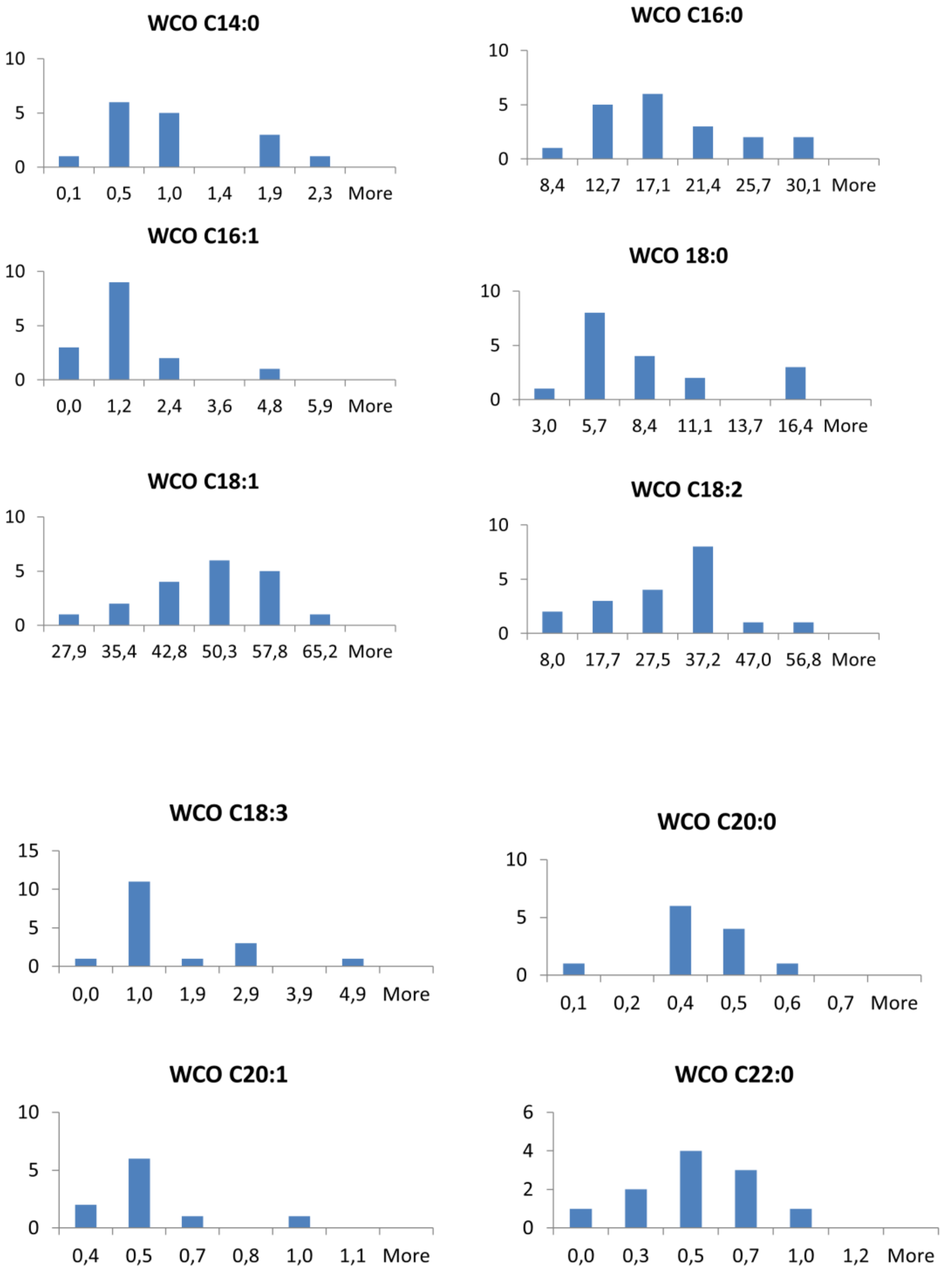

Figure A.IV.4 Histograms of the compositional data for WCO

APPENDIX V: BIODIESEL PROPERTIES VALUES

Table A.V.1 Density, cetane number, iodine value and cold filter plugging point values (average- μ. and standard deviation-σ) of biodiesel (FAME) produced from Pal,. Rapeseed, Soya and WCO adapted from (Hoekman et al. 2012) and oxidative stability adapted from (Giakoumis 2013).

