Computer-Aided Modeling of Lipid Processing Technology

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Ph.D. Thesis

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Preface

This thesis is submitted as partial fulfillment of the requirements for the degree of Doctor of Philosophy (Ph.D.) at the Technical University of Denmark (DTU).

The work has been carried out at the Computer Aided Process-Product Engineering Center (CAPEC) at the Department of Chemical and Biochemical Engineering, from May 2008 to July 2011, under the supervision of Professor Rafiqul Gani (DTU) and Dr. Bent Sarup (Alfa Laval). The project had been founded by three equal parties: Technical University of Denmark, council of Denmark, and the company Alfa Laval Copenhagen A/S.

My gratitude to my supervisors Prof. Rafiqul Gani and Dr. Bent Sarup for granting me the opportunity of being part of this project, for guiding me through it, for the feedback, and for all the interesting discussions that we had over the last years.

My gratitude to Dr. Anton A. Kiss, Assoc. Prof. Jens Abildskov, and Prof. Arturo Jiménez-Gutiérrez for all the insightful comments and critics made on the thesis.

My eternal love and gratitude to God, to my family (David, Isabel, Alexia, Cinthya, Alexander, and Ortensia), to my greatest achievement, Dominika, and to my angels (Raquel, Ortensia, and Jesus) for taking care of me and for all the support given to me all over these years.

I would like to thank all the co-workers from CAPEC that were always willing to provide their assistance whenever it was needed and for all those interesting conversations on different topics that we had.

To Jens Abildskov my gratitude for replying to my very first e-mail; a short reply e-mail that changed my life for good. And, last but not least; to YOU (wherever and however you may be now).

Carlos Axel Díaz-Tovar

July 2011

"If you don't like something, change it;
if you can't change it, change the way you think about it."
Mary Engelbreit

Abstract

Vegetable oils and fats have an important role in human nutrition and in the chemical industry since they are a source of energy, fat-soluble vitamins, and now also in the production of renewable sources of energy. Nowadays as the consumer preferences for natural products and healthier foods increase along with growing interest in biofuels, the oleochemical industry faces in the upcoming years major challenges in terms of design and development of better products and more sustainable processes to make them.

Computer-aided methods and tools for process synthesis, modeling and simulation are widely used for design, analysis, and optimization of processes in the chemical and petrochemical industries. These computer-aided tools have helped the chemical industry to evolve beyond commodities toward specialty chemicals and 'consumer oriented chemicals based products'. Unfortunately this is not the case for the edible oil and biodiesel industries. The oleochemical industry lags behind the chemical industry in terms of thermophysical property modeling and development of computational tools suitable for the design/analysis, and optimization of lipid-related processes.

The aim of this work has been to develop systematic computer-aided methods (property models) and tools (database) related to the prediction of the necessary physical properties suitable for design and analysis of processes employing lipid technologies. The methods and tools include: the development of a lipid-database (CAPEC_Lipids_Database) of collected experimental data from the open literature, data from industry, and, generated data from validated predictive property models; as well as the development of a database user-interface and an external version of this database, for use in commercial process simulators, for fast adoption-analysis of property prediction models and for fast development of process models not available in process simulators.

This was achieved by first identifying and classifying the lipid compounds found in the edible oil and biodiesel industries. Then creating a list of the thermophysical properties needed for model-based design and analysis of edible oil and biodiesel processes. Next, collection of the available experimental data from different sources

for the identified lipid compounds. Finally, selecting and adopting the appropriate models to predict the necessary properties, to fill-out the lipid-database and to make it suitable for application with other computer-aided tools (such as commercial process simulators).

The developed computer-aided methods (property models) and tools (CAPEC_Lipids_Database) have been linked to the proposed methodology for the design/analysis of lipid-related processes. In this PhD thesis the analysis, in terms of their design variables and their impact in the process behavior, of three lipid-related processes has been performed: the solvent recovery section of the extraction of crude soybean oil, the deodorization of palm oil, and the deacidification of soybean oil.

Resumé på Dansk

Planteolier og fedtstoffer spiller en vigtig rolle indenfor human ernæring og i den kemiske industri, fordi de er en kilde til energi, fedtopløselige vitaminer og findes nu også i produktionen af vedvarende energikilder. I disse tider, hvor forbrugerens præferencer for naturlige produkter og sundere fødevarer er stigende, samtidig med en voksende interesse for biobrændsel, står madolieindustrien overfor store udfordringer i de kommende år med hensyn til design og udvikling af bedre produkter og mere bæredygtige processer, der kan fremstille dem.

Computerbaserede metoder og værktøjer til processyntese, modellering og simulering er brugt i stor udstrækning inden for design, analyse og optimering af processer i den kemiske og biokemiske industri. Disse computerbaserede værktøjer har hjulpet den kemiske industri til at udvikle sig fra kun at producere forbrugsartikler til at producere flere specialkemikalier og kemikalier baseret på forbrugerorienteringen. Desværre er dette ikke tilfælde for madolie- og biobrændselsindustrien. Madolieindustrien er derfor bagud i forhold til den kemiske industri med hensyn til at modellere termo-fysiske egenskaber og med hensyn til udvikling af computerbaserede værktøjer velegnede til design/analyse og optimering af fedtstofrelaterede processer.

Formålet med dette arbejde har været at udvikle systematiske computerbaserede metoder (egenskabsmodeller) og værktøjer (databaser) relateret til forudsigelse af de nødvendige fysiske egenskaber, som er velegnede til at designe og analysere processer, der anvender fedtstofrelaterede teknologier. Disse metoder og værktøj inkluderer: Udviklingen af en fedtstofdatabase (CAPEC_Lipids_Database) af eksperimentel data fra åben litteratur, data fra industrien og data genereret af validerede modeller til forudsigelse af egenskaber; udviklingen af en brugerflade til databasen og en ekstern version af denne til brug i kommercielle processimulatorer til hurtig tilpasnings-analyse af modeller, der kan anvendes til forudsigelse af egenskaber, og til hurtig udvikling af procesmodeller, som ikke er tilgængelige i processimulatorerne.

Dette blev opnået ved først at identificere og klassificere fedtstoffer fundet i madolie- og biobrændselsindustrien. Så blev en liste over de termo-fysiske

egenskaber, der er behov for i model-baseret design og analyse af madolie- og biobrændselsprocesser, udarbejdet. Herefter samledes de tilgængelige eksperimentelle data fra de identificerede fedtstoffer, fra de forskellige kilder. Endelig blev de passende modeller til forudsigelse de nødvendige egenskaber valgt og brugt til at udfylde fedtstofdatabasen og gøre den velegnet til anvendelse med andre computerbaserede værktøjer (som for eksempel kommercielle processimulatorer).

Udviklingen af computerbaserede metoder (egenskabsmodeller) og værktøjer (CAPEC_Lipids_Database) er blevet forbundet med den foreslåede metodik til design/analyse af fedtstofrelaterede processer. I denne PhD afhandling er tre fedtstofrelaterede processer blevet analyseret med hensyn til deres designvariable og disses indvirkning på processernes adfærd. De tre fedtstofrelaterede processer er genindvindingen af opløsningsmiddel fra ekstraktionen af råolie fra sojabønner, processen til fjernelse af ildelugtende komponenter i palmeolie og fjernelsen af syrer i sojabønneolie.

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1.
Introduction & Overview

Humans have used vegetable oils and fats in a great variety of applications since prehistoric times because they could be easily isolated from their source and because of their unique properties. These products arose as key components of food, as a heat transfer medium for food processing and to render desirable texture and flavors as well as mouth feel to products. They also have played an important role in human nutrition since they are a concentrated source of energy (carbohydrates, proteins, and fats), as well as carriers of fat-soluble vitamins and fatty acids essential for health that are not manufactured by the human body (O'Brien, 2004; Shahidi, 2005).

Over the past few decades, the world's fats and oils production has been growing rapidly, driven also by demands other than those arising from nutrition needs, such as biofuels (Diaz-Tovar *et al*., 2011). More specifically, the world's production of

natural oils and fats has grown from 79.2 million tons in 1990 (Shahidi, 2005) to over 170 million tons in year 2010 (Oil World Annual 2011). Palm oil, soybean oil, and canola oil are the three with the highest production rate (see Figure 1.1). The growth rate for palm oil production has been particularly remarkable.

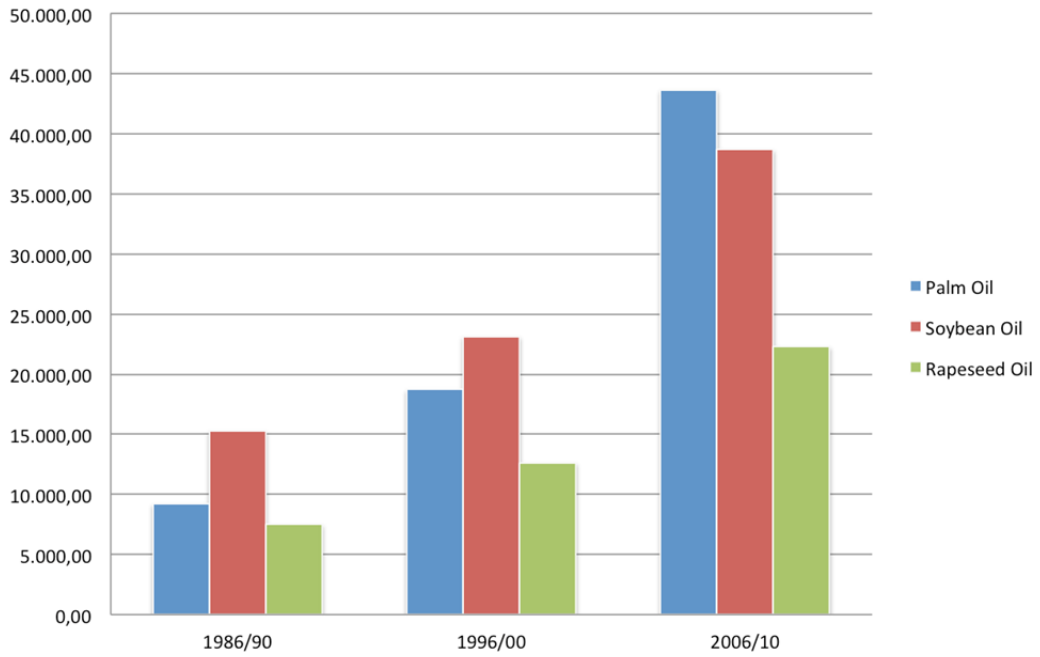


Figure 1.1 World supply of the three most produced commodity oils in thousand metric tons (source http://www.fas.usda.gov)

In years 2008/09 and 2009/10, the world's supply of vegetable oils and fats overcame their demand by almost 0.1 and 0.60 million tons, respectively (Oil World Annual 2011). This increment in the rate of over production combined with the growing consumer preferences for healthier food products and the interest in bio-fuels, had led the industry that processes chemicals derived from plant oilseeds and animal fats (the oleochemical industry) to face major challenges in terms of design and development of better products and more sustainable processes.

Unfortunately, in spite of the fact that the oleochemical industry is mature and based on well-established processes, the complex systems formed by the several different types of chemical compounds (commonly referred to as lipid compounds) present in any vegetable oil or fat, the lack of accurate predictive models for their physical properties and unit operation models for their processing have limited a wide

application of computer-aided methods and tools for process synthesis, modeling, and simulation within this industry.

To appropriately address any given oleochemical process, a step-wise approach is proposed in this PhD project. This approach consists of three steps, from the identification of the main sources of these mixtures to the computer-aided tools suitable for this purpose and they are defined as follows:

1. In the first step, identification of the main sources of vegetable oils and fats and selection of the most representative families of chemical (lipid) species present in the identified sources and their possible industrial application are performed.

2. In the second step, the thermophysical modeling of the selected lipid compounds takes place. This includes: selection, validation, and, if necessary, extension of current predictive models available in the open literature as well as development of predictive models for the missing properties.

3. In the last step, the information and knowledge generated in the first two steps is used together with state of the art lipid processing technology and commercial computer-aided tools (*e.g*. commercial process simulators) to model, simulate, and analyze the selected processing steps that are a key in the oleochemical industry processing steps.

First Step – Vegetable Oils and Fats: Main sources and representative chemical species.

The main sources of vegetable oils and fats are those coming from different animal raw materials (*e.g*. tallow and lard) and vegetable raw materials (*e.g*. oilseeds, tree fruits, and kernels). Among the 17 commodity oils defined by the Oil World Publications (Gunstone, 2002), those coming from vegetable raw materials are the most produced worldwide, with soybean, palm, rapeseed and sunflower oils as the most important ones regarding the amounts involved as shown in Figure 1.2 (Hill, 2000).

Although the terms *fats* and *oils* are used interchangeably, the choice of terms is usually based on the physical state of the material at ambient temperature and

tradition (O'Brien, 2004). Generally, at ambient temperatures fats appear to be solid, while oils appear to be liquid. In the final analysis to determine the suitability of this ingredient in various processes and applications, it is the chemical composition that defines the characteristics of the individual fat or oil.

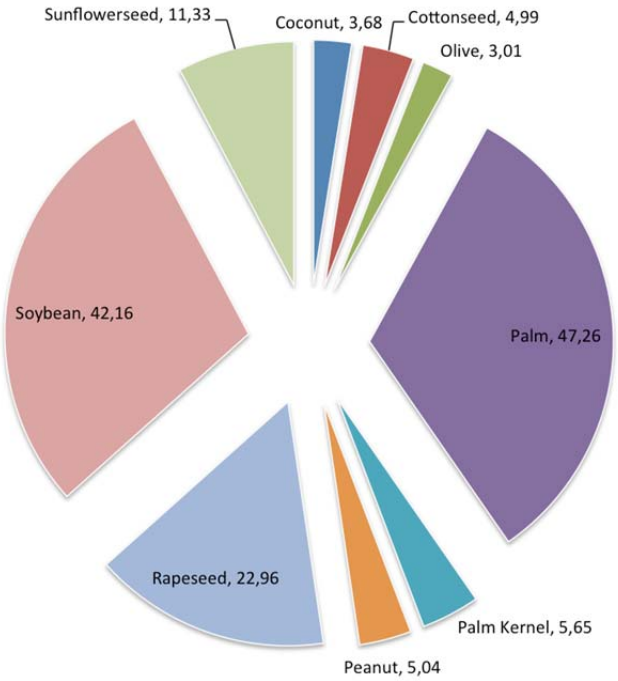


Figure 1.2World Supply and distribution of 9 commodity oils in year 2010 (Source http://www.fas.usda.gov)

The representative chemical species that constitute any given vegetable oil or fat and their potential industrial uses have been widely addressed by different authors (Gunstone, 2002; O'Brien, 2004; Shahidi, 2005). Two different criteria can be used to classify these lipid compounds: i) by the amount in which they are present in any vegetable oil or fat and ii) by the effect (positive or negative) that they have in the quality of the final product (edible oil or fat). The first criterion is helpful for the thermophysical modeling of the mixtures, while the second criterion becomes relevant during the refining processing steps.

In the first classification, lipid compounds are sorted into two different subsets: i) major compounds and ii) minor compounds. In the first group, carboxylic acids (also referred to as fatty acids) with carbon chains ranging from 4 to 26 and glyceryl esters (tri-, di-, and mono-) of these carboxylic acids are found. In the second group,

the nonglyceridic materials are found (*e.g*. phosphatides, sterols, tocopherols, carotenes, and terpenes).

The second classification sorts the compounds also into two groups. In the first group glycerides (which are the main constituents of edible oils/fats), sterols, carotenes and tocopherols (since they are natural antioxidants that improve the shelf life of the final product) are found. The second group is composed by chemical compounds (*e.g*. fatty acids, phosphatides, waxes, gums, *etc*.) that need to be removed from the crude oil/fat as they have a significant negative impact on the vegetable oil processing steps as well as in the quality of the final product.

For the traditional oleochemical industry, the second classification became fundamental as it only aimed to produce good-quality edible oils/fats by removing the undesired compounds. However, and as discussed before, changes in consumer preferences had led this industry to explore new products and process. Fortunately, the widely discussed unique condition of the vegetable oils and fats of been mixtures composed of different chemicals species, allows the oleochemical industry to have a wide range of different unit operations and processes focusing in the potential markets that each one of these compounds may have either as a final (oleochemical) product or as high value raw materials for other industries (see Figure 1.3).For example, triglycerides (TAG) are the main constituents of refined commercial oil. Digliceride oil (DAG) has shown beneficial effects on obesity and weight-related disorders (Lo *et al*., 2008). Monoglycerides are useful in the food industry as emulsifiers (Henry, 1995). Fatty acids are widely accepted in the pharmaceutical and food industries (Shen & Alexander, 1999). Tocopherols, main constituents of natural vitamin E, give oxidative stability to the oil and act as lipid oxidation inhibitors in food and biological systems (Tasan & Demici, 2005). Phospholipids separated with a water degumming process can be dried for lecithin processing (O'Brien, 2004). Sterols are used as starting materials for the synthesis of steroids for pharmaceutical purposes (Ghosh & Bhattachery, 2006). Squalene, based on animal study, has potential as part of a chemotherapeutic regimen for human pancreatic cancer (Top & Rahman, 2000). Finally, carotenes have gained importance in nutrient technology as antioxidants and as natural coloring materials (Peter & Drescher, 2002).

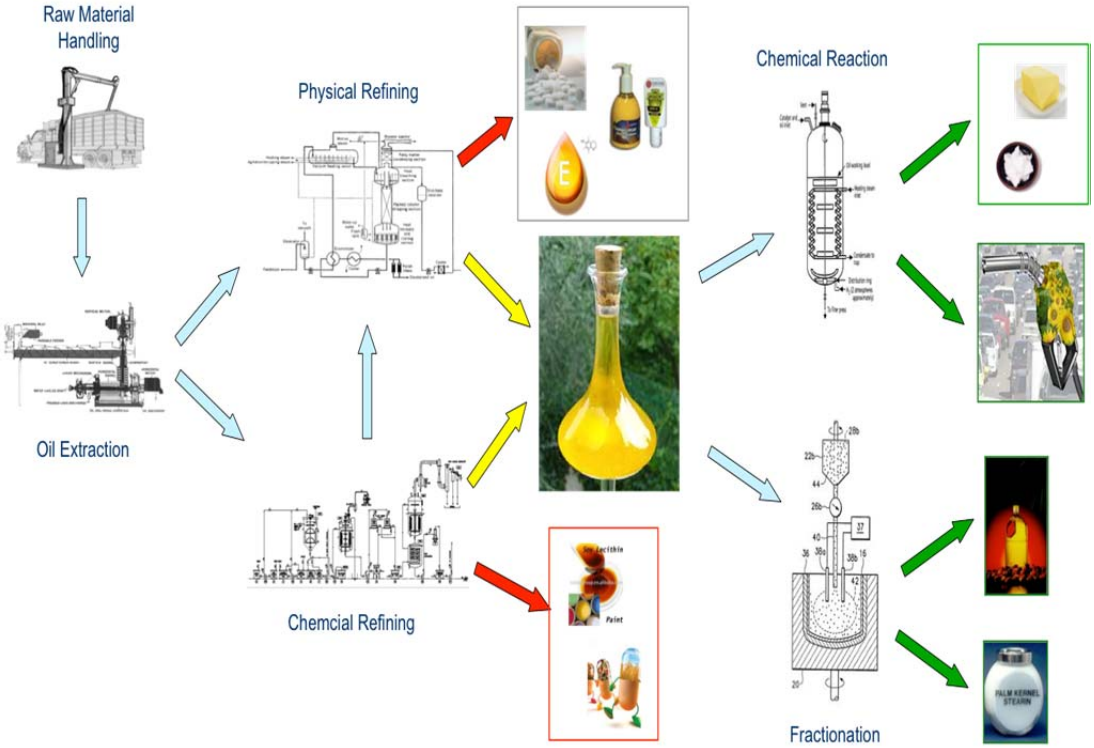


Figure 1.3 Lipid-related products and processes

Second Step –Thermophysical Property Modeling of Lipid Compounds

Knowledge on thermodynamic properties is a key in the understanding of rate and selectivity of chemical processes, including the design of viable industrial chemical processes that undergo some form of transformation (Speybroeck*et al*., 2010). Only few efforts on the development of accurate and robust mathematical models for the prediction/estimation of the thermophysical properties suitable for the design/analysis of processes involving lipid technology have been made.

This lack of accurate and robust predictive models could be, at least to some extent, a consequence of:

i. The few experimental data that is available due to the complexity of the lipid systems, the diversity of chemical species to be analyzed, and the normal processing steps conditions (*e.g*. high temperatures, low pressures, *etc*.).

ii. The models proposed (*e.g*. simple linear equations, Antoine or Andrade equations, *etc*.) that are used to correlate only the generated experimental data and, although the accuracy of the proposed models is significant, their

extension and extrapolation to other lipid compounds is either not possible or leads to great deviations.

At this point, the experimental data collected is not suitable for the design/analysis of oleochemical processes. A well-known alternative to fill-out the gaps in properties of chemicals in databases is the use of property prediction models. A widely used method for the estimation of thermophysical properties is the Group Contribution methods because they are predictive in nature. For example, Joback & Reid (1987), Constantinou and Gani (1994), Marrero and Gani (2001) have proposed different group contribution methods for the estimation/prediction of single value pure component properties based on their molecular structure.

The Group Contribution concept has not exclusively been applied to the estimation/prediction of single value pure compound properties; it has also been used in the estimation/prediction temperature dependent properties. Kolska *et al*. (2008) extended the Marrero and Gani (2001) method and included a term to account for the temperature dependency for estimating liquid heat capacities of organic compounds. Ceriani & Meirelles (2004) established that, even though the families of chemical compounds present in the vegetable oil and fat industry are complex in nature, they could be represented by a small set of already available groups. Based on this hypothesis, they developed a group contribution based method for the estimation of temperature dependent thermophysical properties such as vapor pressure, enthalpy of vaporization, liquid heat capacity, and liquid viscosity.

Diaz-Tovar *et al*. (2011) adopted and extended this idea and proposed a group contribution based method for the estimation of surface tension of lipid compounds. They also established that the most significant minor compounds could also be also described by a small set of 1st, 2nd, and 3rd order groups defined by the Marrero and Gani (2001) method.

Even though group contribution methods have proven to be useful when enough experimental data is not available, this lack of data is also their greatest disadvantage. Properties such as the liquid density of lipids are predicted/estimated by means of other methods rather than the conventional group contribution methods

mentioned above. Halvorsen *et al*. (1993) proposed a method for estimating the liquid density of vegetable oils and fats based on their fatty acid content. The proposed method is based on the modified Rackett equation plus a correction term that accounts for the glycerol part present in the vegetable oils and fats. Zong *et al*. (2010a) developed a method called the Chemical Constituent Fragment Approach that considers the triglycerides as a molecule conformed by two sets of chemical fragments, the first one composed by the tri-, di-, and mono glycerol backbone and the second one that is composed by the free fatty acids that could be attached to the molecule.

If experimental data for the major constituents of vegetable oils and fats is in the best-case scenario scarce, in the case of the minor compounds (tocopherols, sterols, phospholipids, terpenes, *etc*.) it is almost non-existent. Only experimental data on the vapor pressure for this class of compounds have been reported by Shahidi (2005). A commonly employed alternative to overcome this difficulty is the use of equations of state. Privat (2009) developed a method that, based on the Marrero and Gani (2001) groups, computes the three parameters needed by the PC-SAFT EoS in order to calculate the profiles of different properties as a function of temperature.

Third Step – Computer Aided Tools for the Design/Analysis of Oleochemical Processes.

In this final step of the approach, the analysis (through computer-aided tools and state of the art technology) of the current processes employed by the oleochemical industry is to be performed. As previously discussed, the oleochemical industry is mature and based on well-established processes. Throughout the world, processing of vegetable oils and fats, both for food purposes and other oleochemical products, is based on chemical modification of both the carboxyl and unsaturated groups present in fatty acids (Shahidi, 2005) and practically always includes some type of purification to remove impurities. Consequently, innovations and improvements in processing steps such as deodorization, hydrogenation, fractionation, or interesterification have allowed the production of products that can satisfy demanding functional and nutritional requirements (O'Brien, 2004). Ahrens (1999) and Copeland *et al*. (2004) have developed state of the art technologies for the

deodorization of vegetable oil and fats and distillate treatment processes respectively. These contributions have a great impact in the oleochemical industry processing steps as the deodorization process of vegetable oils and fats is a key in determining the quality of the final product (or raw material for other processes such as the transesterification of fats and oils). In the case of the distillate treatment process, the aim is to produce by-product streams with higher purity of selected compounds, and therefore, with a higher commercial value.

Computer-aided methods and tools for process synthesis, modeling, and simulation are widely used for design, analysis, and optimization of processes in the chemical and petrochemical industries. This is, however, not the case for the edible oil and biodiesel industries. Only latest versions of the most commonly used commercial process simulators have started to include small sets of the major constituents of fats, oils, and biodiesels. Therefore, these tools have only to a very limited extent been used to perform the analysis/design of oleochemical (lipid) related processes.

In the last decade, only few authors have made use of computer-aided tools to simulate and analyze lipid related processes. Martinho *et al*. (2008) studied the solvent recovery section of the extraction process of crude soybean oil and performed a sensitivity analysis on the design variables to observe their effect on the system behavior. Ceriani *et al*. (2010) used technical information on the unit operations to setup the simulation model of the deodorization process of palm oil. In their work, the concept of factorial designs was implemented to observe the possible effects of single and combined interaction in the selected response variables. Diaz-Tovar *et al*. (2010) also applied the concept of the full and fractional factorial designs to the solvent recovery section studied by Martinho *et al*. (2008). They concluded that a better understanding of the overall system performance could be obtained when the effects on the selected response variable(s) of single and combined interactions of the design variables are taken into account.

In the upcoming sections, the objective and significance of the PhD project are addressed and a brief description of each one of the chapters that comprise this thesis is given.

1.1. Project Objective

The objective of this PhD project is to develop computer aided methods and tools for the systematic design and analysis of processes that employ lipid technology. These computer-aided methods and tools contain the most representative families of chemical species present in any given vegetable oil or fat, thermophysical pure component property modeling, and the development of validates process simulation models based on state of the art technology.

1.2. Project Significance

In the open literature, the experimental data available of the physical properties needed for the design/analysis of processes involving lipid technology is, in the best case scenario, scarce and the mathematical models used to correlate their behavior is only for the systems analyzed. Hence, these models are not predictive in nature, which limits their scientific and industrial applicability.

On the other hand, the property estimation models found in the open literature are in most of the cases narrowed to a specific family of chemical lipid species or to a very small set of chemical lipid compounds from various lipid families. This limits the possibility of using them as general models for the prediction of all lipid families.

In this PhD project the above-mentioned issue has been addressed through the selection, validation, and extension (if necessary) of thermophysical properties and their impact on the design/analysis of lipid-related processes.

In consequence, the significance of this PhD project both from the scientific and industrial points of view can be divided into two main developments. The first development is the creation of a database that contains:

a) The most representative lipid compounds found in the edible oil and biodiesel industries and their specifics (SMILES, CAS Nr., *etc*.).
b) The collected experimental values available in the open literature.

c) The validated mathematical models for the prediction of single value and temperature dependent physical properties needed for design and analysis of processes involving lipid technology.
d) A user-interface for the fast adoption of the data contained within the database and the link to a well-known commercial simulator.

These developed methods (property models) and tools (database) are employed together with other computer-aided tools (commercial simulators) as input information for the second development. This second development consists of the elaboration of unit operation and process models for the simulation and possible optimization of selected lipid related processes that are a key in the production of edible oils and fats.

1.3. Thesis Structure

Five chapters comprise this PhD thesis. In the current chapter (Chapter 1) an introduction to the lipid processing technology (families of chemical compounds) is given, followed by a discussion on the current state of the art thermophysical models suitable for design/analysis of processes involving lipid technology. Finally, the objectives and the significance of the project are given.

In Chapter 2: Lipid Processing Technology, the chemistry of vegetable oils and fats, their potential industrial and daily-life applications, and the processes used for extraction and purification are described.

In Chapter 3: Property Prediction Methods & Tools, the CAPEC_Lipids_Database is presented and the three features that constitute it are discussed. This includes: the selection of the most representative lipid compounds, the selected thermophysical models suitable for the design/analysis of processes employing lipid technology and their performance with respect to the experimental data available, and finally, the User-Interface for fast adoption of the information contained on it.

In Chapter 4: Design/Analysis Methodology (D/A) & application of the D/A Methodology, the proposed methodology for the design/analysis of lipid related processes is presented.

The applicability of the proposed methodology is highlighted through the analysis of lipid processes that were selected based on their significance for the edible oil and biodiesel industries are analyzed. These three case studies (the solvent recovery section of the solvent extraction process, the deodorization process of palm oil, and the deacidification of soybean oil) are analyzed, simulated, and optimized in terms of their significant design variables.

Finally, in Chapter 5: Conclusion and Future Work, remarks on the work done and the achievements gained with the current PhD project are presented. Recommendations upon the work and improvements that can be carried out as an extension of this work are given.

2.
Lipid Processing Technology

In this chapter the chemistry of vegetable oils and fats, their potential industrial and daily-life applications, and the processes used for extraction and purification are described. From the main sources of vegetable oils and fats to the processes for extraction and refining of them, a review of the different types of vegetable oils and fats, the most representative chemical species which constitute them, and the processes needed to make them suitable for human consumption is given.

Lipid technology refers to products and processes that involve fatty acids, their derivatives, and related substances (Diaz-Tovar *et al*., 2010). As it is known, the production of edible oils and fats involves a great variety of processing steps and unit operations, from crude oil production to the final product. Unit operations include fluid handling, heat transfer, and separation processes such as adsorption,

two-phase separation (liquid-solid, liquid-liquid, and liquid-gas), crystallization, filtration, chemical reactions (interesterification, hydrogenation), steam stripping under vacuum, many more. Consequently, the adequate design of these unit operations is key in the development of sustainable processes that fulfill product specifications and environmental regulations.

World production of oils and fats, currently about 160 million tonnes per annum, comes from vegetable and animal sources (see Table 2.1). Oil World publications have identified 17 commodity oils, of which four are of animal origin; the remainders are from vegetable sources (Gunstone, 2002). Of the total production of oils and fats, about 80% is used for food purposes, 6% is used in animal feed, and the remaining 14% provides the basis for the products from the oleochemical industry (Gunstone & Hamilton, 2001).

Table 2.1 Annual average production of 17 oils and fats in selected five-year periods from 1986/90 with forecasts up to 2016/20 (Gunstone, 2002)

	1986/90	**1996/00**	**2006/10**	**2016/20**
World total	75.66	10.5.05	165.65	184.77
Soybean oil	15.28	23.14	33.60	41.12
Cottonseed oil	3.64	4.00	5.35	6.51
Groundnut oil	3.70	4.55	5.72	6.38
Sunflower seed oil	7.25	9.11	12.43	16.97
Canola oil	7.51	12.64	17.72	22.69
Sesame seed oil	0.64	0.70	0.86	0.96
Corn oil	1.35	1.91	2.49	3.16
Olive oil	1.80	2.47	2.75	2.98
Palm oil	9.22	18.72	31.43	43.36
Palm kernel oil	1.21	2.34	3.84	5.28
Coconut oil	3.07	3.01	3.70	4.55
Butter	6.35	5.81	6.93	7.99
Lard	5.17	6.38	7.93	9.14
Fish oil	1.53	1.25	1.18	11.59
Linseed oil	0.73	0.70	0.81	0.97
Castor seed oil	0.40	0.46	0.71	0.78
Tallow	6.79	7.85	10.06	10.76

With only a limited number of vegetable oils and fats available on a commercial scale, it is not surprising that these are sometimes inadequate to meet the physical, nutritional, and chemical properties required for use in food products. Over a

century or more, lipid technologists have designed and used procedures for overcoming the limitations of a restricted range of natural products. In particular, they have sought to modify the fatty acid composition of their lipids, knowing that such changes will influence the physical, nutritional, and chemical properties of the final vegetable oils and fats products.

As stated elsewhere (Shahidi, 2005; O'Brien, 2004; Gunawan & Ju, 2009), the natural fats and oils are complex chemical mixtures composed of different families of chemicals. Fatty acids (from C4-C24) esterified to glycerol (mono-, di-, and tri-glycerides), are the main constituents of these mixtures. However, during the storage or the physical refining of oils and fats, hydrolysis reactions of glycerides take place and free fatty acids are produced (O'Brien, 2004). These free fatty acids together with another set of chemical species are considered as impurities present in crude vegetable oils and fats that need to be removed in order to make the final product suitable for nutritional purpose or further processing. These impurities can be divided into two different sets: i) high value by-products and ii) quality detrimental by-products. In the former group, chemical species that after a purification step can be sold as high-value products are found; compounds such as: hydratable phosphatides, sterols, tocopherols, tocotrienols, carotenes and terpenes. In the latter group, compounds such as non-hydratable phosphatides, waxes, metals, colored particles and substances, odoriferous components (aldehydes and ketones), pesticides, herbicides, polycyclic aromatic hydrocarbons are found. The amount of these impurities depends on the kind of oil sources, the seed treatment, the extraction process, and the storage conditions. They can negatively influence the taste and smell of oils. Also, they can limit the use and complicate the processing of oils.

2.1. Sources of Vegetable Oils and Fats

During the last 10,000 years humans have learned to cultivate plants and to domesticate animals (O'Brien, 2004). During this period, the evolution of cultivated plants has been shaped to the needs of modern humans. The combined largest source of vegetable oils is the seeds of plants grown in relatively temperate climates (see Figure 2.1). A second source of vegetable oil is oil-bearing trees. All of the oil-

bearing tree fruits require a relatively warm climate (i.e., tropical for coconut and palm and a warm climate for olive trees). The third source is edible meat fats that are supplied almost entirely by three kinds of domesticated animals: lard from pigs, tallow from cattle and sheep, and milk fat or butter from cows. These animals are raised in the greatest quantities where they thrive the best in temperate climates. Animal husbandry has evolved to the stage that these domestic animals require not only a temperate climate but also intensive agriculture to provide a plentiful supply of foodstuffs to produce the desired quality and quantity.

Most of the annual plants and oil-bearing trees not only are cultivated as a source of oil but are also utilized as protein-rich foods. Seed extraction is achieved by pressing and/or by solvent extraction Oils such as palm and olive, on the other hand, are pressed out of the soft fruit (endosperm). Seeds give oils in different proportions. According to the statistics of years 2000/01 (Gunstone, 2002), the world average oil yields are soybean (18.3%); rapeseed (38.6%); sunflower (40.9%); groundnut (40.3%); cottonseed (15.1%); coconut (62.4%); palmkernel (44.6%); sesame (42.4%); linseed (33.5%); average for all oilseeds (25.8%). In addition, yields from palm fruit (45–50%), olive (25–30%) and corn (about 5%) are as indicated. Confirming that the greatest yield is achieved from most of the oil-bearing tree fruits and kernels (O'Brien, 2004).

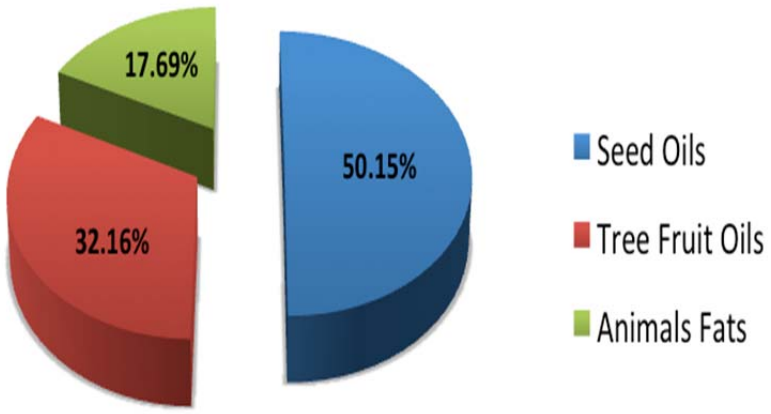


Figure 2.1 Distribution of edible fats and oils produced from different sources in period 2006/10

The chemical and physical properties of fats and oils are largely determined by the fatty acids that they contain and their position within the triglycerol molecule

(O'Brien, 2004). The fatty acid compositions of vegetables oils and fats vary significantly depending not only on the plant or animal species but also within the same species. Among the factors that affect the vegetable oil fatty acid compositions are climate conditions, soil type, growing season, plant maturity, plant health, microbiological conditions, seed location within the flower, and genetic variation of the plant. Animal fat and oil composition varies according to the animal species, diet, health, fat location on the carcass, and maturity. Table 2.2 shows the typical fatty acid range composition of seven vegetable oils and fats. In the first column, the fatty acid carbon chain length and the number of unsaturated bonds are given. For instance, linoleic acid has an 18-carbon-chain length with 2 unsaturated bonds and it is represented as (18:2). In the columns corresponding to each vegetable oil or fat, the minimum and maximum amounts in which a given fatty acid is present is shown. For example, caproic acid (C6:0) is not present in a significant amount (ND) in soybean oil; while it ranges from a non-significant amount (ND) to 0.7% in coconut oil.

Table 2.2 Range of fatty acid composition for major oils (Harwood *et al*., 2007).

Fatty Acid	Soybean	Palm	Rapeseed	Sunflower	Coconut	Tallow
6:0	ND	ND	ND	ND	ND–0.7	ND
8:0	ND	ND	ND	ND	4.6–10.0	ND
10:0	ND	ND	ND	ND	5.0–8.0	ND
12:0	ND-0.1	ND–0.5	ND	ND–0.1	45.1–53.2	0.1-0.2
14:0	ND–0.2	0.5–2.0	ND–0.2	ND–0.2	16.8–21.0	1.4-7.8
16:0	8.0–13.5	39.3–47.5	1.5–6.0	5.0–7.6	7.5–10.2	17.0-37.0
16:1	ND–0.2	ND–0.6	ND–3.0	ND–0.3	ND	0.7-8.8
17:0	ND–0.2	ND–0.2	ND–0.1	ND–0.2	ND	0.5-2.0
17:1	ND–0.1	ND	ND–0.1	ND–0.1	ND	0.8-1.0
18:0	2.0–5.4	3.5–6.0	0.5–3.1	2.7–6.5	2.0–4.0	6.0-40.0
18:1	17.0–30.0	36.0–44.0	8.0–60.0	14.0–39.4	5.0–10.0	26.0-50.0
18:2	48.0–59.0	9.0–12.0	11.0–23.0	48.3–74.0	1.0–2.5	0.5-5.0
18:3	4.5–11.0	ND–0.5	5.0–13.0	ND–0.3	ND–0.2	0.7-2.5
20:0	0.1–0.6	ND–1.0	ND–3.0	0.1–0.5	ND–0.2	0.2-0.5
20:1	ND–0.5	ND–0.4	3.0–15.0	ND–0.3	ND–0.2	0.3-0.5
20:2	ND–0.1	ND	ND–1.0	ND	ND	ND
22:0	ND–0.7	ND–0.2	ND–2.0	0.3–0.5	ND	ND
22:1	ND–0.3	ND	>2.0–60.0	ND–0.3	ND	ND
22:2	ND	ND	ND–2.0	ND–0.3	ND	ND
24:0	ND–0.5	ND	ND–2.0	ND–0.5	ND	ND
24:1	ND	ND	ND–3.0	ND	ND	ND

ND: No significant amount was detected

2.2. The Chemistry of Vegetable Oils and Fats

As stated before, vegetable oils and fats are mixtures composed by several different chemical species (see Figure 2.2). These chemical species can be divided into two sets (major and minor compounds) depending on the actual amount in which they are present in the vegetable oils and fats.

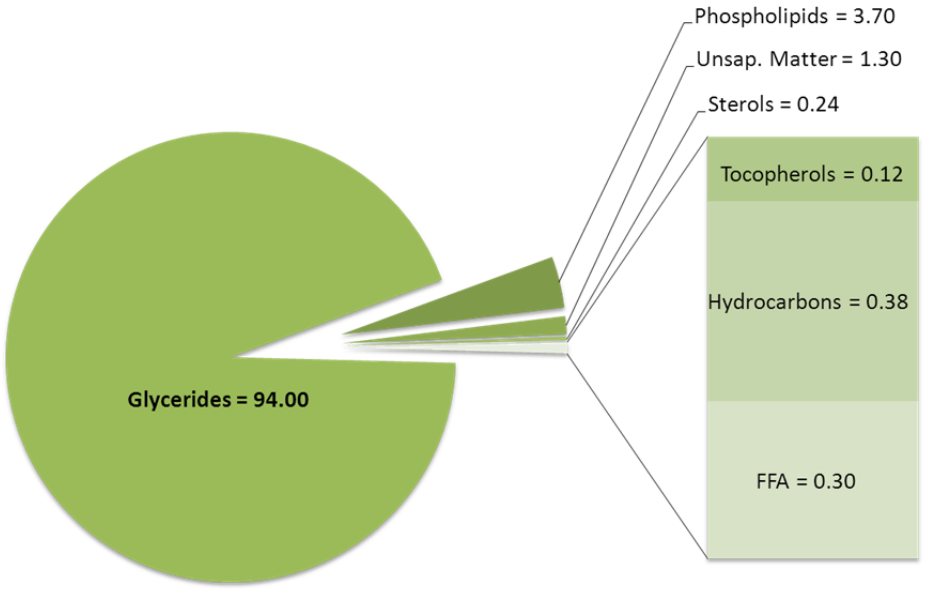


Figure 2.2 Typical glyceride and non-glyceride composition of Soybean Oil (Shahidi, 2005).

In the first set, the major constituents of vegetable oils and fats such as fatty acids and glycerides are included. In the second set, minor compounds such as tocopherols, tocotrienols, phospholipids, carotenoids, and sterols are found. In the upcoming sections, each one of the previously mentioned chemical species is addressed in terms of their chemical structure and their potential industrial use.

2.2.1. Free Fatty Acids

Chemically, all vegetable oils and fats are triglycerides or esters of glycerol and fatty acids. Because all triglycerides have identical glycerol components, the different properties of vegetable oils and fats are contributed by the fatty acids and, hence, the industrial exploitation of them, both for food and oleochemical products, is based on chemical modification of both the carboxyl and unsaturated groups present in fatty acids (O'Brien, 2004; Shahidi, 2005).

Three aspects can differentiate the fatty acid components: i) chain length, ii) the number and position of the double bonds, and iii) the position of the fatty acids

regarding the glycerol. Vegetable oils and fats, for all practical purposes, contain almost entirely straight chain aliphatic carboxylic acids (fatty acids) with carbon chain lengths between 4 and 24 carbon atoms with zero to three double bonds.

Saturated fatty acids have a straight hydrocarbon chain, while unsaturated fatty acids can have i) a *trans*-double bond that is accommodated with little change in shape or ii) a *cis*-double bond that introduces a pronounced bend in the chain (see Figure 2.3). Disregard of the level of saturation or unsaturation, fatty acids have a well-defined basic structure that comprises a hydrophobic hydrocarbon chain with a hydrophilic polar group at one end that endows the acids and their derivatives with distinctive physical and physiological properties (*e.g.* melting point). These properties are reflected in both their food and industrial use. For example, saturated fatty acids are chemically the least reactive and have a higher melting point than do corresponding fatty acids of the same chain length with one or more double bonds. The presence of cis-double bonds markedly lowers the melting point, while trans-acids have melting points much closer to those of the corresponding saturates.

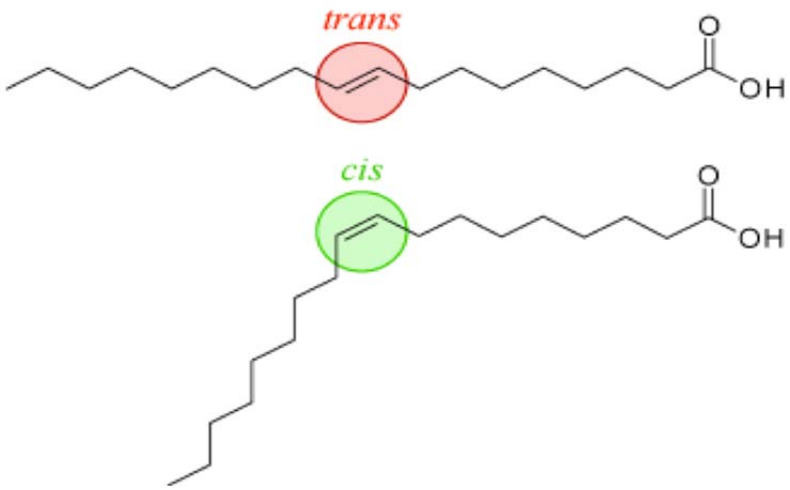


Figure 2.3 *Cis and trans* isomers of unsaturated fatty acids.

Over 1000 fatty acids are known, but 20 or less are encountered in significant amounts in the vegetable oils and fats of commercial importance (Shahidi, 2005). The most common acids are C16 and C18. Below this range, they are characterized as short or medium chain and above it as long-chain acids. Table 2.3 shows the most relevant saturated and unsaturated fatty acids as well as their classification in terms of chain length. As for Table 2.2, the first column shows the fatty acid carbon chain

length and the number of unsaturated bonds. For example, stearic acid has an 18-carbon chain length and no double bounds that are represented as 18:0.

The saturated fatty acids with only 4 to 10 carbon atoms occur principally in milk fats, coconut, and palm kernel oils. These short-chain fatty acids have little or no effect upon serum cholesterol and all are liquids at room temperature. Palm kernel and coconut are also sources of medium-chain fatty acids, referred to as lauric oils. Commodity oils contain fatty acids with chain lengths between C16 and C22, with C18 fatty acids dominating in most plant oils. Oleic fatty acid is the most widely distributed natural fatty acid. Olive, peanut, and palm oils as well as lard and tallow, have high-oleic fatty acid contents. Liquid oils with higholeic fatty acid contents normally have good flavor and frying stability; however, oils with more than 65% oleic fatty acid lose some of the characteristic fried-foods flavor. Saturated fatty acids with carbon chains longer than those of stearic fatty acids are major components of only a few vegetable oils. Arachidic (C-20:0), behenic (C-22:0), and lignoceric (C-24:0) are minor components of peanut oil for a total content of 5 to 8% of C-20 and higher fatty acids. Rapeseed oil contains erucic fatty acid (~41%), which hydrogenates to behenic fatty acid.