Property	**Palm**		**Rapeseed**		**Soya**		**WCO**	
	μ	**σ**	**μ**	**σ**	**μ**	**σ**	**μ**	**σ**
Density (kg m^{-3})	873	8	879	10	882	7	879	10
CN	61.9	3.6	53.7	2.9	51.3	4.6	56.9	4.2
IV(g I_2/100 g)	54	6.1	116.1	6.7	125.5	5.4	88.9	16.2
CFPP (ºC)	9	5	-12	6	-4	2	1	5
OS (hours)	11.4	2.38	7.4	1.81	5	2.59	5.0	3.28
No of References	**27**		**20**		**39**		**19**	

APPENDIX VI: BIODIESEL BLENDING OPTIMIZATION MODEL PARAMETERS

Table A.VI.1 Parameters used in the model for each technical constraint. For FA j=1,2,3 and 7 there is no coefficient for the properties and for the sake of simplicity are excluded from the table

Property $l \in L$ **(with lower bound)**	**Property** $m \in M$ **(with upper bound)**	**Prop Coef for each j** 4 C14:0	5 C16:0	6 C16:1	8 C18:0	9 C18:1	10 C18:2	11 C18:3	12 C20:0	13 C20:1	14 C20:2	15 C22:0	16 C22:1	17 C24:0	18 C24:1	**Property Constant**	**Property Threshold** a)
Dens	Dens	n.a.	n.a.	0.917	n.a.	0.917	0.183	0.275	n.a.	0.917	0.183	n.a.	0.917	n.a.	0.917	869.3	860/900
CN	n.a.	0.088	0.133	-0.101	0.152	-0.039	-0.243	-0.395	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	61.1	51
n.a.	OS b)	n.a.	n.a.	n.a.	n.a.	n.a.	1	1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0	34.59
n.a.	IV	n.a.	n.a.	0.95	n.a.	0.860	1.732	2.616	n.a.	0.785	n.a.	n.a.	0.723	n.a.	n.a.	0	120
n.a.	CFPP	n.a.	0.314	n.a.	1.57	n.a.	n.a.	n.a.	3.14	n.a.	n.a.	4.71	n.a.	6.28	n.a.	-16.5	0 c)

a) Threshold stablished according the EN 14214 (CEN 2008)

b) based on the rearrangement of equation 2.11

c) Grade B for temperate climates

n.a. - not applicable

APPENDIX VII: MAIN INPUT INVENTORY DATA

Table A.VII.1 Main inventory data for the cultivation of 1 kg of palm fruit, soybean and Rapeseed in different locations.

	Palm Fruit Colombia (Castanheira et al. 2014)	**Palm Fruit Malaysia** (Jungbluth et al. 2007)	**Soybean Argentina** (Castanheira and Freire 2013)	**Soybean Brazil** (Castanheira et al. 2015)	**Soybean US** (Jungbluth et al. 2007)	**Rapeseed Germany** (Malça et al. 2014)	**Rapeseed France** (Malça et al. 2014)	**Rapeseed Spain** (Malça et al. 2014)	**Rapeseed Canada** (Malça et al. 2014)	**Rapeseed US** (Jungbluth et al. 2007
N-fertiliser - ureia (g N)	7.18	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	29.6	18.32
N-fertiliser - Ammonium nitrate (g N)	n.ap.	n.ap.	n.ap.	2.73	n.ap.	41.0	50.0	57.2	15.2	25.3
N-fertiliser- Urea ammonium nitrate (g N)	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	5.8	n.ap.
N-fertiliser- ammonium sulfate (g N)	n.ap.	6.3	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	3.9	n.ap.
Nitrogen Fertilizer (g N)	n.ap.	n.ap.	n.ap.	n.ap.	1.6	n.ap.	n.ap.	n.ap.	n.ap.	7.44
P-fertilizer (g P2O5, single super phosphate)	3.08	n.ap.	n.ap.	27.30	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.
P-fertilizer (g P2O5, triple super phosphate)	n.ap.	n.ap.	1.87	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.
P-fertilizer (g P2O5, monoammonium phosphate)	n.ap.	n.ap.	1.94	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.
P-fertilizer (g P2O5, Ammonium nitrate phospate)	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	7.4	13.4	9.8	18.3	n.ap.
Phosphate fertilizer (g P2O5)	n.ap.	1.28	n.ap.	n.ap.	5	n.ap.	n.ap.	n.ap.	n.ap.	19.02
K-fertilizer, Potassium chloride (g K2O)	12.82	n.ap.	n.ap.	27.30	9.3	23.9	10.0	87.1	n.ap.	28.4
K-fertilizer, Potassium sulphate (g K2O)	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	9.8	3.5	n.ap.
Limestone (g)/Lime	n.ap.	1.72	n.ap.	38.23	94.3	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.
Pyretroid-compounds (g)	n.ap.	2.8 E-3	4.1E-2	1E-3	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.
Benzimidazole-compounds(g)	n.ap.	3.7 E-5	n.ap.	1.7E-2	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.
[Thio]carbamate-compounds (g)	n.ap.	2.04E-2	n.ap.	1.0e-2	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	1.15E-2
Glyphosate(g)	n.ap.	n.ap.	0.97	0.34	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.

Table A.VII.1 (cont) Main inventory data for the cultivation of 1 kg of palm fruit, soybean and Rapeseed in different locations.