A special classification of fatty acids includes those acids that are essential nutrients that the human body cannot synthesize and must obtain from the diet. Humans and several other animals are unable to create fatty acids with double bonds beyond the ninth carbon from the carboxyl end of the compound. Linoleic (C-18:2) fatty acid, with double bonds in the 9 and 12 positions, and linolenic (C-18:3) fatty acid, with double bonds in the 9, 12, and 15 positions, are classified as essential for human health. These fatty acids, also known as omega- 6 (linoleic) and omega-3 (linolenic), form an important part of the human diet to i) help prevent eczema, psoriasis, hair loss, impaired immune functions, and neurological dysfunction; ii) improve circulatory, reproductive, and integumentary health; iii) decrease low-density lipoprotein cholesterol; and iv) help fetal growth and development. Only the *cis* form has the essential activity, and isomerization of these fatty acids to form positional or *trans*-fatty acids results in the loss of these health-promoting characteristics.

Table 2.3 Nomenclature and structure of most the recurrent saturated and unsaturated fatty acid (Shahidi, 2005).

Fatty acid	Common name	Formula	Chain length
4:0	Butyric	$CH_3(CH_2)_2CO_2H$	Short
6:0	Caproic	$CH_3(CH_2)_4CO_2H$	Short
8:0	Caprylic	$CH_3(CH_2)_6CO_2H$	Short/medium
10:0	Capric	$CH_3(CH_2)_8CO_2H$	Medium
12:0	Lauric	$CH_3(CH_2)_{10}CO_2H$	Medium
14:0	Myristic	$CH_3(CH_2)_{12}CO_2H$	Medium
16:0	Palmitic	$CH_3(CH_2)_{14}CO_2H$	Medium/long
18:0	Stearic	$CH_3(CH_2)_{16}CO_2H$	Long
18:1 9c	Oleic	$CH_3(CH_2)_7CH=CH(CH_2)_7CO_2H$	Long
18:2 9c12c	Linoleic	$CH_3(CH_2)_4(CH=CH)_2(CH_2)_6CO_2H$	Long
18:3 9c12c15c	Linolenic	$CH_3CH_2(CH=CH)_3(CH_2)_6CO_2H$	Long
20:0	Arachidic	$CH_3(CH_2)_{18}CO_2H$	Long
22:0	Behenic	$CH_3(CH_2)_{20}CO_2H$	Long
24:0	Lignoceric	$CH_3(CH_2)_{22}CO_2H$	Long
22:1 13c	Erucic	$CH_3(CH_2)_7CH=CH(CH_2)_{11}CO_2H$	Long
20:5 5c8c11c14c17c	EPA*	$CH_3CH_2(CH=CHCH_2)_5(CH_2)_2CO_2H$	Long
20:6 4c7c10c13c16c19c	DHA*	$CH_3CH_2(CH=CHCH_2)_6CH_2CO_2H$	Long

*Abbreviations of the systematic names eicosapentanoic acid and docosahexaenoic acid.

2.2.2. Glycerides

Fatty acids in vegetable oils and fats are found esterified to glycerol. These compounds are named glycerides and, as previously mentioned, they are the main constituents of vegetable oils and fats.

Seed oils and animal adipose tissue consist chiefly (98%) of triglycerides with the fatty acids distributed among different molecular species (Shahidi, 2005). During storage of vegetable oils and fats, hydrolysis reaction of triglycerides may take place and production of free fatty acids and partial glycerides takes place. These partial glycerides (mono- and di-) are not significant components of good quality vegetable oils and fats, elevated levels may be found in badly stored seeds. Although this reaction in vegetable oils and fats is highly undesired, partial glycerides had proven to have beneficial effects on obesity and weight-related disorders (Lo *et al*., 2008). These compounds can be produced at an industrial scale are by partial hydrolysis or glycerolysis of triglycerides.

Triglycerides (TAGs)

Triglycerides are the major constituents of vegetable oils and fats that consist of three fatty acids esterified to a glycerol backbone. Triglycerides with three identical

fatty acids are called monoacid triglycerides (O'Brien, 2004), while those containing more than one type of fatty acid are called mixed triglycerides.

As the distribution of fatty acids on the glycerol backbone is not random and, in order to designate the stereochemistry of glycerol containing components, the carbon atoms of glycerol are numbered stereospecifically: 1, 2, and 3 from top to bottom (Harwood *et al*., 2007). Molecules that are stereospecifically numbered in this fashion have the prefix "*sn*" immediately preceding the term "glycerol" in the name of the compound to distinguish them from compounds that are numbered in a conventional fashion (see Figure 2.4).

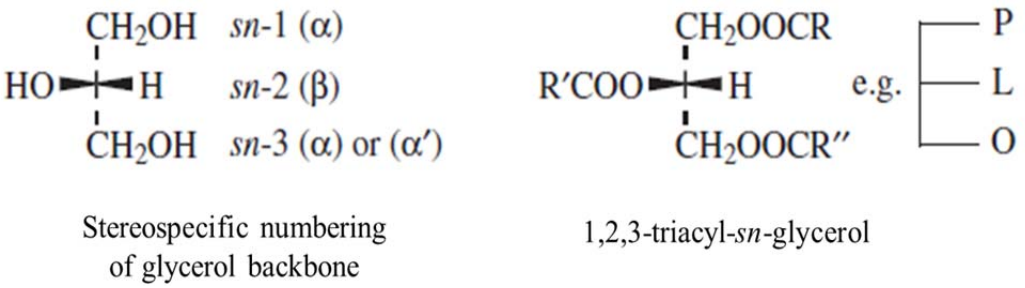


Figure 2.4 Structure and stereospecific numbering of triglycerides (adapted from Shahidi, 2005)

As stated before, glycerides have the same glycerol backbone structure. This means that the triglycerides are affected by the position of the fatty acid linkage to the glycerol, whether the three fatty acids are the same or different, and by the position of each. In vegetable oils, unsaturated acids predominate at the sn-2 position, with more saturated acids at sn-1 and sn-3. The distribution of fatty acids at the sn-1 and sn-3 positions is often similar, although not identical (Shahidi, 2005). All of these fatty acid and structural variations affect the chemical and physical properties of the resulting triglycerides; therefore, fatty acid and triglyceride composition analyses provide the best characterization of fats and oils products.

A commonly used physical property that generally reflects that expected fatty acid composition is melting behavior of triglycerides. Oils with similar fatty acid composition may have different solid fat content, polymorphic forms, and melting behavior as a result of a different triglyceride composition.

Diglycerides (DAGs)

Diglycerides are esters of the trihydric alcohol glycerol in which two of the hydroxyl groups are esterified with fatty acids. They can exist in two structural isomers namely, *sn*-1,2-diglyceride and 1,3-diglycerideDAG (see Figure 2.5). 1,3- DAG is more thermodynamically stable because of the steric effect of the molecule. In general, the melting point of 1,3-DAG is approximately 10°C higher than TAG, and 1,2-DAG is approximately 10°C lower than 1,3-DAG, of the same fatty composition (Lo *et al*., 2008). The causes of these melting point differences are the strength of hydrogen bonding of the hydroxyl group and fatty acid chain arrangement of the DAG isomers.

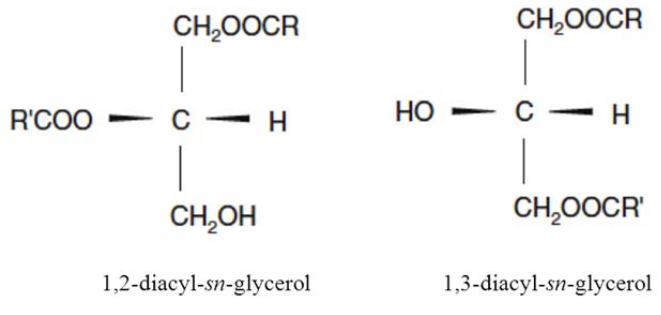


Figure 2.5 Structural isomers of diglycerides.

Diglyceride based-oil (DAG oil) has metabolic characteristics that are distinct from triglyceride based-oils (TAG oil). The consumption of DAG oil is claimed to reduce postprandial serum TAG levels and thus is beneficial for the prevention and management of obesity (Lo *et al*., 2008).

The versatility of DAG oil is evident as numerous applications (*e.g*. as cooking oil, salad oil, shortenings, chocolates, among others). Furthermore, in patent literature it is possible to find tailor-made DAG oils with a defined composition that may: i) exhibit excellent inhibitory effect on body fat accumulation, ii) capable of reducing arteriosclerotic factors in the blood, or iii) capable of lowering blood sugar level, improve insulin resistance, and reduce the effect of leptin (Lo *et al*., 2008).

Monoglycerides

These are fatty acid monoesters of glycerol and exist in two isomeric forms (see Figure 2.6). Monoglycerides are the most polar components of simple lipids and,

thus, need care to prevent their loss in hydrophilic solutions (Gunawan & Ju, 2009). This property is fundamental as it allows these compounds to be used as emulsifiers in food, pharmaceutical and cosmetic industries (Hwang *et al*., 2009). Owing to their excellent lubricating and plasticizing properties, these partial glycerides are also used in textiles processing, the production of plastics and in the formulation of oils for different types of machinery.

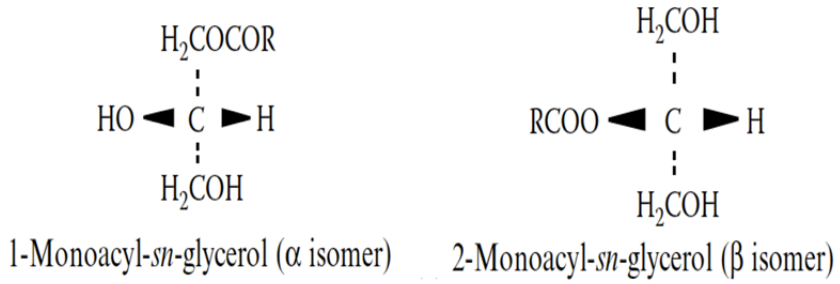


Figure 2.6 Structural isomers of monoglycerides (adapted from Harwood *et al*., 2007).

The crude fats and oils recovered from oilseeds, fruits, nuts, and animal tissues can vary from pleasant-smelling products that contain few impurities to quite offensive-smelling, highly impure materials (see Table 2.4). Although, the presence of most of these impurities in edible oil and fats is undesired, these chemical species have proven to be valuable raw materials in the production of high-value cosmetic/pharmaceutical products.

Table 2.4 Vegetable oils and fats nonglyceride components (O'Brien, 2004).

Vegetable Oil or Fat	Phosphatides (%)	Sterols (ppm)	Cholesterol (ppm)	Tocopherols (ppm)	Tocotrienols (ppm)
Soybean	2.2±1.0	2965±1125	28±7	1293±300	86±86
Canola	2.0±1.0	8050±3230	53±27	692±85	—
Corn	1.25±0.25	15,050±7100	57±38	1477±183	355±355
Cottonseed	0.8±0.1	4560±1870	68±40	865±35	30±30
Sunflower	0.7±0.2	3495±1055	26±18	738±82	270±270
Safflower	0.5±0.1	2373±278	7±7	460±230	15±15
Peanut	0.35±0.05	1878±978	54±54	482±345	256±218
Olive	<0.1	100	<0.5	110±40	89±89
Palm	0.075±0.025	2250±250	16±3	240±60	560±140
Tallow	<0.07	1100±300	1100±300	—	—
Lard	<0.05	1150±50	3500±500	—	—
Coconut	<0.07	805±335	15±9	6±3	49±22
Palm	kernel	<0.07	1100±310	25±15	3±30±30

2.2.3. Tocopherols and Tocotrienols

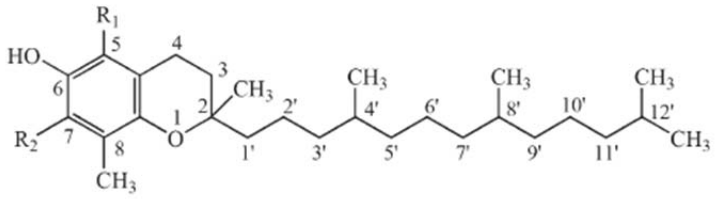
Tocopherols and tocotrienols, also called tochromanols, are fat-soluble organic compounds found in plant material and, consequently, also in the extracted oils, especially in seed oils (Gunawan & Ju, 2009; Tasan & Demirci, 2005). These compounds are important because they retard the oxidation and spoilage of plant matter and because the control the oxidative stability of the oil. Tocopherol and tocotrienol contents and pattern of oils are characteristic and depend on plant genotype, climatic conditions of growth and harvest, polyunsaturated fatty acid content of oil, and processing and storage conditions (Tasan & Demirci, 2005).

Tocochromanols are also components of vitamin E and possess similar general structural features. Tocochromanols generally have aromatic chromanol head and 16-carbon hydrocarbon tail (phytyl in the case of tocopherols, isoprenyl in the case of tocotrienols). The number and position of methyl substituents in the chromanol nucleus give rise to the α-, β-, γ-, and δ- homologues (see Figure 2.7). The structural features of each from govern their metabolic fate and biological activities, which is the measure of potency or functional use in the body.

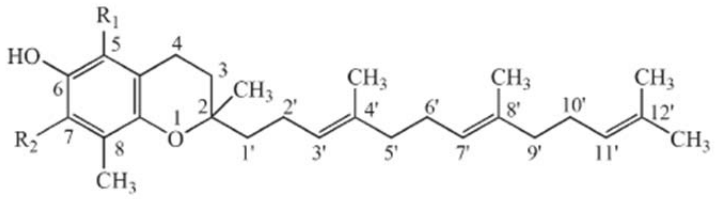
Such activities include platelet aggregation and antioxidant functions. The main function of α-tocopherol is that of a radical-chainbreaking antioxidant in membranes and lipoproteins. It is also the most active form of vitamin E in humans (Gunawan & Ju, 2009). Due to its antioxidant potential and various functions at the molecular level, it is believed to reduce the risk of cardiovascular diseases and of certain types of cancer (Schwartz *et al*., 2008). A mixture of α-, γ-, and δ- isomers containing 60 wt% tocopherols is widely utilized as an additive to various kinds of foods including fats and oils.

Despite lower plasma concentrations, other tocopherols are still capable of exerting antioxidant and biological activities. γ-tocopherol, for instance, has been reported to be more potent than α-tocopherol in decreasing platelet aggregation and delaying intra-arterial thrombus formation. Likewise, tocotrienols have been shown to inhibit cholesterol biosynthesis and are discussed in the context of reducing the risk of breast cancer (Gunawan & Ju, 2009).

Tocopherols and tocotrienols are two classes of compounds that have shown to play a role in immune function, in DNA repair, and other metabolic processes. Also they are known to have a beneficial effect on the level of cholesterol in the bloodstream.



Tocopherols (T)



Tocopherols (T3)

Tocopherols	Tocotrienols	R_1	R_2
α-Tocopherol (α-T) (5,7,8-Trimethyltocol)	α-Tocotrienol (α-T3) (5,7,8-Trimethyltocotrienol)	CH_3	CH_3
β-Tocopherol (β-T) (5,8-Dimethyltocol)	β-Tocotrienol (β-T3) (5,8-Dimethyltocotrienol)	CH_3	H
γ-Tocopherol (γ-T) (7,8-Dimethyltocol)	γ-Tocotrienol (γ-T3) (7,8-Dimethyltocotrienol)	H	CH_3
δ-Tocopherol (δ-T) (8-Monomethyltocol)	δ-Tocotrienol (δ-T3) (8-Monomethyltocotrienol)	H	H

Figure 2.7 Natural occurring tochromanols (adapted from Gunawan & Ju, 2009)

2.2.4. Phospholipids

This chemical specie is a major component of biological membranes and consists of polyhydric alcohols esterified with fatty acids and phosphoric acid, which is combined with a nitrogen-containing compound (O'Brien, 2004; Wang, 2009). The chemical composition of the various phospholipids classes determines their physical properties, which can affect the biological function of membranes (Wang, 2009).

Phospholipids, also known as phosphatides, are present in crude plant oils at levels ranging from 0.1 to 1.8% where they behave as emulsifiers (Przybylski, 1991). In terms of the effect that water has on them, phospholipids are divided into two categories: i) hydratable (phosphatidylcholine and phosphatidylinositol) and ii)

nonhydratable (phosphatidic acid and lysophosphatidic acid). The hydratable phosphatides can be separated from the oil phase with water. The nonhydratable phosphatides and the calcium and magnesium salts of these acids remain in the oil after water degumming. A typical water degumming process will remove the hydratable phosphatides to a level of 200 ppm phosphorus for soybean and canola oils. Pretreatment of good-quality crude oils with phosphoric or citric acid before refining is successful in removing both nonhydratable and hydratable phosphatides to a phosphorus level of approximately 20 to 30 ppm. Two common phosphatides occurring in vegetable oils are the lecithins and cephalins, which may be considered triglycerides that have one fatty acid replaced with phosphoric acid.

Unlike other non-glyceride compounds, the presence of phospholipids in the final product is undesirable because they can cause several problems during the processing of the crude vegetable oils or fats and in the product. Some of these problems are listed below (O'Brien, 2004; Przybylski, 1991):

- Hinder the separation of oil and water phases in the chemical refining process.
- Produce losses in neutral lipids during neutralization.
- Interfere with bleaching.
- Contribute to discoloration of the oil during deodorization.
- Catalyst poisons, shorten shelf life, and foul equipment surfaces.

In spite of the negative influence that this chemical specie has on the processing of vegetable oils and fats, the phospholipids removed during the degumming stage of refining have a high industrial value. These phospholipids are the basis for an industry that uses these chemicals extensively in food products, in animal feeds, and in industrial processes. The major members are phosphatidylcholines, phosphatidylethanolamines, and phosphatidylinositols (see Figure 2.8) and are accompanied by smaller proportions of other phospholipids. Soybean oil, rapeseed oil, and sunflower seed oil are the main sources of commercial lecithins, especially soya lecithin. Palm oil contains little or no phospholipids.

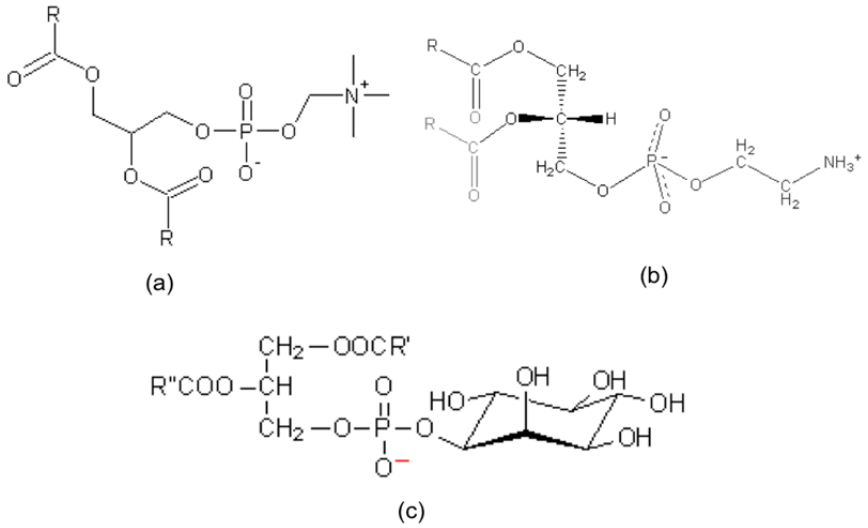


Figure 2.8 Major phospholipids used in food products: (a) phosphatidylcholines (b) phosphatidylethanolamines (c) phosphatidylinositols

2.2.5. Carotenoids

Carotenoids are the most important group of natural coloring materials most widely occurring in plants and animals at more or less elevated concentrations (*e.g.* up to 0.2% in palm oil) (Peter *et al.*, 2002). Carotene is the carotenoid that has been known for the longest time, after it was isolated for the first time by H. Wackenroder (in 1831) from carrots. In 1931, Kuhn found that naturally occurring carotene is composed of three isomers: α-carotene, β-carotene and γ-carotene (see Figure 2.9).

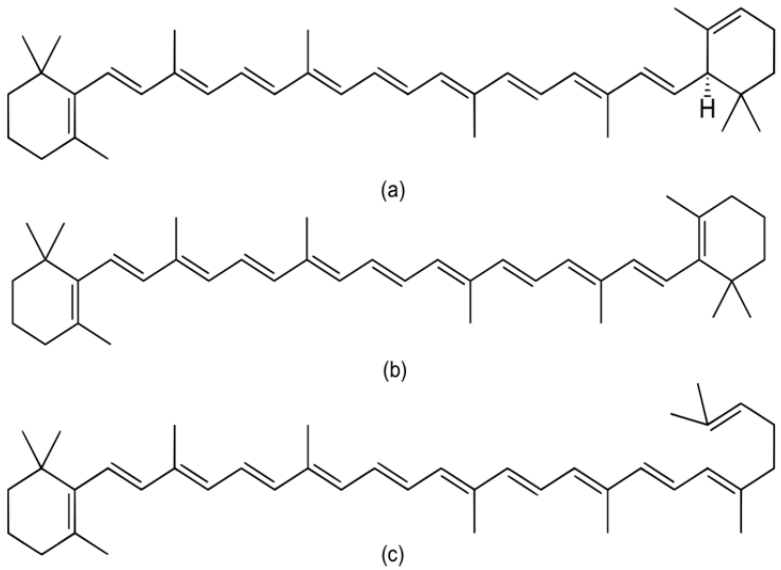


Figure 2.9 Natural occurring carotene isomers (a) α-carotene, (b) β-carotene and (c) γ-carotene

Carotenoids are fat-soluble, nitrogen-free, and yellow to violet materials composed by linear tetraterpenoid hydrocarbons comprising eight C5 isoprene units with an extensive conjugated polyene chain as the light absorbing chromophore which gives them their brilliant colors (Bonnie & Choo, 1999). The structures of carotenoids confer on them many important physiological properties, such as antioxidant activity. They, therefore, play role in protecting cells and organisms against lipid peroxidation.

Carotene isomers possess the same fundamental structure, comprising one β-ionone ring structure at one molecule end, 9 conjugated double bonds and 8 branchings. They differ only in the structure of the other molecule end. Depending on its origin, carotene is a varying mixture of the structurally isomeric polyene hydrocarbons C 40 H 56: all-trans-α-carotene, all-trans-β-carotene, all-trans-γ-carotene. Depending on processing and starting material, cis isomers may also occur.

Palm oil is the richest plant source of carotenoids in terms of retinol equivalent with 500-700 ppm (Wei *et al*., 2005). Depending on their origin and freshness condition, palm oils have a bright yellow (predominantly α-carotene), red (lycopene), orange (predominantly β-carotene) or reddish brown (presence of chlorophyll) coloration.

Carotenoids have been proven to be beneficial to human health apart from having pro-vitamin A which prevents xeropthlamia, a night blindness disease (Wei *et al*. 2005). Carotenoids also play an important role as anti-oxidant by scavenging free radicals and as singlet oxygen quencher. They are also found to be capable of inhibiting growth of certain cancer cells such as the colon cancer. Carotenes, themselves have gained importance in nutrient technology as antioxidants and as natural colouring materials (Peter *et al*., 2002). They predominantly serve for coloring fats and oils, for vitamin enrichment of margarine, nutrient preparations, and pharmaceuticals, as an addition to concentrated feed in rearing young animals and to ice creams or sherbets and milk preparations.

2.2.6. *Sterols*

Plant sterols, also called phytosterols, have been reported to include over 250 different sterols and related compounds in various plants and marine materials

(Piironen *et al*., 2000)**.** Phytosterols resemble cholesterol both in their chemical structure and their biological function, which makes them essential components of the membranes of all eukaryotic organisms.

These plant materials are steroid alcohols that mainly occur as free steryls (see Figure 2.10), esterfied steryls, and steryl glycosides, which can be esterified to acylated steryl glycosides (see Figure 2.11) (Piironen *et al*., 2000). The most common representatives of this chemical specie are sitosterol, stigmasterol and campesterol (4-desmethyl sterols). The 4-methyl sterols and 4,4-dimethyl sterols are usually only minor components in most plant sources. Sitosterol is the principal sterol in plant materials, but in addition to its 22-dehydro analogue stigmasterol and campesterol, brassica- and avenasterols occur in many plant materials.

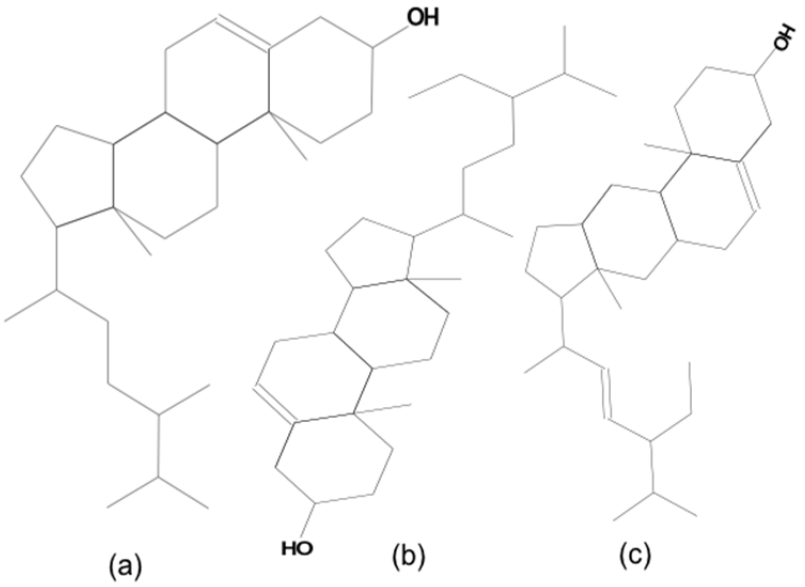


Figure 2.10 Examples of natural occurring sterols (a) Campesterol (b) Sitosterol (c) Stigmasterol

Like cholesterol in mammalian cells, free sterols and to some extent also steryl glycosides and acylated steryl glycosides are incorporated into cell membranes performing an important role in the structure and function of cell membranes. Thus the vegetable oils are rich in plant steryl esters. In addition to their important role in maintaining adequate function of plant cell membranes, plant sterols are precursors of a group of plant growth factors.

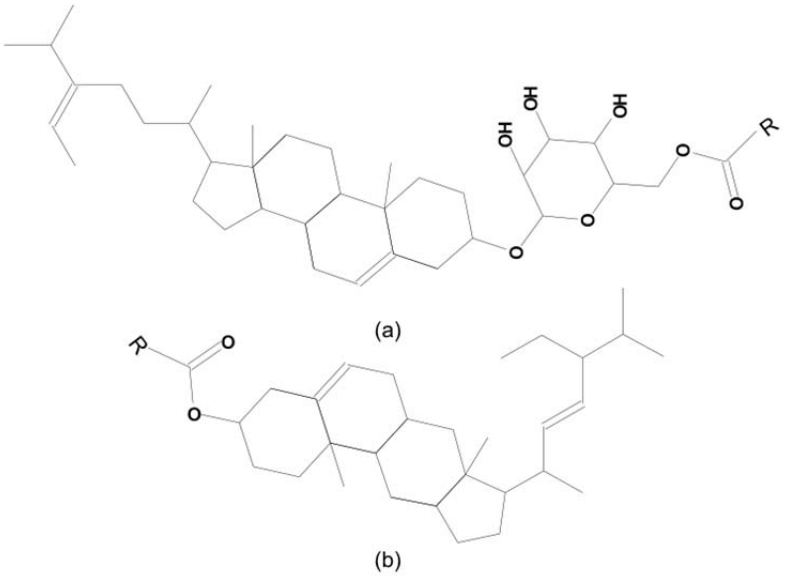


Figure 2.11 Examples of natural occurring (a) steryl glycoside (b) esterified steryl

The usual human diet contains currently around 200±300 mg/day of plant sterols (Akihisa, 1991). The higher the dietary intake of plant sterols from the diet, the lower is cholesterol absorption and the lower is the serum cholesterol level. Diets rich in plant materials have become recommended in the majority of public health education programs, not only because of the presence of endogenous and exogenous plant sterols and stanols, but also because of the presence of antioxidants (Piironen *et al*., 2000).

2.3. Lipid-Related Processes: From Oil Extraction to Oil Refining

Edible oils and fats have been produced and used since time immemorial. The first fats were probably obtained by rendering animal waste products since this is a relatively easy operation that only involves simmering fatty animal tissue (Harwood *et al*., 2007). Although, crushing nuts and oilseeds is a more sophisticated way of producing edible oils, sesame seeds and linseed were already pressed in Egypt around 259 BCE and some 75 years later, screw and wedge presses were used in ancient Rome for the production of quite a variety of nut and seed oils and of course olive oil.

Although some oils such as virgin olive oil are used without further treatment, most of the crude fats and oils recovered from oilseeds, fruits, nuts, and animal tissues can

vary from pleasant-smelling products that contain few impurities to quite offensive-smelling, highly impure materials (O'Brien, 2004). However, it was not but until 1842 that Schmersal patented the refining of cottonseed oil with caustic soda and in 1858 that Bareswil started to deacidify cottonseed oil with a 30% caustic solution (Harwood *et al*., 2007). Physical refining began in 1891 when Eckstein operated a steam deodorization process operating at atmospheric pressure. An improved version of the process that used vacuum was introduced by Bataille and Wesson. Therefore, it is fair to say the refining of edible oils (neutralization, bleaching, and deodorization), has only been practiced for just over a century, but it has had a great impact on eating habits.

Throughout the world, processing of fats and oils, both for food and oleochemical products, is based on chemical modification of both the carboxyl and unsaturated groups present in fatty acids and practically always includes some type of purification to remove impurities; such as gums, free fatty acids, pigments, metal complexes, and other undesirable materials (Shahidi, 2005). The choice of processing equipment and techniques can depend upon source oils handled, quality of raw materials, available manpower, governmental regulations, and a number of other considerations. Nowadays, innovations such as deodorization, hydrogenation, fractionation, and interesterification, along with improvements in other processes, have allowed the production of products that can satisfy demanding functional and nutritional requirements (O'Brien, 2004).

Figure 2.12 shows the typical processing steps followed to produce en edible vegetable oil or fat. The first processing step is related to the recovery of vegetable oils and fats, while the rest of the processing steps relate to the purification of the recovered vegetable oils and fats.

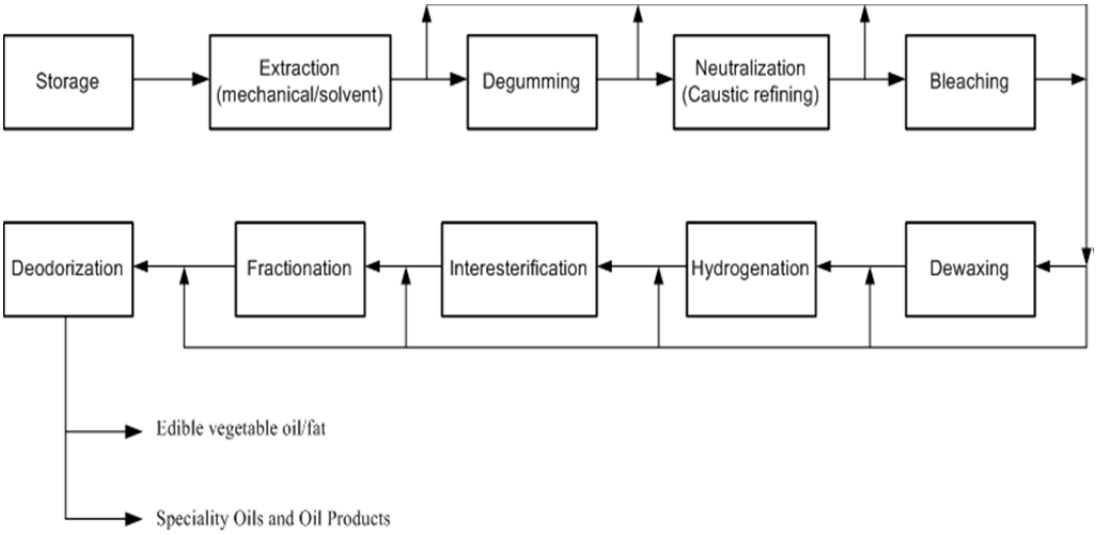


Figure 2.12 Integrated processing facility (adapted from Shahidi, 2005)

2.3.1. *Vegetable Oils and Fats Recovery*

The purpose of all fats and oils recovery processes is to obtain triglycerides in high yield and purity and to produce co-products of maximum value. The oilseeds are processed by one of two types of processes: i) expeller or screw press extraction (mechanical extraction) and ii) prepress solvent extraction. Animal tissues may be wet- or dry rendered to separate the fats.

Mechanical Extraction

The mechanical extraction process is used for four primary reasons (Shahidi, 2005):

- This type of extraction process can be furnished in very small scale, as low as 10 tons per day. The capital cost for small mechanical extraction facilities is considerably less than small solvent extraction facilities.
- There is a niche, high-value market for natural oils that have not been in contact with solvents or chemicals, requiring the use of mechanical extraction.
- Mechanical extraction can create a high bypass protein meal for ruminant animals that sells at a price premium over solvent extracted meal.
- Finally, mechanical extraction is often considered more reliable than solvent extraction when processing difficult materials (copra and palm kernel) in hot, tropical climates.

Most full presses are capable of processing 10 to 100 tons of oleaginous materials per day. To be highlighted that olive oil industry is the only oilseed industry still

using hydraulic presses today. This is possible because of the price premium paid for natural olive oil, processed without the use of heat or chemicals.

Solvent Extraction

Because of comparatively poor oil yields, sole use of mechanical extraction to separate the oil and meal fraction is not as commonly used as solvent extraction (Shahidi, 2005). The mechanical extraction process can reduce the oil in meal to 5% to 10% by weight, whereas the solvent extraction process reduces the oil in meal to less than 1% by weight.

As the value of the oil fraction is typically two to three times the value of the meal fraction by weight, the loss of yield is very costly. The mechanical extraction process also has comparatively higher energy and maintenance costs per ton of oleaginous materials processed. The major drawback of solvent extraction is the high initial capital cost to construct a facility. Solvent extraction facilities constructed today are commonly in the size range of 1000 to 5000 tons per day.

Direct solvent extraction removes the oil directly from conditioned oilseeds with an organic solvent. The theory of extraction is very simple (O'Brien, 2004): Leach the oil out of the cake, flakes, or collets with a solvent, usually hexane. Even though elevated temperatures reduce oil viscosity and enhance diffusion, the hexane vapor pressure limits the practical operating temperatures of the extractor and its contents to approximately 50 to 55°C. Separation of the oil and solvent is accomplished by conventional distillation methods. The full miscella, which is the solvent and oil mixture, is distilled to free the oil from the solvent. The recovered solvent is separated from the accumulated moisture in a gravity separation tank and reused in the solvent extraction operation. The hexane-free oil is cooled and filtered before storage or further processing.

2.3.2. *Vegetable Oils and Fats Refining Processes*

Crude edible oil and fats contain variable amounts of nonglyceride impurities, such as fatty acids, non-fatty materials generally classified as "gums", and color pigments (Carr, 1978). Most of these impurities are detrimental to end product fresh and aged quality characteristics, hence must be eliminated by purification process.

The refining processes remove undesirable materials but may also remove valuable minor components, which were discussed in the previous sin section 2.2. Some of the useful minor components can be recovered from side streams to give valuable products. Figure 2.13 shows a typical two-way path for the refining of edible oils and fats and the by-products of each step.

For relatively cheap oils, like soybean oil, the higher oil yield with the physical refining is less important than the higher bleaching earth consumption, making chemical refining more attractive. For other unsaturated oils with a higher value, such as peanut oil and sunflower seed oil, physical refining will be more attractive.

Degumming Process

Degumming may be considered the first step in the refining process and it is designed for the treatment of oils with water, salt solutions or dilute acids to remove phosphatides, waxes and other impurities that interfere with subsequent processing (Shahidi, 2005).

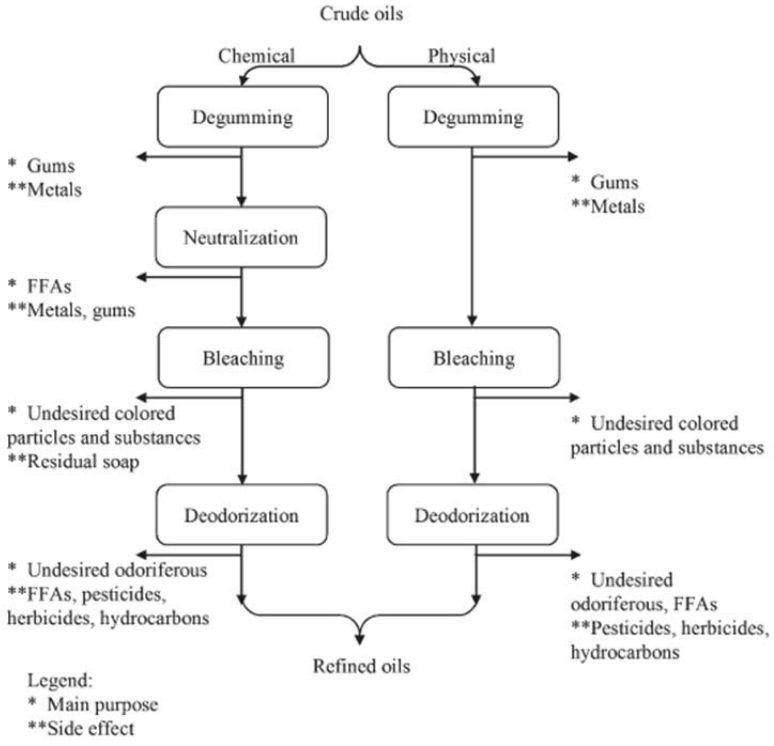


Figure 2.13 Full refining processing steps and their influence on the product (adapted from Gunawan & Ju, 2009)

Depending on the aim of the process, several types of degumming processes are used for the refining of edible oils and fats (Harwood *et al*., 2007):

a) Water degumming: This process is aimed to target those phosphatides that have greater affinity for the water phase (hydratable phosphatides) rather than for the oil phase. The process has two different aims: to produce lecithin from crude soya bean oil and to control the phosphorus content of crude oils, such as sunflower seed oil and rapeseed oil at just below 200 ppm.
b) Dry degumming: The process makes use of the fact that strong acids displace weaker acids from their salts. In the presence of bleaching earth, these metal ions will be chemisorbed by the acidic sites in the earth.

   The dry degumming process constitutes the main treatment for palm oil, lauric oils, and low phosphatide animal fats, such as tallow and lard.
c) Acid-water degumming: In this process crude oil is mixed with 0.005-0.01% citric acid and 1-2% water at 70°C (O'Brien, 2004). The acid water degumming mixture is then cooled and allowed to hydrate for 1 hour. The water-soluble substances are then separated from the oil. Degummed oil goes to the bleaching process.

Dry degumming process allows crude oil to be fully refined in only two steps: dry degumming and physical refining. This makes the dry degumming route the cheapest provided the auxiliary costs, such as the cost of bleaching earth and its subsequent disposal, do not escalate

Neutralization

This refining step is the processes designed to neutralize free fatty acids present in the oil by introduction of an alkali, such as caustic soda (sodium hydroxide), and centrifugal separation of the heavy-phase insoluble material (O'Brien, 2004). The purpose of the alkali refining process is manifold. If there are still phosphatides present in the oil, the alkali refining process should remove them. The process should remove free fatty acids present by converting them into soaps that are oil-insoluble and can be separated from the oil by settling or centrifugal separation. In addition, the process should remove coloring compounds and/or their precursors so that bleaching the alkali-refined oil requires less bleaching earth and color fixation during subsequent high temperature treatments is avoided.

Bleaching

The purpose of bleaching is not only to provide lighter colored oil but also to purify it in preparation for further processing (O'Brien, 2004). Refined oil contains traces of a number of undesirable impurities either in solution or as colloidal suspensions. In many cases, the bleaching process is performed more for the removal of the nonpigment materials such as soap, gums, and pro oxidant metals, which hinder filtration, poison hydrogenation catalyst, darken the oils, and affect finished oil flavor. The key parameters for the bleaching process are i) procedure, ii) adsorbent type and dosage, iii) temperature, iv) time, v) moisture. The three most common types of contact bleaching methods used for edible fats and oils are batch atmospheric, batch vacuum, and continuous vacuum.

Dewaxing

This process refers to the removal of high-melting-point ‘‘waxes’’ extracted from certain oilseeds, such as corn, sunflower, and canola (Shahidi, 2005). While the wax usually does not negatively affect the functionality of the products, the presence of wax affects the appearance of the product.

The classical dewaxing process consists of carefully cooling the oil to crystallize the waxes for removal by filtration (O'Brien, 2004). The cooling must be done slowly under controlled conditions.

Hydrogentaion

Hydrogenation is generally performed for one of two specific purposes (Shahidi, 2005; O'Brien, 2004). The first is to provide taste and smell stability and to enhance the shelf life for unsaturated products. The second is to increase oxidative stability. Flavor stability is necessary to maintain product acceptability for prolonged periods after processing and packaging and for use as an ingredient in a finished product.

Simply stated, hydrogenation is designed to saturate (to the degree desired) double bonds in the fatty ester of the triglyceride molecule. Hydrogenation also promotes isomerization of the *cis* orientation to the *trans* position.

Interesterification

Emulsifiers are usually made either by alcoholysis or by direct esterification. Indirect esterification, fatty acids and polyalcohols are reacted together under controlled conditions to form esters. In alcoholysis, fats are reacted with polyalcohols to make the surfactants. For example, the production of mono- and diglycerides from fat is an alcoholysis reaction with glycerine as the alcohol.

Fractionation

Today, edible vegetable oils and fats are fractionated for one of the following reasons: i) to remove waxes and other nonglycerides, ii) to remove naturally occurring highmelting-point triglycerides, or iii) to remove high-melting-point materials formed during hydrogenation (Shahidi, 2005). Separation of a vegetable oil or fat into fractions can also provide two or more functional products from the same original product (O'Brien, 2004).

Deodorization Process

Deodorization process (steam distillation) and its parameters have a great relevance in lipid processing technology since they have significant impact on the quality of the finished oil as it stripes from the relatively nonvolatile oil, volatile odor- and color-causing substances (Maza *et al*., 1992; Bailey, 1941).

The physical refining of vegetable oils is a distillation process in which, under low absolute pressure of 2 to 10mbar and high temperatures of 240 to 270°C, the accompanying lower boiling compounds are distilled off from the triglycerides by using unsaturated open steam as the effective stripping agent.

For lauric oils and palm oil physical refining is preferred in terms of both operating cost and refining loss (Shahidi, 2005). In the case of soybean and rapeseed oils, physical refining is suitable only for crude oils of a high quality, i.e., with a low degree of oxidation and a sufficiently low. Another important factor is the free fatty acid content of the crude oil. In general, physical refining only becomes advantageous when the acidity of the crude oil is sufficiently high.

3.
Property Prediction Methods & Tools

In this chapter, the development of methods (algorithms and models) and tools (computer software) used to solve design/analysis problems of lipid-related processes is discussed. This includes: i) the development of a lipids database (CAPEC_Lipids_Database) that contains of the most representative lipid compounds and their molecular description, the parameters of the validated models that correspond to the identified thermophysical properties suitable for design/analysis of lipid related compounds; ii) A User-Interface of the database that is used for fast adoption and retrieval of the information contained in the database, and the creation of an external version of it for use in commercial computer-aided tools (such as process simulators).

The chemical or process engineer, in particular, finds knowledge of physical properties of fluids essential to the design of many kinds of products, processes, and industrial equipment (Poling *et al*. 2001). This set of physical and thermodynamic data and properties of compounds in a process that undergoes some form of transformation is a key in the understanding, design, and simulation of many chemical processing units (Marrero & Gani, 2001).

Unfortunately, the complexity of the chemical systems present in any lipid process together with the normal operating conditions found in lipid processes have limited the availability of experimental data of the needed properties. Consequently, the development of methods and tools to overcome this lack of experimental data has become indispensable for the design/analysis of lipid-related processes.

In the particular case of the edible oils/fats and biodiesel industries there is an increasing need for reliable predictive methods for physical properties of fatty compounds present in vegetable oils and those related to the biofuels. Due to the complexity of the fatty systems, many efforts have been made (Halvorsen *et* al., 1993; Goodrum, 2002; Ceriani *et al.,* 2004; Zo *et al.*, 2010a) to describe their behavior based experimental observation and through mathematical modeling. In this PhD thesis, this need is addressed, at least for the pure component properties, by means of a three step-wise methodology.

The first step involves the creation of a lipid-database (CAPEC_Lipids_Database [Diaz-Tovar *et al.*, 2011]). This database contains the most representative chemical compounds found in the edible oil and biodiesel industries, their molecular description, and the collected experimental data of the selected single value and temperature dependent pure component thermophysical properties. Table 3.1 gives an overview of the lipid compounds contained in the database and a complete description of it is given in Section 3.1.

In this state, however, the database cannot be used for process synthesis/design where not only the database needs to be totally filled but also, for new chemicals or process conditions, the necessary property data need to be predicted. In the second step, the gaps found in the lipid-database have been filled through adopted GC-

based property models, which are predictive in nature. These properties are divided into pure component single value properties and temperature dependent properties. Whenever enough data was not available, the PC-SAFT EoS was used to generate pseudo-experimental data for the temperature dependent properties for regression of the GC-based model parameters. It is to be highlighted that in this work mixture properties are not addressed as they are out of the scope of it; nevertheless, the predictive accuracy of the original UNIFAC and UNIFAC-CI for SLE and VLE of some lipid systems is briefly discussed in Appendix F.

Latest versions of commercial simulators (*e.g.* PRO/II ®, ASPEN®, etc.) provide friendly user-interfaces to define user-added compounds. In consequence, in the third step, the contents of the CAPEC_Lipids_Database (lipid compounds, their molecular description, single value properties, and temperature dependent model parameters) have been adapted for use in an external software, PRO/II. Through this database, PRO/II can be used to simulate and optimize edible oil process flowsheets.