	Palm Fruit Colombia	Palm Fruit Malaysia	Soybean Argentina	Soybean Brazil	Soybean US	Rapeseed Germany	Rapeseed France	Rapeseed Spain	Rapeseed Canada	Rapeseed US
Fipronil (g)	n.ap.	n.ap.	n.ap.	0.11	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.
2,4 D (g)	n.ap.	n.ap.	0.11	0.40	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.
Organophosphorus-compounds (g)	n.ap.	4.2E-2	0.16	0.14	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	5.04E-3
Cyclic N-compounds (g)	n.ap.	n.ap.	4.0E-3	3.4E-2	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.
Pesticide unspecified (g)	n.ap.	1.1 E-4	4.9E-2	n.ap.	0.52	0.24	0.6	2.2	3.34	0.10
Sulfony (urea compounds) (g)	n.ap.	n.ap.	1E-3	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.
Triazine-compounds (g)	n.ap.	n.ap.	4E-3	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.
Di nitroanilina compound	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	0.42
Phenoxy compound (g)	n.ap.	5.8E-3	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.
Dolomite (g)	n.ap.	3.2	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.
Ammonia (g)	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	53
Diesel (g)	2.81	1.38	11.15	13.86	3.50	23.40	19.80	22.10	11.60	35.18
Gasoline (g)	8.0E-2	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.
Electricity (MJ)	n.ap.	n.ap.	n.ap.	n.ap.	0.09	4.0E-2	0.148	0.023	0.023	n.ap.
Heat (fuel)(MJ)	n.ap.	n.ap.	n.ap.	n.ap.	n.ap.	0.38	n.ap.	n.ap.	n.ap.	n.ap.
Heat (natural gas) (MJ)	n.ap.	n.ap.	n.ap.	n.ap.	0.08	n.ap.	n.ap.	0.372	0.372	n.ap.

Table A.VII.2 Main inventory data for the extraction of 1 kg of palm fruit, soybean and Rapeseed.

	Palm (Castanheira et al. 2014)	**Soybean** (Castanheira et al. 2015)	**Rapeseed** (Castanheira and Freire 2016b)
Palm fruit (kg)	4.70	n.ap.	n.ap.
Soybean (kg)	n.ap.	5.13	n.ap.
Rape seed (kg)	n.ap.	n.ap.	2.60
Electricity (MJ)	0.31	0.58	0.35
Heat (natural gas) (MJ)	n.ap.	2.61	1.68
Heat (fuel oil) (MJ)	n.ap.	0.48	0.11
Hexane (g)	n.ap.	7.88	2.24

n.ap. - not applicable

Table A.VII.3 Distance and type of transportation used to transport of palm oil, soybean and Rapeseed from the different locations to the biodiesel plant in Portugal.

	Palm Oil Colombia	**Palm Oil Malaysia**	**Soybean Argentina**	**Soybean Brazil - MT**	**Soybean US**	**Rapeseed Canada**	**Rapeseed US**	**Rapeseed Germany**	**Rapeseed France**	**Rapeseed Spain**
FROM	PLANTATION	PLANTATION	PLANTATION	PLANTATION	PLANTATION	PLANTATION	PLANTATION	PLANTATION	PLANTATION	PLANTATION
Transportation mode	**lorry 16-32t EURO3**					**Train**	**lorry 16-32t EURO3**	**lorry 16-32t EURO4**		
Distance (km)	**1300**	**1300**	**403**	**2228**	**1300**	**4500**	**1000**	**2860**	**1620**	**1190**
TO	**Country Port**							**BIODIESEL PLANT**		
FROM										
Transportation mode	**Transoceanic freighter**									
Distance (km)	**7077**	**14744**	**10244**	**8371**	**6019**	**5320**	**6019**			
TO	**Lisbon Port**									
FROM										
Transportation mode	**lorry 16-32t EURO4**									
Distance (km)	**100**									
TO	**BIODIESEL PLANT**									

Table A.VII.4 Main Inventory data for the refining of 1 kg of virgin and waste cooking oils.

	Vegetable virgin oil (Castanheira et al. 2015	**WCO high FFA** (Jungbluth et al, 2007)	**WCO low FFA** (Caldeira et al. 2015)
Crude vegetable oil (kg)	1.03	1.13	1.13
Electricity (kWh)	0.01	0.05	0.005
Heat (natural gas) (MJ)	0.27	0.77	n.ap.
Phosphoric acid, 85% in water (g)	1.60	n.ap.	n.ap.
Sodium hydroxide, 50% in water (g)	4.55	n.ap.	n.ap.
Citric acid (g)	0.40	n.ap.	n.ap.
Bleaching earth [a] (also called fuller's earth) (g)	1.20	n.ap.	n.ap.
Methanol (g)	n.ap.	27	n.ap.
Glycerin (g)	n.ap.	110	n.ap.
Sulfuric acid	n.ap.	2.10	n.ap.

n.ap. - not applicable