Table 3.1 Chemical species contained in the CAPEC_Lipids_Database (Diaz-Tovar *et al.*, 2011)

Chemical Family	Chemical Specie	Carbon Length	Number of Compounds
Glycerides	Tri-	C31-C57	73
	Di-	C17-C43	41
	Mono-	C11-C25	15
Fatty	Acids	C6-C24	29
	Methyl Esters	C7-C25	29
	Ethyl Esters	C8-C26	29
Minor Compounds	Tocopherols	C27-C29	4
	Tocotrienols	C27-C29	4
	Phospholipids	C41,C45	2
	Terpenes	C30-C40	9
	Sterols	C27-C29	4
	Sterol Esters	C41,C47	2
	Sterol Glycoside	C35,C53	2
		Total	243

3.1. Database

The CAPEC_Lipids_Database is a computer-aided tool designed for the storing, predicting, and retrieving of physical property data suitable for design and analysis of processes employing lipid technology.

This computer-aided tool consists of three main features (see Figure 3.1): the first feature includes the most representative lipid compounds, their molecular description in terms of the original UNIFAC Method (Fredenslund *et al.,* 1975) and the Marrero and Gani (2001) method groups, and the collected experimental data from the open literature and confidential data from industry for a range of physical properties (see Table 3.2); the second feature consists of validated predictive property models and their correspondent model parameters; while the third feature contains a user-interface for fast and easy retrieval of the information contained in the database.

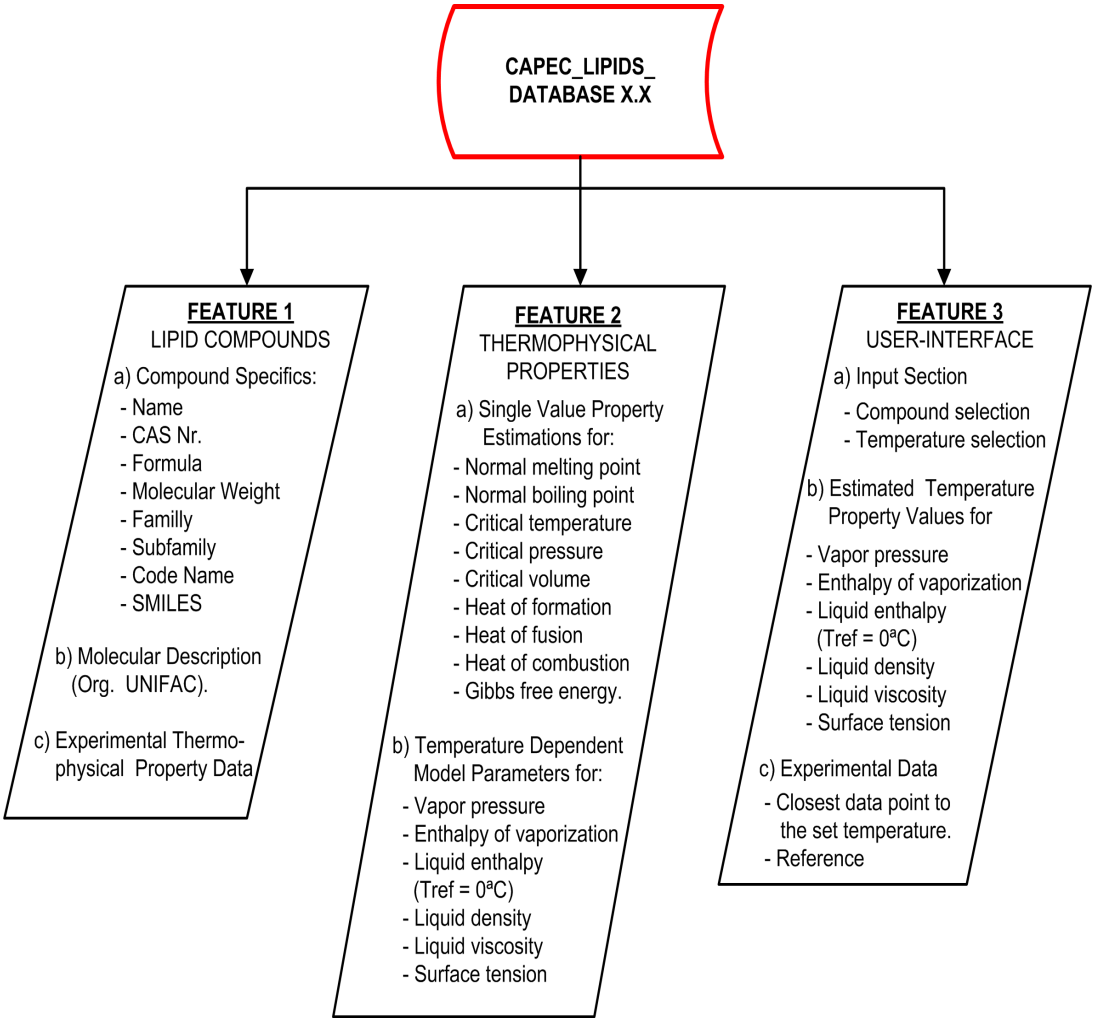


Figure 3.1 CAPEC_Lipids_Database feature contents

3.1.1. Feature 1: Lipid Compounds

This first feature of the database contains the specifics of the world's most produced 14 vegetable oils and fats. Figure 3.2 shows these identified fats and oils, classified

by their source (oilseeds, tree fruits and kernels, or animals) as discussed in Chapter 2, and the representative families of chemical species found in them (acylglycerides, fatty acids, fatty esters, or minor compounds). Note that Figure 3.2 only shows the diglyceride contents in the identified vegetable oils and fats, the information regarding the rest of the compounds can be seen in Appendix D.

As shown in Table 3.2, a total of 2531 data points collected for the identified pure component properties, single value and temperature dependent, for a total of 243 lipid compounds are contained in the lipids database (see Table 3.1). Among them 73 are triglycerides (C31-C63), 41 are diglycerides (C27:C43), 15 are monolglycerides (C11:C17), 29 are free fatty acids (C6:C24), 29 are methyl esters (C7-C25), 29 are ethyl esters (C8-C26), 4 are tocopherols (C27-C29), 4 are tocotrienols (C27-C29), 9 are terpenes (C30-C40), and 8 are sterols (C27-C53).

The molecular description of each the lipid compounds contained in the lipid library obtained through the Marrero and Gani (2001) method for fatty acids is shown in Figure 3.3. The rest of the information is presented in Appendix D.

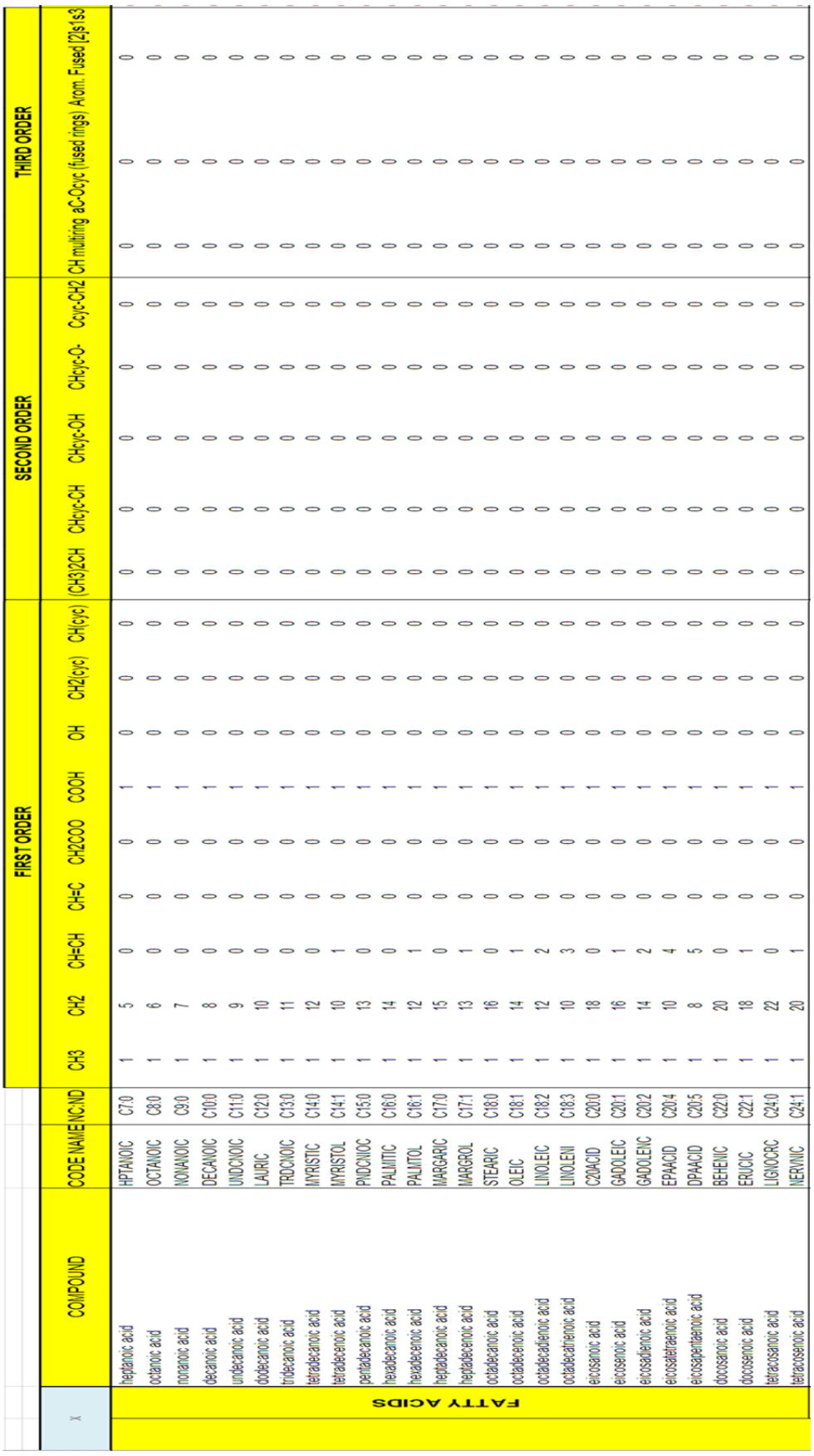
Finally, Figure 3.4 and Figure 3.5 show a partial set of the experimental data set contained for vapor pressure of fatty acids and liquid heat capacity for triglycerides respectively.

Table 3.2 Experimental data points available in the database.

	Basic & Critical	Heats of Formation	Vapor Pressure	Liquid Heat Capacity	Liquid Density	Liquid Viscosity	Surface Tension
Acylglycerides	4	-	53	9	76	118	137
Fatty Acids	58	20	562	120	49	284	46
Fatty Esters	56	8	339	98	41	264	186
Minor Compounds	-	-	3	-	-	-	-

X								SOURCE														
								OIL SEEDS									TREE FRUITS AND KERNELS				ANIMALS	
FAMILIES		COMPOUND	ABVT	NC:ND	C	H	O	SOYBEAN	COTTON SEED	PEANUT	CORN	SUNFLOWER	RICEBRAN	SAFFLOWER	CASTOR	CANOLA	OLIVE	PALM	COCONUT	PALM K.	LARD	TALLOW
	DIGLYCERIDES	1-octanoyl-2-octadecenoyl-sn-glycerol	CpO-	C26:1	29	54	5	-	-	-	-	-	-	-	-	-	-	-	X	-	-	-
		1-dodecanoyl-2-hexadecanoyl-sn-glycerol	LP-	C28:0	31	60	5	-	-	-	-	-	-	-	-	-	-	X	X	X	-	-
		1,2-ditetradecanoyl-sn-glycerol	MM-	C28:0	31	60	5	-	-	-	-	-	-	-	-	-	-	-	-	X	-	-
		1-decanoyl-2-dodecanoyl-3-octadecenoyl-sn-glycerol	CO-	C28:1	31	58	5	-	-	-	-	-	-	-	-	-	-	-	X	-	-	-
		1-dodecanoyl-2-octadecanoyl-sn-glycerol	LS-	C30:0	33	64	5	-	-	-	-	-	-	-	-	-	-	-	X	-	-	-
		1-tetradecanoyl-2-hexadecanoyl-sn-glycerol	MP-	C30:0	33	64	5	-	X	-	-	-	-	-	-	-	-	X	-	X	-	-
		1-dodecanoyl-2-octadecenoyl-sn-glycerol	LO-	C30:1	33	62	5	-	-	-	-	-	-	-	-	-	-	X	X	X	-	-
		1,2-dihexadecanoyl-sn-glycerol	PP-	C32:0	35	68	5	X	X	X	X	-	X	X	-	-	X	X	-	X	-	-
		1-tetradecanoyl-2-octadecenoyl-sn-glycerol	MO-	C32:1	35	66	5	-	X	-	-	-	-	-	-	-	-	X	X	X	-	-
		1-tetradecanoyl-2-octadecadienoyl-sn-glycerol	LiM-	C32:2	35	64	5	-	X	-	-	-	-	-	-	-	-	X	-	X	-	-
		1-hexadecanoyl-2-octadecanoyl-sn-glycerol	PS-	C34:0	37	72	5	-	X	-	-	-	X	-	-	-	X	X	-	-	-	-
		1-hexadecanoyl-2-octadecenoyl-sn-glycerol	PO-	C34:1	37	70	5	X	X	X	X	X	X	X	-	X	X	X	-	X	-	-
		1-hexadecanoyl-2-octadecadiienoyl-sn-glycerol	PLi -	C34:2	37	68	5	X	X	X	X	X	X	X	-	X	X	X	-	X	-	-
		1-hexadecanoyl-2-octadecatrienoyl-sn-glycerol	PLn -	C34:3	37	66	5	X	-	-	X	-	-	-	-	X	X	-	-	-	-	-
		1-heptadecanoyl-2-octadecenoyl-sn-glycerol	MgO-	C35:1	38	72	5	-	-	-	-	-	-	-	-	-	X	-	-	-	-	-
		1-heptadecenoyl-2-octadecenoyl-sn-glycerol	MoO-	C35:2	38	70	5	-	-	-	-	-	-	-	-	-	X	-	-	-	-	-
		1-hexadecanoyl-2-eicosanoyl-sn-glycerol	PA-	C36:0	39	76	5	-	-	-	-	-	-	-	-	-	X	-	-	-	-	-
		1,2-dioctadecanoyl-sn-glycerol	OS-	C36:1	39	74	5	X	X	X	X	X	X	X	-	X	X	X	-	-	-	-
		1-octadecanoyl-2-octadecedienoyl-sn-glycerol	OO-	C36:2	39	72	5	X	X	X	X	X	X	-	-	X	X	X	-	X	-	-
		1,2-dioctadecenoyl-sn-glycerol	SLi -	C36:2	39	72	5	-	X	X	-	-	-	X	-	-	-	-	-	-	-	-
		1-octadecanoyl-2-octadecadienoyl-sn-glycerol	OLi -	C36:3	39	70	5	X	X	X	X	X	X	X	-	X	X	X	-	X	-	-
		1-octadecenoyl-2-octadecadienoyl-sn-glycerol	LiLi-	C36:4	39	68	5	X	X	X	X	X	X	X	-	X	X	-	-	-	-	-
		1,2-dioctadecadienoyl-sn-glycerol	OLn-	C36:4	39	68	5	-	-	-	-	-	-	-	-	X	-	-	-	-	-	-
		1-octadecenoyl-2-octadecadienoyl-sn-glycerol	LiLn-	C36:5	39	66	5	X	X	-	X	-	-	X	-	X	-	-	-	-	-	-
		1-octadecadienoyl-2-octadecatrienoyl-sn-glycerol	LnLn-	C36:6	39	64	5	-	-	-	-	-	-	-	-	X	-	-	-	-	-	-
		1,2-dioctadecatrienoyl-sn-glycerol	PBe-	C38:0	41	76	5	-	-	X	-	-	-	-	-	-	-	-	-	-	-	-
		1-hexadecanoyl-2-docosanoyl-sn-glycerol	OA-	C38:1	41	76	5	X	-	X	-	-	-	-	-	X	X	-	-	-	-	-
		1-octadecenoyl-2-eicosenoyl-sn-glycerol	ALi-	C38:2	41	74	5	-	-	X	-	-	-	X	-	-	-	-	-	-	-	-
		1-octadecadienoyl-2-eicosenoyl-sn-glycerol	OGa-	C38:2	41	74	5	-	-	-	-	-	-	-	-	X	-	-	-	-	-	-
		1-octadecenoyl-2-eicosenoyl-sn-glycerol	LiGa-	C38:3	41	72	5	-	-	-	-	-	-	-	-	X	-	-	-	-	-	-
		1-octadecadienoyl-2-eicosenoyl-sn-glycerol	OBe-	C40:1	43	80	5	X	-	X	-	-	-	-	-	-	-	-	-	-	-	-
		1-octadecenoyl-2-docosanoyl-sn-glycerol	LiBe-	C40:2	43	78	5	-	-	X	-	-	-	-	-	-	-	-	-	-	-	-
		1-octadecadienoyl-2-docosanoyl-sn-glycerol	OEr-	C40:2	43	78	5	-	-	-	-	-	-	-	-	X	-	-	-	-	-	-
		1-octadecenoyl-2-docosenoyl-sn-glycerol	LiEr-	C40:3	43	76	5	-	-	-	-	-	-	-	-	X	-	-	-	-	-	-

Figure 3.2 Selected commodity oils/fats and the significant chemical species contained in the CAPEC_Lipids_Database



			FIRST ORDER								SECOND ORDER					THIRD ORDER		
	COMPOUND	CODE NAME	NC:ND	CH3	CH2	CH=CH	CH=C	CH2COO	COOH	OH	CH2(cyc)	CH(cyc)	(CH3)2CH	CHcyc-CH	CHcyc-OH	CHcyc-O-	Ccyc-CH2	CH multiring	aC-Ocyc (fused rings)	Arom.. Fused [2]s1s3
FATTY ACIDS	heptanoic acid	HPTANOIC	C7:0	1	5	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0
	octanoic acid	OCTANOIC	C8:0	1	6	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0
	nonanoic acid	NONANOIC	C9:0	1	7	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0
	decanoic acid	DECANOIC	C10:0	1	8	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0
	undecanoic acid	UNDCNOIC	C11:0	1	9	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0
	dodecanoic acid	LAURIC	C12:0	1	10	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0
	tridecanoic acid	TRDCNOIC	C13:0	1	11	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0
	tetradecanoic acid	MYRISTIC	C14:0	1	12	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0
	tetradecenoic acid	MYRISTOL	C14:1	1	10	1	0	0	1	0	0	0	0	0	0	0	0	0	0	0
	pentadecanoic acid	PNDCNOIC	C15:0	1	13	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0
	hexadecanoic acid	PALMITIC	C16:0	1	14	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0
	hexadecenoic acid	PALMTOL	C16:1	1	12	1	0	0	1	0	0	0	0	0	0	0	0	0	0	0
	heptadecanoic acid	MARGARIC	C17:0	1	15	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0
	heptadecenoic acid	MARGROL	C17:1	1	13	1	0	0	1	0	0	0	0	0	0	0	0	0	0	0
	octadecanoic acid	STEARIC	C18:0	1	16	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0
	octadecenoic acid	OLEIC	C18:1	1	14	1	0	0	1	0	0	0	0	0	0	0	0	0	0	0
	octadecadienoic acid	LINOLEIC	C18:2	1	12	2	0	0	1	0	0	0	0	0	0	0	0	0	0	0
	octadecatrienoic acid	LINOLENI	C18:3	1	10	3	0	0	1	0	0	0	0	0	0	0	0	0	0	0
	eicosanoic acid	C20ACID	C20:0	1	18	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0
	eicosenoic acid	GADOLEIC	C20:1	1	16	1	0	0	1	0	0	0	0	0	0	0	0	0	0	0
	eicosadienoic acid	GADOLENIC	C20:2	1	14	2	0	0	1	0	0	0	0	0	0	0	0	0	0	0
	eicosatetraenoic acid	EPAACID	C20:4	1	10	4	0	0	1	0	0	0	0	0	0	0	0	0	0	0
	eicosapentaenoic acid	DPAACID	C20:5	1	8	5	0	0	1	0	0	0	0	0	0	0	0	0	0	0
	docosanoic acid	BEHENIC	C22:0	1	20	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0
	docosenoic acid	ERUCIC	C22:1	1	18	1	0	0	1	0	0	0	0	0	0	0	0	0	0	0
	tetracosanoic acid	LIGNOCRC	C24:0	1	22	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0
	tetracosenoic acid	NERVNIC	C24:1	1	20	1	0	0	1	0	0	0	0	0	0	0	0	0	0	0

Figure 3.3 Molecular description of lipid compounds through the M&G (2001) method

×	COMPOUND	CODE NAME	EXPERIMENTAL VALUES												
FATTY ACIDS	hexanoic acid	HEXANOIC	Temperatue (K)	284.65	306.15	307.15	332.15	334.85	345.05	355.95	359.65	362.65	366.15	367.75	371.25	372.65
			Value (Pa)	1.33	10.01	13.33	100.07	133.32	266.64	533.29	666.61	666.61	1000.72	1066.58	1253.23	1333.23
			Reference	11	12	11	12	4	4	4	11	8	12	4	2	11
	heptanoic acid	HPTANOIC	Temperatue (K)	295.15	318.65	338.35	345.15	348.05	351.15	358.45	369.45	373.15	374.45	380.15	381.45	386.35
			Value (Pa)	1.33	13.33	66.66	100.07	133.32	133.32	266.64	533.29	666.61	666.61	1000.72	1066.58	1333.23
			Reference	11	11	11	12	4	8	4	4	11	8	12	4	8
	octanoic acid	OCTANOIC	Temperatue (K)	305.65	330.65	351.05	358.15	360.65	365.45	371.05	382.25	386.65	387.25	393.15	394.45	397.15
			Value (Pa)	1.33	13.33	66.66	100.07	133.32	133.32	266.64	533.29	666.61	666.61	1000.72	1066.58	1333.22
			Reference	11	11		12	4	8	4	4	11	8	12	4	8
	nonanoic acid	NONANOIC	Temperatue (K)	318.15	342.15	362.35	370.15	372.05	382.75	394.35	399.15	406.15	407.15	410.55	411.85	420.65
			Value (Pa)	1.33	13.33	66.66	100.07	133.32	266.64	533.29	666.61	1000.72	1066.58	1333.23	1333.23	2133.16
			Reference					4	4	4			4			4
	decanoic acid	DECANOIC	Temperatue (K)	328.15	344.35	352.15	372.75	381.15	383.45	394.25	405.85	410.15	418.15	418.65	421.85	425.35
			Value (Pa)	1.33	6.67	13.33	66.66	100.07	133.32	266.64	533.29	666.61	1000.72	1066.58	1333.23	1333.23
			Reference	11	13	13	11	12	4	4	4	11	12	4	11	8
	undecanoic acid	UNDCNOIC	Temperatue (K)	391.15	392.95	404.25	416.45	429.15	429.65	443.95	459.25	470.35	476.25	480.35	485.65	495.35
			Value (Pa)	100.07	133.32	266.64	533.29	1000.72	1066.58	2133.16	4266.32	7999.36	8532.63	10007.20	13332.27	17065.26
			Reference		4	4	4		4	4	4		4			4
	dodecanoic acid	LAURIC	Temperatue (K)	325.15	339.35	345.15	364.15	371.15	371.65	392.75	401.15	403.35	414.95	427.25	431.15	439.15
			Value (Pa)	0.13	0.69	1.33	6.67	13.33	13.33	66.66	100.07	133.32	266.64	533.29	666.61	1000.72
			Reference									4	4	4		
	tridecanoic acid	TRDCNOIC	Temperatue (K)	360.15	382.15	411.15	410.95	413.05	424.65	437.35	439.45	449.15	450.95	454.15	465.35	468.95
			Value (Pa)	1.00	10.01	100.07	133.32	133.32	266.64	533.29	666.61	1000.72	1066.58	1333.23	2133.16	2666.45
			Reference	12	12	12	8	4	4	4	8	12	4	8	4	8
	tetradecanoic acid	MYRISTIC	Temperatue (K)	341.15	357.15	362.65	372.85	382.75	389.15	389.65	393.15	410.95	417.65	422.35	434.25	447.05
			Value (Pa)	0.13	0.77	1.33	3.60	7.77	13.33	13.33	17.33	66.66	102.66	133.32	266.64	533.29
			Reference	13	13	13	13	13	11	13	13	11	13	4	4	4
	pentadecanoic acid	PNDCNIOC	Temperatue (K)	430.95	442.85	455.95	469.95	474.25	485.15	501.25	519.55	541.15	565.85	594.35	612.25	
			Value (Pa)	133.32	266.64	533.29	1066.58	1330.00	2133.16	4266.32	8532.63	17065.26	34130.53	68261.05	101325.23	
			Reference	4	4	4	4		4	4	4	4	4	4	4	
	hexadecanoic acid	PALMITIC	Temperatue (K)	355.65	371.85	377.95	393.15	395.15	405.15	405.65	416.65	427.85	438.15	440.55	452.15	465.35
			Value (Pa)	0.13	0.73	1.33	5.33	5.93	13.33	13.33	30.00	66.66	100.07	133.32	266.64	533.29
			Reference	13	13	13	13	13	13	11	13	11	12	4	4	4
	heptadecanoic acid	MARGARIC	Temperatue (K)	448.25	460.75	473.95	488.05	492.85	503.85	521.05	539.75	561.55	587.45			
			Value (Pa)	133.32	266.64	533.29	1066.58	1330.00	2133.16	4266.32	8532.63	17065.26	34130.53			
			Reference	4	4	4	4		4	4	4	4	4			
	octadecanoic acid	STEARIC	Temperatue (K)	349.65	369.15	386.15	392.15	414.95	417.35	420.65	421.15	444.06	456.15	456.75	469.05	482.35
			Value (Pa)	0.01	0.13	0.77	1.33	7.95	10.27	13.33	13.33	66.66	100.07	133.32	266.64	533.29
			Reference	11	11	13	11	13	13	11	13	11	13	4	4	4
	octadecenoic acid	OLEIC	Temperatue (K)	449.65	481.65	487.65	496.15	497.15	506.65	513.15	523.15	530.35	537.15	542.95	550.15	559.15
			Value (Pa)	133.32	666.61	1000.00	1330.00	1333.23	1999.84	2666.45	3999.68	5332.91	6532.81	7999.36	10000	13332.26675
	octadecadienoic acid	LINOLEIC	Temperatue (K)	406.15	497.15	497.15	503.15									
			Value (Pa)	9.33	1330.00	1333.23	2133.16									
			Reference													
	octadecatrienoic acid	LINOLENI	Temperatue (K)	497.15	497.65	504.15										
			Value (Pa)	1330.00	1333.23	2266.49										
			Reference													
	eicosanoic acid	C20ACID	Temperatue (K)	382.15	394.75	408.15	425.95	477.15	487.65	519.05	601.15					
			Value (Pa)	0.13	0.38	1.33	5.53	133.32	266.65	1330.00	101325.00					
			Reference	13	13	13	11	11	11		11					
	eicosapentaenoic acid	DPAACID	Reference													
	docosanoic acid	BEHENIC	Temperatue (K)	395.15	415.15	418.55	421.15	449.65	486.85	532.45	589.35	663.15				
			Value (Pa)	0.13	0.70	1.00	1.33	10.01	100.07	1000.72	10007.20	100000.00				
			Reference	13	13	12	13	12	12	12	12	12				
	docosenoic acid	ERUCIC	Temperatue (K)	512.85	520.55	537.65	543.75	558.15	554.15	562.25	573.35	579.65	587.55	609.65	631.95	654.25
			Value (Pa)	666.61	1000.00	1999.84	2666.45	4000.00	4199.66	5332.91	7999.36	10000.00	13332.27	26664.53	53329.07	100000.00
			Reference													
	tetracosanoic acid	LIGNOCRC	Temperatue (K)	530.15	544.15	558.15	572.15									
			Value (Pa)	532.96	532.96	532.96	532.96									

Figure 3.4 Experimental vapor pressure data for different fatty acids

x	COMPOUND	CODE NAME	EXPERIMENTAL VALUES																									
TRIACYLGLYCERIDES	1,2,3-trioctanoyl-sn-glycerol	CP-CP-CP	Reference	8	9	8	8	9	8	8	9																	
			Temperature (K)	324.15	338.15	373.15	388.15	413.15	423.15																			
			Value (J/gmolK)	921.10	921.10	983.90	979.71	979.71	1176.49																			
			Reference	9	8	9	8	8	9																			
			Temperature (K)	313.15	325.15	363.15	373.15	388.15	423.15																			
	1,2,3-tridecanoyl-sn-glycerol	C-C-C	Value (J/gmolK)	1109.50	1155.56	1189.05	1230.92	1184.86	1289.53																			
			Reference	8	9	8.00	9.00	8.00	9.00																			
			Temperature (K)	323.15	339.15	346.85	348.15	353.15	355.05	362.65	370.25	373.15	373.15	393.15	398.15	413.15	433.15	453.150								
	1,2,3-tridodecanoyl-sn-glycerol	L-L-L	Value (J/gmolK)	1306.28	1364.46	1377.83	1293.72	1338.34	1388.54	1401.91	1417.97	1369.59	1364.90	1400.84	1394.20	1432.02	1463.27	1494.45								
			Reference	8	5	5	8	10	5	5	5	10	8	10	8	10	10	10								
			Temperature (K)	331.55	333.15	338.45	353.15	358.15	358.45	365.05	373.15	383.15	393.15	408.15	413.15	433.15	453.15									
	1,2,3-tritetradecanoyl-sn-glycerol	M-M-M	Value (J/gmolK)	1556.27	1482.13	1568.39	1544.40	1528.18	1604.72	1616.83	1576.80	1620.29	1609.20	1599.36	1641.60	1673.92	1706.29									
			Reference	5	8	5	10	8	5	5	10	8	10	8	10	10	10									
			Temperature (K)	338.85	343.15	345.95	353.15	359.95	368.15	369.15	373.15	393.15	413.15	418.15	433.15	453.15										
	1,2,3-trihexadecanoyl-sn-glycerol	P-P-P	Value (J/gmolK)	1754.29	1666.35	1774.57	1757.72	1801.61	1729.15	1821.89	1797.69	1837.65	1877.61	1892.43	1917.49	1957.46										
			Reference	5	8	5	10	5	8	5	10	10	10	8	10	10										
			Temperature (K)	323.15	333.15	353.15	373.15	393.15	413.15	433.15	453.15															
	1,2-dihexadecanoyl-3-octadecenoyl-sn-glycerol	P-P-O	Value (J/gmolK)	1702.28	1796.70	1838.37	1880.04	1921.71	1963.37	2005.04	2046.71															
			Reference	10	10	10	10	10	10	10	10															
			Temperature (K)	333.15	353.15	373.15	393.15	413.15	433.15	453.15																
	1-hexadecanoyl-2-octadecanoyl-3-octadecenoyl-sn-glycerol	P-S-O	Value (J/gmolK)	1851.63	1892.89	1934.24	1975.59	2016.85	2058.20	2099.46																
			Reference	10	10	10	10	10	10	10																
			Temperature (K)	333.15	353.15	373.15	393.15	413.15	433.15	453.15																
	1-hexadecanoyl-2,3-dioctadecenoyl-sn-glycerol	P-O-O	Value (J/gmolK)	1787.40	1832.77	1876.15	2000.87	1968.90	2014.28	2059.66																
			Reference	10	10	10	10	10	10	10																
			Temperature (K)	352.15	353.15	361.95	371.65	373.15	378.15	393.15	403.15	413.15	428.15	433.15	453.15	453.15										
	1,2,3-trioctadecanoyl-sn-glycerol	S-S-S	Value (J/gmolK)	1978.23	1940.96	2000.62	2023.02	1985.09	2085.03	2029.22	2068.28	2073.34	2068.28	2117.38	2147.83	2161.51										
			Reference	5	10	5	5	10	8	10	8	10	8	10	8	10										
			Temperature (K)	333.15	353.15	373.15	393.15	413.15	433.15	453.15																
	1,2-dioctadecanoyl-3-octadecenoyl-sn-glycerol	S-S-O	Value (J/gmolK)	1915.93	1957.20	1998.48	2039.75	2081.02	2122.29	2163.56																
			Reference	10	10	10	10	10	10	10																
			Temperature (K)	333.15	353.15	373.15	393.15	413.15	433.15	453.15																
	1,2,3-trioctadecedienoyl-sn-glycerol	O-O-O	Value (J/gmolK)	1844.12	1879.53	1914.95	1950.37	1985.79	2021.21	2056.62																
			Reference	10	10	10	10	10	10	10																
			Temperature (K)																							
	1,2,3-trieicosanoyl-sn-glycerol	A-A-A	Value (J/gmolK)																							
			Reference																							

Figure 3.5 Experimental liquid heat capacity data for different triglycerides

3.1.2. Feature 2: Thermophysical Properties

This second feature was developed by means of a two-step methodology. In the first step (Section 3.1.2.1), the thermophysical property modeling of lipid compounds was made. From the selected single value properties to the relevant temperature dependent properties, a description of their significance to the edible oil and biodiesel industries, the state of the art mathematical models for estimating them, and an analysis of their performance is carried out.

In the second step (Section 3.1.2.2) the validated thermophysical models are used to generate two different databases: i) in the first database, the single value pure component property experimental (if available) or predicted data are contained. ii) In the second database the computed temperature dependent model parameters that are used to fill-out the lipid-database and to make it suitable for application with other computer-aided tools (such as commercial process simulators) are contained.

3.1.2.1. Thermophysical Property Modeling of Lipid Compounds

I. Thermophysical Property Modeling Needs

The first step toward the thermophysical property modeling of any given mixture has its basis in the modeling of pure component properties. In this work the most significant pure component properties, both single-value and temperature dependent, have been considered by means of validated models from the literature and by extending these models whenever needed (see Table 3.3).

a. Single Value Pure Component Properties

Estimation of pure compound single value properties has been widely performed through group contribution (GC) methods (Marrero & Gani, 2001). Methods proposed by Joback and Reid (1987), Lydersen (1955), Ambrose (1978), Klincewicz and Reid (1984), Lyman *et al.* (1990) and Horvath (1992), define the property of a compound as a function of structurally dependent parameters, which are determined by summing the frequency of each group occurring in the molecule times its contribution. These methods provide the advantage of quick estimates without requiring substantial computational resources. In spite of this advantage, it has been widely discussed that their applicability is greatly limited by the oversimplification of the molecular structure representation.

Table 3.3 Selected Thermophysical Properties suitable for design/analysis of lipid processes

		Property	Model
Single Value	Basic	Normal Melting Point	Marrero and Gani (2001)
		Normal Boiling Point	Marrero and Gani (2001)
	Critical	Temperature	Marrero and Gani (2001)
		Pressure	Marrero and Gani (2001)
		Volume	Marrero and Gani (2001)
	Standard Enthalpy	Formation	Marrero and Gani (2001)
		Fusion	Marrero and Gani (2001)
		Combustion	Marrero and Gani (2001)
	Other	Gibbs Energy of Formation	Marrero and Gani (2001)
Temperature Dependent		Vapor Pressure	GDT (Diaz *et al* 2010), CAPEC_PC-SAFT(2010)
		Enthalpy of Vaporization	Ceriani & Meirelles (2004)
		Liquid Heat Capacity	GDT (Diaz *et al* 2010),
		Viscosity	GDT (Diaz *et al* 2010),
		Surface Tension	GDT (Diaz *et al* 2010),
		Density	Modified Rackett Equation (Halvorsen, *et al.*, 1993), CCFA (Zong *et al.* 2010b), CAPEC_PC-SAFT(2010)

In order to consider, to some extent, the proximity effects and to distinguish among isomers, Constantinou and Gani (1994) proposed a method that performs the estimation at two levels: the basic level uses contributions from first-order simple groups, while the second level uses a small set of second-order groups having the first-order groups as building blocks. Following the concept of incorporating higher-order groups to account for polyfunctional and structural groups, Marrero and Gani (2001) (see section 3.1.2.1.II.a) developed a GC method to estimate the properties of an organic chemical at three levels.

The advantage of using the Marrero and Gani (MG) GC method is that, even though lipid-related compounds are complex molecules, this type of chemical species are described by a small set of already available first-order (i.e. CH_3, CH_2, COOH, CH=, COO, OH, $(CH_3)_2CH$), second-order (i.e. Ccyc-CH_3, Ccyc-CH_2), and third-order functional groups [*i.e.* -CHncyc (fused rings), aC-Ocyc (fused rings)]. Table 3.4 shows the molecular description of α-Tocopherol and methyl palmitate through the MG groups.

Table 3.4 Marrero and Gani (2001) depiction of α-Tocopherol and methyl palmitate (ME-C16H32)

Level	Group	Frequency	
		α-Tocopherol	ME-C16H32
First Order	CH_3	5	2
	CH_2	9	14
	CH	3	0
	COO	0	1
	aC	2	0
	aC-CH_3	3	0
	aC-OH	1	0
	CH_2(cyc)	2	0
	C(cyc)	1	0
	O(cyc)	1	0
Second Order	$(CH_3)_2CH$	1	-
	Ccyc-CH_3	1	-
	Ccyc-CH_2	1	-
Third Order	-CHncyc (fused rings)	1	-
	aC-Ocyc (fused rings)	1	-

b. Temperature Dependent Pure Component Properties

The use of GC-based methods for estimating thermophysical properties has not been limited to single value pure component properties. Different authors have used this approach for estimating different thermophysical temperature dependent properties such as vapor pressure (Ceriani and Meirelles, 2004), enthalpy of vaporization (Basarova and Svoboda, 1995; Ceriani *et al.*, 2010), liquid heat capacity (Kolská *et al.*, 2008; Ceriani *et al.*, 2010), and surface tension (Diaz-Tovar *et al*., 2011).

A later method to estimate thermophysical properties of glycerides was introduced by Zong *et al.* (2010). In their method, the Chemical Constituent Fragment Approach (CCFA), the glycerides (tri-, di-, and mono-) are considered to be compounds comprised of a backbone glycerol fragment with one, two, or three fatty acid fragments attached (see Figure 3.6). The thermophysical properties of a glyceride component are calculated from the composition of the constituent fragments and sets of fragment-specific parameters.

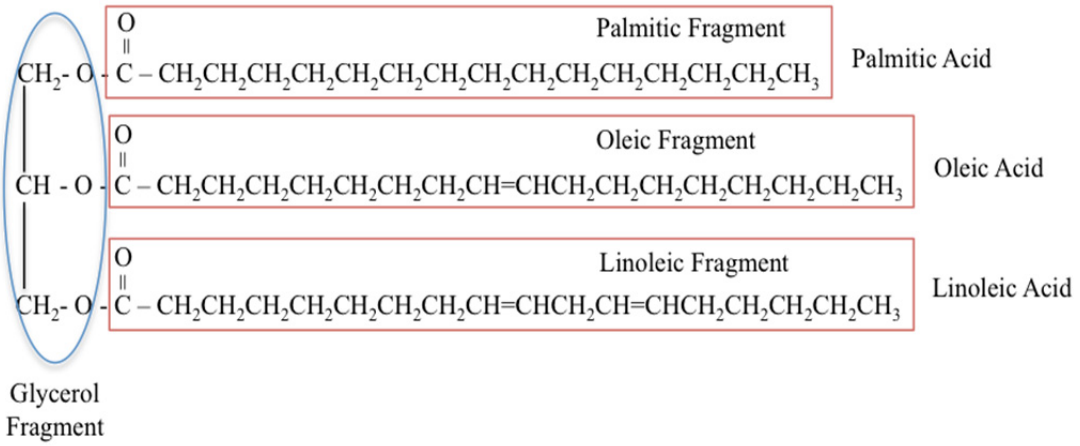


Figure 3.6 Fragment characterization of a triglyceride (Adapted from Zong *et al.*, 2010a)

b.1 Vapor Pressure

Vapor pressure (P_i^{sat}) of a given compound is the pressure of a vapor in thermodynamic equilibrium with its condensed phases in a closed system (Poling *et al.*, 2001). This thermophysical property plays a key role not only in processes used for the production of edible oils and fats, but also in those used for the production of biodiesel. In the former case, it is significant in processes that involve vapor-liquid equilibra such as the solvent recovery section of solvent-based extraction process or the physical refining. The latter case, it is of interest for two main reasons (Goodrum & Geller, 2002; Goodrum, 2002):

i) It is used to estimate atomization characteristics of fuels.
ii) Vapor pressures and boiling points of selected methyl esters and vegetable oils are proposed as quality control metrics for biodiesel.

Vapor pressures of the fatty compounds are usually very low, and thus measurements must be performed using an accurate technique (Perry *et al.*, 1949).

Ceriani and Meirelles (2004) developed a GC-base model to estimate the vapor pressure of lipid compounds. In their model, there are two main contributions:

i) The proposal of a new group to account for the glycerol backbone of the glycerides (CH_2-CH-CH_2).

ii) The addition of a "perturbation term" to account for the influence of compound chain length on its vapor pressure and, as proposed by Tu (1996), a "correction term" to describe the effect of some molecular structures (double bounds, side chain) and functional groups such as –OH and –COOH.

The parameters of the GC-based model were regressed from a database consisting of 1300 experimental values, among which 528 are fatty acids, 307 are fatty esters, 332 are fatty alcohols, 47 are triglycerides, and 6 monoglycerides. This robust data set allows the model to be applied not only for the prediction of glycerides but also for the prediction of fatty acids and esters, as well as to account the impact of the level of unsaturation in the carbon chains.

Zong *et al.* (2010a) apply their fragment-based method (CCFA) and the Clausius-Claperyon equation to estimate vapor pressures of triglyceride. To be highlighted that, due to the lack of experimental data for vapor pressures of unsaturated triglycerides, the fragment-based approach assumes that both saturated and unsaturated fatty acid chains of the same number of carbon atoms have identical vapor pressures (*e.g.* stearic acid, oleic acid, linoleic acid, and linolenic acid*)*.

Su *et al.* (2011) compared the behavior of the two proposed models and concluded that accuracy of both models is similar (see Table 3.5). However, in this work, the Ceriani and Meirelles (2004) model was selected for two reasons: i) the predictive nature of the model is not constraint only to glycerides but can be used to other lipid compounds (*e.g.* acids and esters) and ii) the assumption of considering identical behavior of same carbon chain-length saturated and unsaturated acids may become a serious limitation when an oil (such as soybean oil) rich in both type of acids is analyzed.

Table 3.5 Average Relative Deviation (ARD) of vapor pressure predictions

Glyceride	Zo *et al.* (2010)	Ceriani & Meirelles (2004)	Data Points	Temp. Range (ºC)
Simple TAG	13.02	17.76	135	45-313
Mixed TAG	18.63	10.08	226	189-317
MAG	9.19	9.05	6	175-211
Total	**16.41**	**12.88**	**367**	**-**

b.2 Enthalpy of Vaporization

The determination of enthalpies of formation in the gaseous state and comparisons of acidities, basicities, and reactivities in the gaseous state and in solution require the knowledge of the enthalpies of vaporization (ΔH_i^{vap}) of the involved species (Fuchs & Peacock, 1980). Much of the enthalpy of vaporization available in the literature consists of estimates based on various schemes and experimental values using methods with large uncertainties.

Based on the Clausius-Claperyon equation and the group contribution method of Ceriani and Meirelles (2004), Ceriani *et al*. (2010) developed a model for predicting the enthalpy of vaporization of lipid compounds. The database of experimental data used to verify the accuracy of the estimations of the method consists of 264 experimental values. Among them 119 are saturated fatty acids, 1 is unsaturated fatty acid, 98 are fatty esters, 37 are fatty alcohols, and 9 are glycerides.

The GC-based method proposed by Basarova and Svoboda (1995) and the linear equation proposed by Pitzer *et al.* (1955) use the critical temperature and the acentric factor for estimating the heat of vaporization over a wide range of substances and temperature.

The requirement of acentric factor and critical temperature when using Pitzer *et al.* (1955) and Basarova and Svoboda (1995) makes them less convenient for predictive applications. However, we find that the predictions by Ceriani *et al.* (2010) show an unexpected increase of the heat of vaporization with increasing temperature. As the temperature increases, the heat of vaporization should decrease.

b.3 Liquid Heat Capacity

Liquid heat capacity (C_{Pi}) is a measure of the amount of energy required by a unit mass (or mole) of a substance to raise its temperature by a unit degree. This thermophysical property of pure compounds is need in the evaluation of heating and cooling duties.

Morad *et al.* (2000) proposed the Rowling-Bondi equation to compute the liquid heat capacity. This equation requires as input the ideal gas heat capacity of, the universal gas constant, the reduced temperature, and the acentric factor. The

computation of these parameters follows the procedure proposed by Halvorsen *et al*. (1993) for the estimation of liquid density of triglycerides and oil mixtures based on the fatty acid composition. In their work experimental data were employed to determine the *Correction Factor*, which in turn is used to increase the accuracy of the model. The limitation of this model is that it cannot be extrapolated to predict the liquid heat capacity of other fatty compounds, such as fatty alcohols and fatty esters.

Kolská *et al.* (2008) and Ceriani *et al.* (2010) developed GC-based models to estimate the liquid heat capacity of lipid compounds. In the former model, the multilevel GC approach proposed by Marrero and Gani (2001) GC was taken as the basis and then extended by including additional parameters to account for the temperature dependence in the form of an empirical polynomial equation. In the later model, a significant database containing saturated and unsaturated fatty acids, fatty alcohols and esters, as well as hydrocarbons and triglycerides was used to regress the parameters of the equation.

These last two models could be equally used to predict the liquid heat capacity of the fatty compounds. Although, it is necessary to establish that, even though the model proposed by Kolská *et al.* (2008) has a wider range of applicability, the model proposed by Ceriani *et al.* (2009) has a higher accuracy.

b.4 Liquid Density

The prediction of the behavior of liquid oils under processing conditions depends on measuring bulk properties (density and viscosity). Liquid density (ρ_i) is important in the design and sizing of numerous chemical engineering unit operations of the lipid industry such as reactors, distillation columns, or storage tanks. Density data are relevant because injection systems, pumps, and injectors must deliver the amount of fuel precisely adjusted to provide proper combustion (Pratas *et al*, 2010).

Two criteria's are important for estimating the density of fatty acids (Halvorsen *et al.,* 1993). First, saturated and unsaturated fatty acids must be included in the density estimation scheme. Second, the estimation scheme must account for the temperature dependency of density. Both criteria are important for the design of vegetable oil

processing facilities and are frequently missing from previous fatty acid density estimation methods.

Halvorsen *et al.* (1993) use the Racket equation modified by Spencer and Danner (1973) that is commonly used for liquid density estimation and has been employed by different authors to accurately predict the liquid density of vegetable oils and fats based on their fatty acid composition (Ceriani *et al*, 2008; Noureddini *et al.*, 1992a). Density is first estimated as that of a liquid mixture of free fatty acids and then a correction factor to describe the triglyceride form is added. The accuracy of the density estimations obtained through this method (see Section 3.3.3) for oils, free fatty acids, and fatty esters is remarkable. However, extending the model for the computation of partial glycerides is not feasible as no correction factors were given.

Zong *et al.* (2010b) proposed the fragment-based approach to estimate thermophysical properties of di- and mono- glycerides. In the case of the liquid density, the liquid molar volume of each fragment is calculated with a temperature-dependent correlation and fragment parameters, and then estimate the overall liquid molar volume based on the composition and contribution of each. Their model is used in this work to compute the density of partial glycerides.

b.5 Liquid Viscosity & Surface Tension

Liquid viscosity and surface tension are thermophysical properties that are widely used in the design of chemical products and the processes. Knowledge and understanding of these properties are a key in detailed design of unit operations such as heat exchangers, distillation towers, *etc.*, where transport phenomena of mass and/or energy, wetting, adhesion, friction, spraying, and many more take place.

Liquid viscosity (μ_i^l) is a measure of the internal fluid friction, which tends to oppose any dynamic change in the fluid motion (Poling *et al*. 2001). An applied shearing force will result in a large velocity gradient at low viscosity. Increased viscosity causes each fluid layer to exert a larger frictional drag on adjacent layers that in turn decreases the velocity gradient. For the edible oil/fat and biodiesel industries, this is relevant not only because it is a reference of the internal friction to

resist flow, but also because the reduction of viscosity is the major reason why vegetable oils and fats are transesterified to biodiesel (Rabelo *et al.*, 2000).

Different authors (Noureddini *et al.,* 1992b; Valeri & Meirelles, 1997; Rabelo *et al.,* 2000; Boyaci *et al.*, 2002;) use the Andrade equation, or a modified version of it, to correlate the experimental data of liquid viscosities of different vegetable oils, fatty acids (from C12:0 to C22:1), and fatty acids methyl esters. Although, authors have reported great accuracy of their model predictions, their model parameters are not eligible for extrapolation. A more robust model to predict the liquid viscosity of different types of fatty compounds (acids, esters, and triglycerides) was developed by Ceriani *et al*. (2007) based on Ceriani and Meirelles (2004) GC-based model.

Surface tension (σ_i) is a measure of the property of liquids arising from unbalanced molecular cohesive forces at or near the surface, as a result of which the surface tends to contract. The relevance of this physical property is highlighted in the investigation of emulsions and in the design of biodiesel and equipment involving gas-liquid contact (Chumpitaz *et al.*, 1999; Allen *et al.*, 1999). In spite of the relevance of this property has in the edible oil and fat industry, as well as in the development of new biofuels, it has received very little attention. Only few studies have been published and what had been published is relatively old.

Three predictive models are available in the open literature to predict the surface tension of fatty compounds. Chumpitaz *et al.* (1999) use a van de Waals-type equation to correlate their experimental database containing different fatty acids and triglycerides. Allen *et al.* (1999) suggested the Sudgen expression to correlate this physical property to the experimental values of saturated methyl esters. Diaz-Tovar *et al.* (2011) applied the GC-based model proposed by Ceriani and Meirelles (2004) to predict the surface tension of lipid compounds. The advantage of this model is the capability of predicting surface tension of the different fatty compounds (glycerides, fatty acids, and fatty esters).

II. Thermophysical Property Models

a. Marrero and Gani (MG) Group Contribution Method

In this method, the molecular structure of a compound is considered to be a collection of three types of groups. The first-order groups have a large set of simple groups describing a wide variety of organic compounds. The second-order groups permit a better description of the polyfunctional compound structure that is not provided by the first-order groups and thus corrects the estimates at the first-order. The second-order groups are based on conjugation and, hence, account for distinctions among a class of isomers but not for *cis-trans* isomers. A final adjustment to the prediction of the property is performed through the third-order groups. These groups allow a quite detailed representation of systems of fused aromatic rings, systems of fused aromatic and nonaromatic rings, and systems of non-fused rings joined by chains in which can occur in different functional groups. Like the second-order groups, the third-order groups also use the first-order groups and do not represent the entire molecular structure of the chemical.

To some extent, second- and third-order groups can be considered as corrections to the general first-order contributions, as these last ones are considered to estimate satisfactorily the property values of relatively simple compounds whereas, for properties of more complex compounds, additional levels are needed to obtain more accurate estimations. This multilevel approach is illustrated in Figure 3.7, in which each region symbolizes a specific type of compounds.

The property-estimation model has the following (equation) form:

$$f(X) = \sum_r M_r C_r + w \sum_t N_s D_s + z \sum_t O_t E_t \qquad (3.1)$$

In Eq.(3.1), C_r is the contribution of the first-order group of type-*r* that occurs M_r times, D_s the contribution of the second-order group of type-*s* that occurs N_s times and E_t is the contribution of the third-order group of type-*t* that has O_t occurrences in a compound.

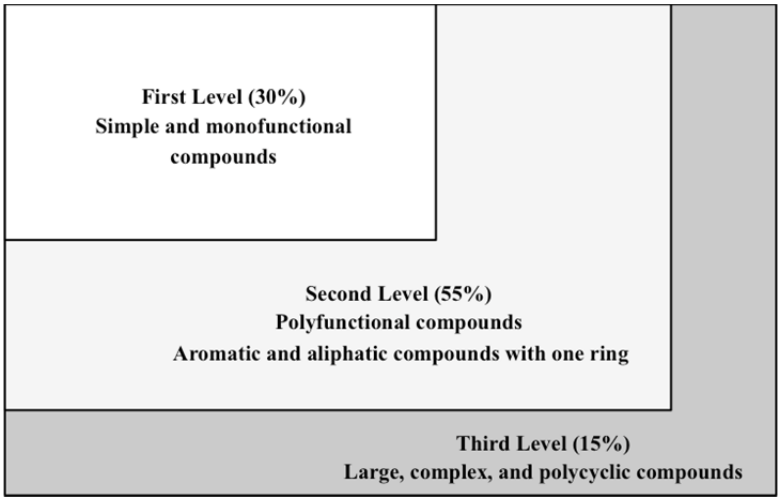


Figure 3.7 A multilevel approach for property estimation from group-contributions (adapted from Marrero & Gani, 2001)

The left-hand side of Eq. (3.1) is a simple function *f(X)* of the target property *X*. Table 3.6 shows the selected function for each single value pure component property. The selection of this function has been based on the following criteria.

a) The function has to achieve additivity in the contributions C_r, D_s, and E_t.
b) It has to exhibit the best possible fit of the experimental data.
c) It should provide good extrapolating capability and therefore, a wide range of applicability.

Table 3.6 Selected function for the single value property model

Property	**Left-hand side of Eq. 3.1**
Normal melting point (T_m)	$\exp\left(\frac{T_m}{147.45}\right)$
Normal boiling point (T_b)	$\exp\left(\frac{T_b}{222.543}\right)$
Critical temperature (T_c)	$\exp\left(\frac{T_b}{231.239}\right)$
Critical pressure (P_c)	$\left(P_c - 5.9827\right)^{-0.5}$
Critical volume (V_c)	$V_c - 7.95$
Standard Gibbs Energy at 298K (G_f)	$G_f + 34.697$
Standard enthalpy of formation at 298K (H_f)	$H_f - 5.549$
Standard enthalpy of vaporization at T_b (H_v)	$H_v - 11.733$
Standard enthalpy of fusion at 298K (H_{fus})	$H_{fus} + 2.806$

According to these criteria, the selected functions are the same as used by Constantinou and Gani (1994). Additional adjustable parameters of the estimation models or universal constants are (T_{m0}, T_{b0}, T_{c0}, P_{c1}, P_{c2}, V_{c0}, G_{f0}, H_{f0}, H_{v0}, H_{fus0}) also regressed.

The determination of the adjustable parameters of the models, that is, the contributions C_r, D_s, and E_t has been divided into a three-step regression procedure.

a) Regression is carried out to determine the contributions (C_r) of the first-order groups and the universal constants of the models while *w* and *z* are set to zero
b) Then, *w* is set to unity, *z* is set to zero and another regression is performed using the C_r and the universal constants calculated in the previous step to determine the contributions (D_s) of the second-order groups.
c) Finally, both *w* and *z* are assigned to unity and, using the universal constants of the models (C_r and D_s obtained as results of the previous steps), the contributions (E_t.) of the third-order groups are determined.

b. Temperature Dependent Pure Component Properties

b.1 General Temperature Dependent (GTD) Model (vapor pressure, liquid heat capacity, liquid viscosity, and surface tension)

A general model to predict the following temperature dependent properties - vapor pressure (Ceriani & Meirelles, 2004), liquid viscosity (Ceriani *et al.*, 2007), and liquid heat capacity (Ceriani *et al.*, 2009) - has been developed from GC-based models. Also, using the same model equation and functional groups, a model for surface tension as a function of temperature has been developed (Diaz-Tovar *et al.*, 2011). This general model is represented by Eqs. (3.2)-(3.6). It is to be highlighted that for the case of temperature dependent properties, a new functional group (CH_2-CH-CH_2), proposed by Ceriani and Meirelles (2004), has been added as a new functional group to represent the glycerol part of the glycerides.

$$f(X) = \sum_k N_k \left(A_{1k} + \frac{B_{1k}}{T^{-a1}} - a_2 C_{1k} \cdot \ln T - a_3 D_{1k} \cdot T \right) + c_1 \left[MW_i \sum_k N_k \left(A_{2k} + \frac{B_{2k}}{T^{-b1}} - b_2 C_{2k} \cdot \ln T - b_3 D_{2k} \cdot T \right) \right] + c_3 Q \tag{3.2}$$

where N_k is the number of groups k in the molecule; MW_i the component molecular weight that multiplies the "perturbation term"; A_{1k}, B_{1k}, C_{1k}, D_{1k}, A_{2k}, B_{2k}, C_{2k}, D_{2k} are parameters obtained from the regression of the experimental data; k represents the groups of component i; and Q is a correction term expressed as

$$Q = \xi_1 \cdot q + \xi_2 \tag{3.3}$$

where ξ_1 and ξ_2 are related to each class of lipid compounds.

In Eq. (3.3), q is function of the temperature, expressed as

$$q = \alpha + \frac{\beta}{T^{d1}} - d_2 \cdot \gamma \cdot \ln T - d_3 \cdot \delta \cdot T \tag{3.4}$$

where, α, β, γ, and δ are parameters obtained by regression.

In Eq. (3.3), ξ_1 is a function of the total number of carbon-atoms (N_c) in the molecule and is calculated as follows:

$$\xi_1 = f_0 + N_C \cdot f_1 \tag{3.5}$$

Where, f_0 and f_1 are optimized constants.

The term ξ_2 (see Eq. (3.3)) describes the differences between the values in the properties of the isomers of esters at the same temperature, and is related to the number of carbons of the substitute fraction (N_{cs}) as follows:

$$\xi_2 = s_0 + N_{CS} \cdot s_1 \tag{3.6}$$

Where, s_0 and s_1 are regressed constants. Eq. (3.6) is mainly used to account for the effect of the alcoholic portion of the fatty esters. Since they are obtained from the reaction of fatty acids and short-chain alcohols (C1–C4), the molecule can be split in two parts; N_{cs} represents the number of carbons of the alcoholic part.

The values of the coefficients (a_1, a_2, a_3, b_1, b_2, b_3, c_1, and c_2) that define the specific algebraic form of the model for each property type are listed in Table 3.7. In all other references to this model, the term "GTD-model" will be used.

Table 3.7 GTD model coefficients for vapor pressure, liquid heat capacity, liquid viscosity, and surface tension.

Coefficient	Vapor Pressure	Liquid Heat Capacity	Liquid Viscosity	Surface Tension
a_1	1.5	-1.0	1.0	-1.0
a_2	1.0	0.0	1.0	0.0
a_3	1.0	0.0	1.0	0.0
b_1	1.5	-1.0	1.0	-1.0
b_2	1.0	0.0	1.0	0.0
b_3	1.0	0.0	1.0	0.0
c_1	1.0	0.0	1.0	1.0
c_2	1.0	0.0	1.0	1.0
d_1	1.5	0.0	1.0	-1.0
d_2	1.0	0.0	1.0	0.0
d_3	1.0	0.0	1.0	0.0

b.2 Clausius–Clapeyron Equation (Enthalpy of Vaporization)

The enthalpy of vaporization (ΔH_i^{vap}) of a compound *i* is estimated by the Clausius–Clapeyron equation as a function of its vapor pressure (P_i^{sat}) and the temperature (T) (Joback & Reid, 1987):

$$\frac{dP_i^{sat}}{dT} = \frac{\Delta H_i^{vap}}{T\left(V^v - V^l\right)} \tag{3.7}$$

Assuming that, at low pressures, V^l is small compared to V^v and that the vapor phase shows an ideal behavior, Eq. (3.7) reduces to the simplified form given as

$$\frac{dP_i^{sat}}{dT} = \frac{P_i^{sat}\Delta H_i^{vap}}{RT^2} \tag{3.8}$$

By substituting the coefficients given for the vapor pressure in Table 3.7, Eq. (3.2) is reduced to:

$$P_i^{sat} = \exp\left[A_i^{'} + \frac{B_i^{'}}{T^{1.5}} - C_i^{'} \cdot \ln T - D_i^{'} \cdot T\right] \tag{3.9}$$

The term dP_i^{sat}/dT in Eq. (3.8) is obtained from Eq. (3.9) by differentiating the right hand side of the equation with respect to T:

$$\frac{dP_i^{sat}}{dT} = -P_i^{sat}\left(\frac{1.5 \cdot B_i^{'}}{T^{2.5}} + \frac{C_i^{'}}{T} + D_i^{'}\right) \tag{3.10}$$

The final expression for ΔH_i^{vap} as a function of T is then obtained as

$$\Delta H_i^{vap} = -R\left(\frac{1.5 \cdot B_i^{'}}{T^{0.5}} + C_i^{'} \cdot T + D_i^{'} \cdot T^2\right) \tag{3.11}$$

where R is the gas constant (8.3144 J/gmolK for ΔH_i^{vap} in J/gmol).

Values of the model parameters B'_i, C'_i, and D'_i of Eq. 3.11 are the same as reported by Ceriani and Meirelles (2004). At high temperatures and, consequently, high vapor pressures, the simplifications assumed in Eq. (3.8) are no longer valid, and ΔH_i^{vap} falls rapidly to zero. In these cases, a correction term should be included as proposed by Haggenmacher (Ceriani *et al.,* 2010), and Eq. (3.11) becomes

$$\Delta H_i^{vap} = -R\left(\frac{1.5 \cdot B_i^{'}}{T^{0.5}} + C_i^{'} \cdot T + D_i^{'} \cdot T^2\right) \cdot \left(1 - \frac{T_c^3 \cdot P_i^{sat}}{T^3 \cdot P_{ci}}\right)^{0.5} \tag{3.12}$$

b.3 Liquid Density

i. Modified Rackett Equation

The model form used by Halvorsen *et al.* (1993) is given in Eq. (3.13). When computing the density of oils, a correction factor, F_c, is added to account for the triglyceride form of the fatty acids in the oil,

$$\rho_i^l = \left(\sum_i x_i MW_i\right)\left\{R\left(\frac{\sum_i x_i T_{c_i}}{P_{c_i}}\right)\left(\sum_i x_i Z_{RA_i}\right)^{\left[1+(1-T_r)^{2/7}\right]}\right\}^{-1} + F_c \tag{3.13}$$

Where, x_i is the mole fraction of each component.

The Rackett parameter, Z_{RA}, is a unique correlating parameter for each compound. This parameter can be estimated with a reference density, ρ_{ref}, at a given temperature,

$$Z_{RA_i} = \left[\frac{MW_i \cdot P_{c_i}}{\rho_{ref} \cdot R \cdot T_{c_i}}\right]^{\left[1+(1-T_r)^{2/7}\right]^{-1}} \tag{3.14}$$

A simple molar average of the critical temperatures and pressures is used for the pseudo-critical properties,

$$T_{c,mix} = \sum_i x_i T_{c_i} \tag{3.15}$$

$$P_{c,mix} = \sum_i x_i P_{c_i} \tag{3.16}$$

The correction factor equation for oils with molecular weight greater than 875 is given by Eq. (3.17). For molecular weights lower than 875 the correction factor is given by Eq. (3.18):

$$F_c = 0.0236 + 0.000082\left|875 - MW_{oil}\right| \tag{3.17}$$

$$F_c = 0.0236 + 0.00098\left|875 - MW_{oil}\right| \tag{3.18}$$

where,

$$MW_{oil} = 3\sum_i x_i MW_i + 38.0488 \tag{3.19}$$

Setting the mole fraction, x_1, in Eqs. (3.13), (3.15), (3.16) and the correction factor, F_c, in Eq. (3.13) to be one and zero respectively, the pure component liquid densities of fatty acids and fatty esters are also obtained. Table 3.8 shows the model parameters of different short, medium, and long carbon chain free fatty acids.

Table 3.8 Modified Racket Equation parameters for different fatty acids

Fatty Acid	Carbon Chain Length	T_c (K)	P_c (bar)	Z_{RA}
Caprylic Acid	C8:0	694.26	27.79	0.25001
Capric Acid	C10:0	723.00	22.50	0.24347
Lauric Acid	C12:0	743.30	19.40	0.24200
Myristic Acid	C14:0	765.00	16.44	0.23517
Palmitic Acid	C16:0	785.22	14.68	0.23379
Stearic Acid	C18:0	804.00	13.60	0.23518
Oleic Acid	C18:1	781.00	13.90	0.23849
Linoleic Acid	C18:2	775.00	14.10	0.23800
Arachidic Acid	C18:3	821.00	12.40	0.23288
Behenic Acid	C20:0	855.00	11.00	0.22588

ii. Chemical Constituent Fragment (CCF) Approach

In the Chemical Constituent Fragment Approach (CCFA), liquid molar volumes of mono- and diglycerides are calculated from the fragment composition and the fragment-specific parameters:

$$V^{l} = \sum_{A} N_{frag,A} V_{A}^{l}(T) \tag{3.20}$$

Where V^{lm}_{A} is the liquid molar volume of fragment A in the component, m^3/kmol; $N_{frag,A}$ is the number of fragments A in the component.

The Van Krevelen model[20] is used to estimate liquid molar volume of fragment A:

$$V_{A}^{lm} = \frac{1 + B_{2,A} \cdot T}{B_{1,A}} \tag{3.21}$$

Where $B_{1,A}$ and $B_{2,A}$ are temperature dependency correlation parameters of fragment A; T is the temperature, K.

The parameters $B_{1,A}$ and $B_{2,A}$ for the monoglyceride fragment are regressed against experimental density data of monoacetate [C2:0] with a temperature range from 283.15 to 343.15 K. The acetic acid fragment parameters are extrapolated from the relationships between the fragment parameters $B_{1,A}$, $B_{2,A}$ and the carbon number of the fatty acid fragments. The parameters $B_{1,A}$ and $B_{2,A}$ for the diglyceride fragment are regressed against experimental density data of diacetate. Table 3.9 lists the calculated parameters $B_{1,A}$ and $B_{2,A}$ for the three glycerol and the FFA fragments.

Table 3.9 Calculated liquid molar volume parameters for the mono-, di-, and tri fragments and the fatty acid fragments

Fragments	Carbon Chain Length	$B_{1,A}$ (kmol/m^3)	$B_{2,A}$ (1/K)
monoglycerol		17.412	6.9785E-04
diglycerol		18.939	9.5032E-04
triglycerol		20.048	7.6923E-04
caproic acid	C6:0	12.476	1.2385E-03
caprylic acid	C8:0	9.396	1.2232E-03
capric acid	C10:0	7.700	1.2345E-03
lauric acid	C12:0	6.579	1.2687E-03
myristic acid	C14:0	5.758	1.3154E-03
palmitic acid	C16:0	5.052	1.3008E-03
palmitoleic acid	C16:1	5.052	1.3008E-03
stearic acid	C18:0	4.633	1.4091E-03
oleic acid	C18:1	4.292	9.8650E-04
linoleic acid	C18:2	4.168	7.4102E-04
linolenic acid	C18:3	4.323	8.1078E-04
arachidic acid	C20:0	4.117	1.5393E-03
behenic acid	C22:0	3.769	1.6875E-03
erucic acid	C22:1	3.769	1.6875E-03

b.4 PC-SAFT Equation of State

The PC-SAFT EoS (Gross & Sadowski, 2001) provides an alternative for the prediction of properties when no experimental data are available. The *Statistical associated-fluid theory* (SAFT) is based in the first-order perturbation theory of Wertheim. The essence of this theory is that the residual Helmholtz energy is given by a sum of expressions to account not only for the effects of short repulsions and long-range dispersion forces but also for two other effects: chemically bonded aggregation and association and/or solvation between different molecules (Gross & Sadowski, 2001).

This PC-SAFT EoS requires as input three pure compound parameters that can be obtained through the GC-method. The CAPEC_PC-SAFT (Privat, 2009) software has been developed as a quick and easy application for chemicals with little or no experimental data. The procedure employed to generate the PVT calculations is given below:

i. Define the molecular structure with the Marrero-Gani groups.
ii. Calculate the PC-SAFT EoS parameters (m, sigma, epsilon/k) with the GC-based method
iii. Use the PC-SAFT EoS to generate the PVT data.

Application of the PC-SAFT EoS is highlighted for α-tocopherol (see Figure 3.8).

i. The compound is defined by:
   The group representation of alpha-tocopherol is given in Table 3.4.
ii. Calculated values of the three parameters are:
   m = 1.62410; sigma = 7.74050; epsilon/k = 824.06522
iii. Figure 3.9 shows the vapor pressure and the enthalpy of vaporization profiles as a function of temperature.

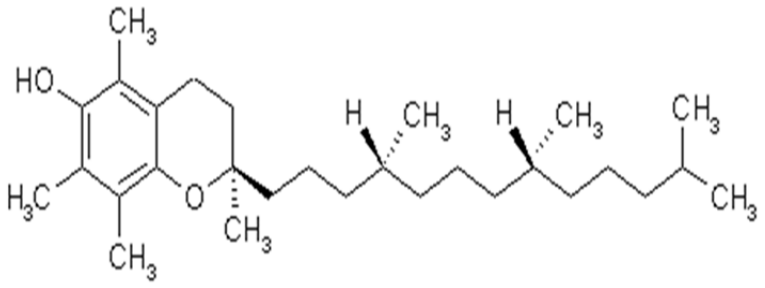


Figure 3.8 2D schematic representation of α-Tocopherol

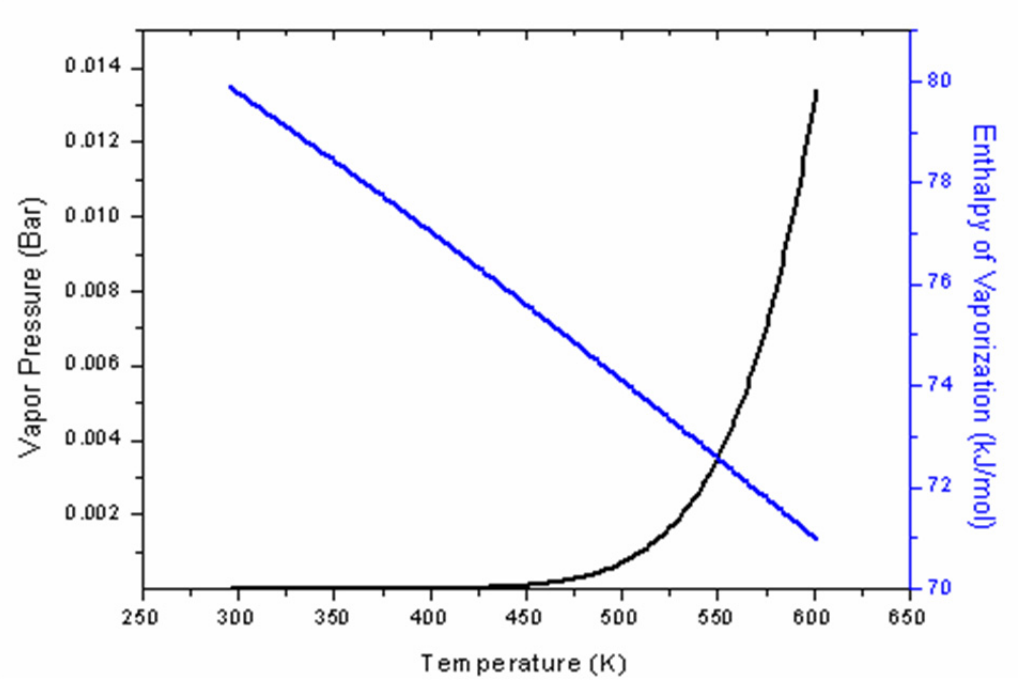


Figure 3.9 Vapor pressure and enthalpy of vaporization profiles for α-tocopherol computed with CAPEC PC-SAFT.

III. Model Performance

a. Single Value Pure Component Properties

Table 3.4 shows the higher-order Marrero and Gani (2001) functional groups and their times of occurrence needed to describe the compound α-Tocopherol.

After defining the functional groups it is possible to compute the single value properties mentioned above. Note that although, Eq. (3.1) is a general model for all the properties, the definition of *f(X)* is specific for each property.

In this work the normal melting and normal boiling points, critical temperature, pressure, and volume properties as well as the energies of formation were computed by means of the software ICAS ProPred®. Note that more experimental data is available in the lipid database for fatty acids and esters than the other lipid compounds. The compared predicted and experimental values of properties, such as, normal melting point and enthalpy of formation show that the accuracy of the model is decreasing as the length of the carbon chain increases (see Table 3.10), but the extrapolation error is still within acceptable limits. Also, the deviations for the rest of the properties that can be predicted by means of this method have been found to be within 1-10%.

Table 3.10 Marrero and Gani (2001)] model performance for single value properties of fatty compounds

Compound	Property	Exp.	Deviation (%)
Lauric Acid	Normal Melting Point (K)	316.35	1.01
Monosterain		332.15	10.93
Methyl Myristate		292.15	2.91
Ethyl Oleate		278.95	4.68
Capric Acid	Critical Temperature (K)	723.00	0.36
Palmitic Acid		785.22	0.62
Stearic Acid		805.09	1.05
Methyl Caprate		671.00	0.53
Caproic Acid	Gibbs Energy of Formation (KJ/mol)	-338.00	0.41
Undecanoic Acid		-296.63	0.54
Myristic Acid		-278.00	0.39
Methyl Caprate		-254.70	3.69
Heptanoic Acid	Enthalpy of Formation (KJ/mol)	-536.20	0.19
Oleic Acid		-764.80	15.73
Linolenic Acid		-508.80	18.93
Methyl Caprate		-573.80	2.07

b. General Temperature Dependent Model

b.1 Vapor Pressure

The performance evaluation of the GTD-model for the prediction of vapor pressure of fatty compounds has been done by analyzing the average relative deviation (ARD) (see Eq. (3.22)). For fatty acids, fatty esters and monoglycerides this was found to be within 10%; while for triglycerides, the ARD is almost 18%. For different long-chain triglycerides, the boiling points have been estimated from GTD-model by specifying the known vapor pressure values. These calculated values have been compared with experimental data and the results are given in Table 3.11. Very low errors were obtained. Figure 3.10 compares the experimental data with predicted values (with the GTD-model) for different medium and long-chain fatty methyl esters. Figure 3.11 shows the experimental and predicted normal boiling points of different short, medium, and long carbon chain triglycerides.

$$ARD(\%) = \frac{1}{N}\sum_{j=1}^{N}\left[\frac{\left|x_j^{\exp} - x_j^{\mathrm{val}}\right|}{x_j^{\exp}}\right]\cdot 100 \qquad (3.22)$$

were:

- N is the total number of experimental data points;
- x_j^{exp} is j-th experimental data point; and
- x_j^{pred} is the j-th predicted data point.

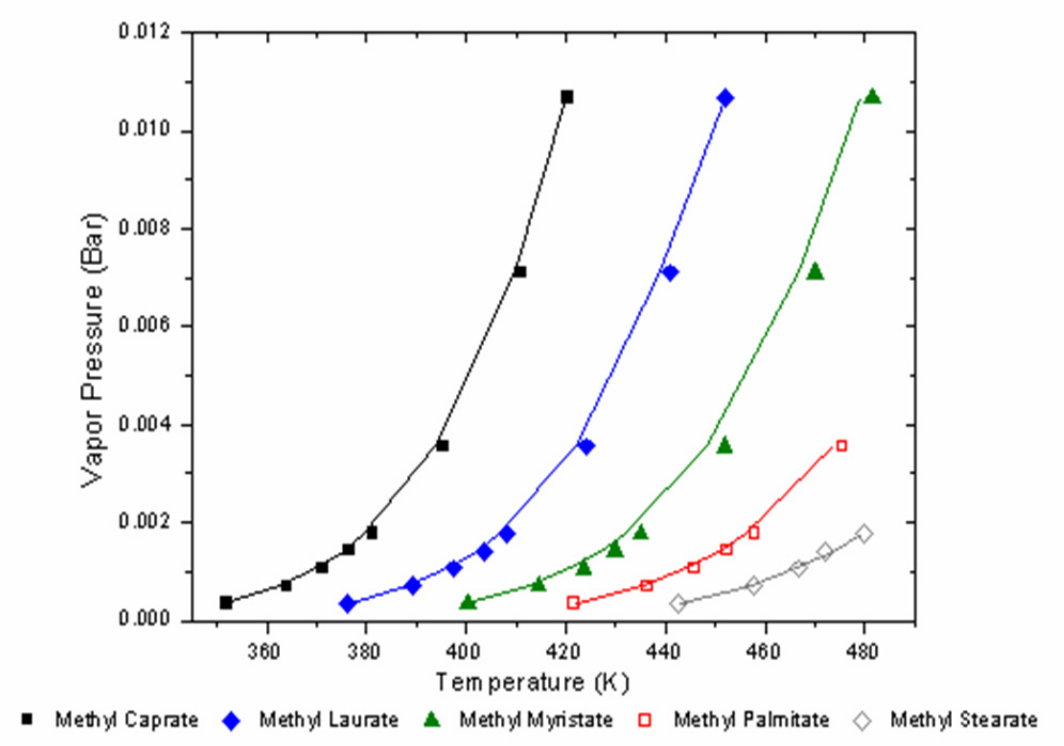


Figure 3.10 Experimental and calculated values (GTD-model) of vapor pressures of medium and long-chain FAME

Table 3.11 Boiling temperatures for long-chain TAGs at a given pressure using the GTD-Model.

Triglyceride	Pressure (mmHg)	Predicted Values (K)	Literature Values (K)	Deviation (%)
Trilaurin	0.050	519.81	517.15	0.5144
	0.001	462.25	461.15	0.2385
Trimyristin	0.050	547.00	548.15	0.2098
	0.001	491.58	489.15	0.4968
Tripalmitin	0.050	568.77	571.15	0.4167
	0.001	512.44	512.15	0.0566
Tristearin	0.050	587.61	586.15	0.2491
	0.001	533.66	526.15	1.4200

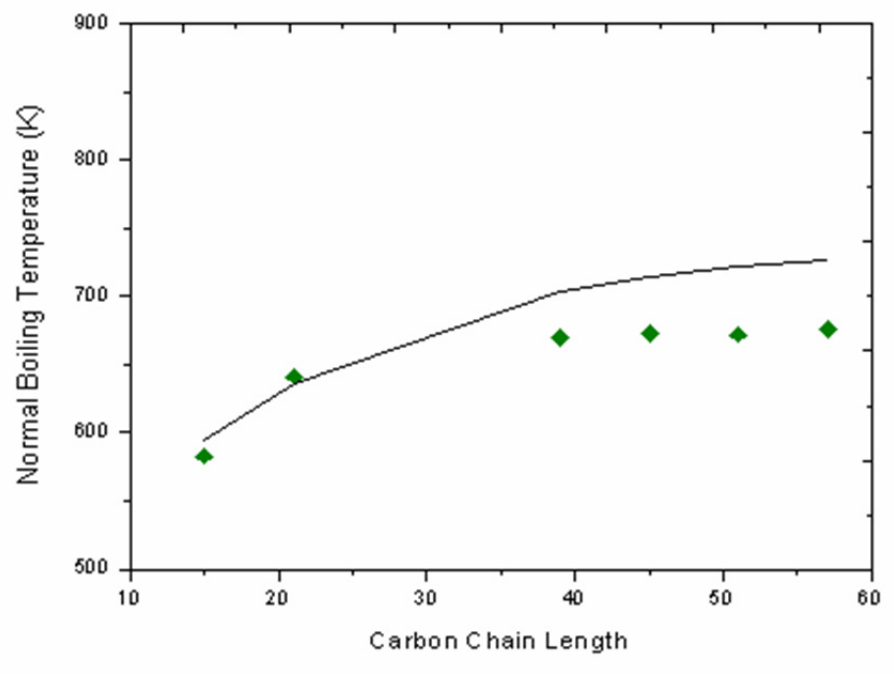


Figure 3.11 Normal boiling point of different TAGs (predicted and calculated)

b.2 Liquid Heat Capacity

For liquid heat capacities, the performance of the GTD-model is highlighted through the average relative deviations (ARD) for different classes of lipid compounds in Table 3.12. It can be noted that the fatty alcohols have the largest ARD (3.15%) while the fatty esters have the smallest ARD (0.46%). The limitations of this model are the incapability to extend it to mono- and di- glycerides and that there is no "perturbation term" to distinguish between the fatty ester isomers. Figure 3.12 and Figure 3.13 compare the performance of the GTD-model against experimental data for different medium and long-chain triglycerides for a wide range of temperature and for different methyl esters of n-alkanoic acids (C7-C20), respectively.

Table 3.12 ARD for liquid heat capacities of fatty compounds using the GTD-Model

Family	Number of Data Points	Carbon Length	TDG Model
Triglycerides	168	21-57	2.82
Fatty Acids	150	5-26	2.79
Fatty Esters	125	8-21	0.46
Fatty Alcohols	557	5-22	3.15
Hydrocarbons	395	6-50	2.32
Total	**1395**	**6-57**	**2.60**

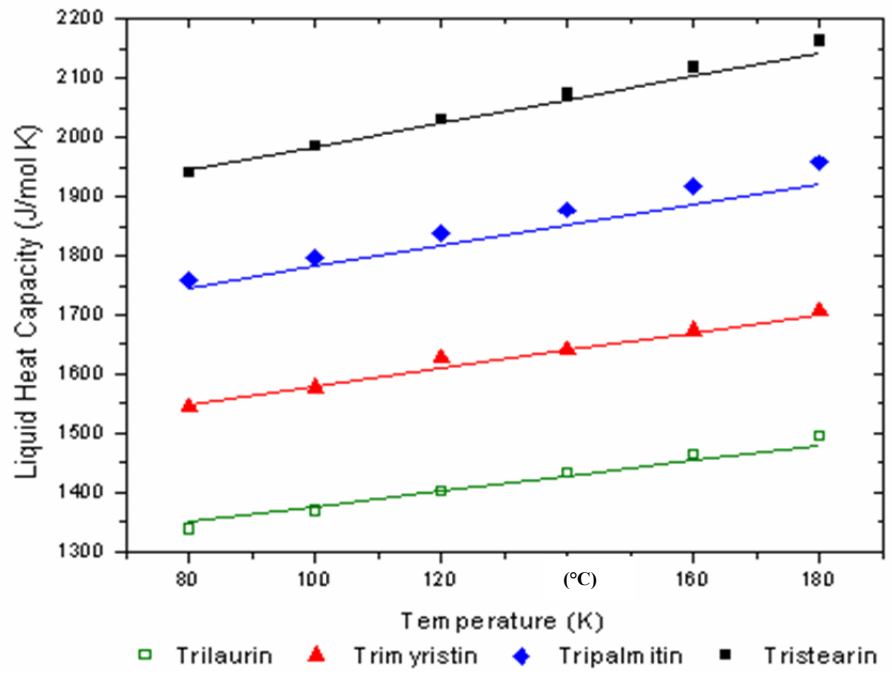


Figure 3.12 Experimental and predicted values (GTD-model) of liquid heat capacities of saturated triglycerides.

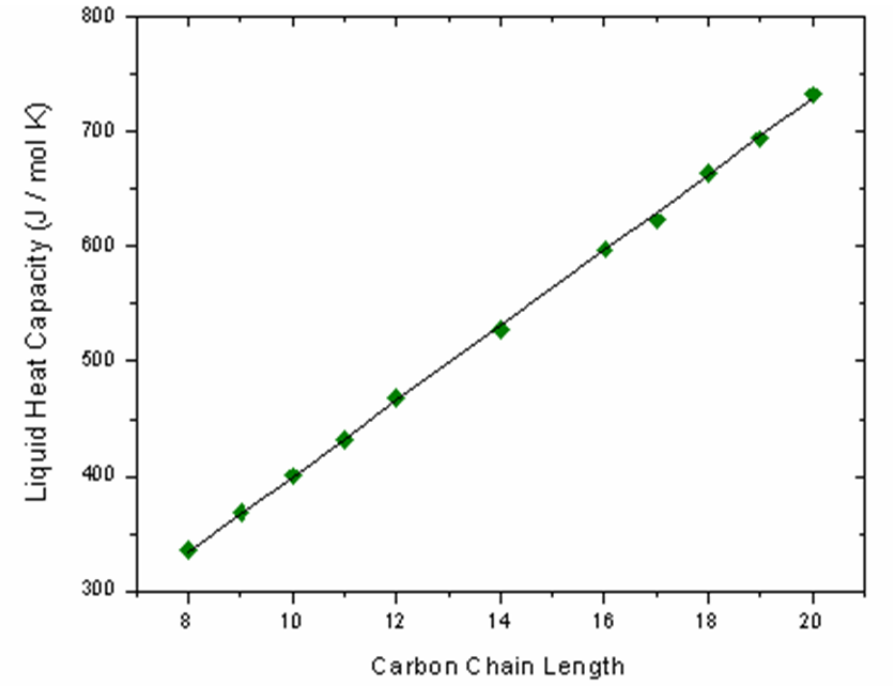


Figure 3.13 Experimental and predicted values of liquid heat capacities different methyl esters of n-alkanoic acids (C7-C20)

b.3 Liquid Viscosity

The GTD-model performance for prediction of different fatty compounds is analyzed through the average relative deviation (ARD) (see Table 3.13). The different classes of fatty compounds showed similar ARD (4-6%). The GTD-model for the prediction of this property has two main limitations: First, the model is

unable to distinguish between the mono- and di- glycerides; and second, the range of temperature (20-170°C) of the experimental data may lead to higher deviations when extrapolated to other process conditions (e.g. temperatures above 220°C found in the deodorization process). Figure 3.14 compares experimental data of different fatty acid methyl esters with the predicted values from the GTD-model.

Table 3.13 ARD for dynamic viscosity of fatty compounds using GTD-Model

Family	Number of Data Points	Carbon Length	ARD(%)
Saturated Fatty Acids	284	6-22	5.71
Fatty Esters	264	7-21	4.50
Fatty Alcohols	97	6-14	3.98
Triglycerides	118	21-57	4.85
Total	**763**	**6-57**	**4.86**

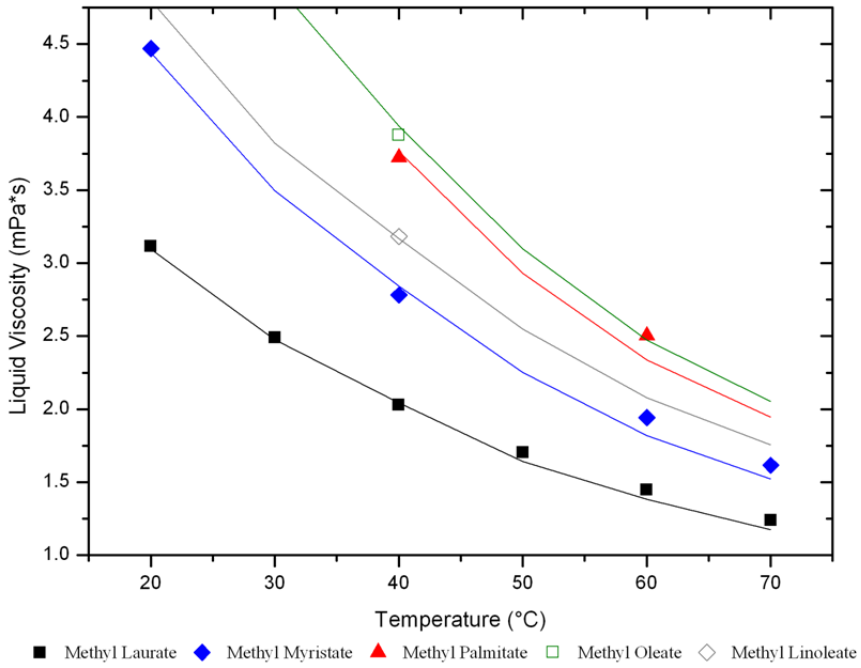


Figure 3.14 Experimental and calculated values (GTD-model) of dynamic viscosities of various fatty methyl esters

b.4 Surface Tension

GTD-model parameters for surface tension are presented in this work for the first time. Table 3.14 shows the regressed values for the parameters given in Eqs. (3.2)-(3.6).

Table 3.14 Surface Tension adjusted parameters for the GTD-Model

Group	A_{1i}	B_{1i}	A_{2i}	B_{2i}
CH3	4.44360E+03	-1.72984E+00	1.40269E+00	1.13988E-01
CH2	-8.29208E+00	2.81576E-01	8.58228E-04	-2.12011E-06
CH=	-1.44411E+01	2.67474E-01	6.24537E-03	1.48730E-06
COO	-7.53105E+02	1.07682E+01	-2.25435E+00	-2.47943E-01
COOH	-4.31989E+03	2.59566E+01	-1.98166E+00	-3.95035E-01
OH	3.72079E+03	8.25908E+00	-8.75560E-01	-1.33909E-01
CH2-CH-CH2	-1.11465E+04	-2.43862E+01	3.12202E+00	3.87547E-01
Family	f_0	f_1	s_0	s_1
Acids	-1.38639E+01	3.25665E-03	-8.09212E+03	-1.71779E-01
Esters	-3.44765E+01	8.54674E+00		
Glycerides	2.42268E+00	-1.84330E-01		
	q			
	α	**β**		
	1.78095E+00	4.28859E-01		

The accuracy of the GTD-model is analyzed in terms of the average relative deviation (ARD) for the predicted values and the corresponding experimental data for different fatty compounds (see Table 3.15). Diglycerides have the largest ARD (≈4.65%). The smallest ARD (≈0.81%) is found for the fatty acids. The limitation of the GTD-model for this property is mainly that, due to the lack of data for the regression analysis, any extrapolation for the prediction of surface tension of mono- and poly-unsaturated partial glycerides would be uncertain. Figure 3.15 compares the GTD-model performance with the corresponding experimental data for different fatty acid methyl esters and a wide range of temperatures.

Table 3.15 ARD for surface tension of fatty compounds using the GTD-Model

Family	Number of Data Points	Carbon Length	Unsaturated Compounds	ARD(%)
TAGs	104	21-51	30	2.55
DAGs	9	16	0	2.76
MAGs	21	6-18	0	4.65
Fatty Acids	46	6-18	8	0.81
Fatty Esters	186	7-19	0	1.45
Total	**366**	**6-51**	**38**	**1.92**

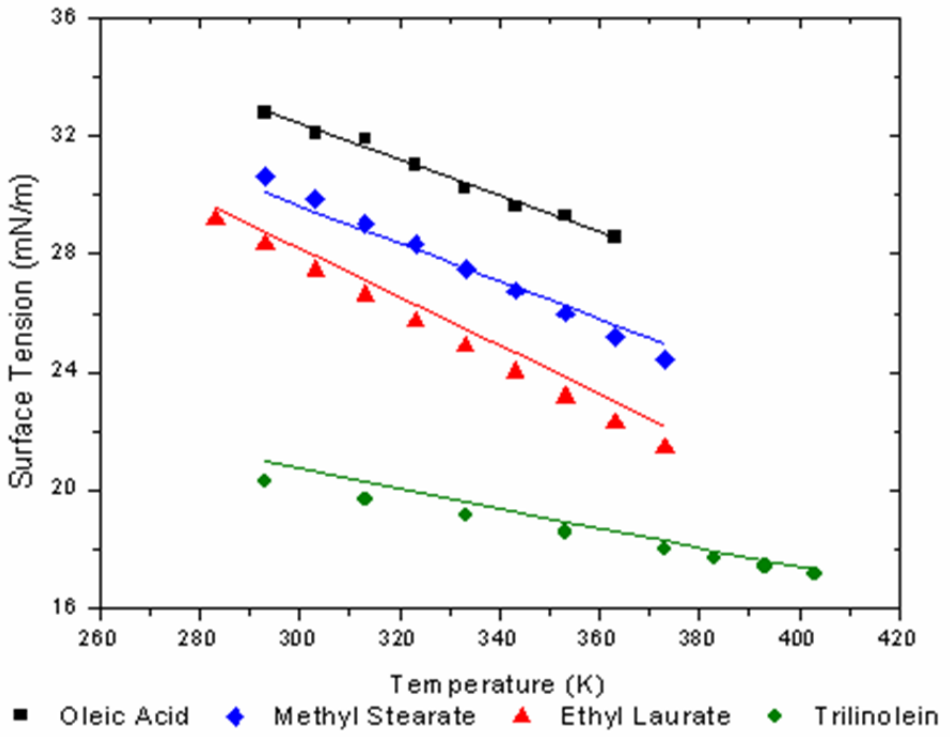


Figure 3.15 Predicted and experimental surface tension values for different lipid compounds

c. Enthalpy of Vaporization

The enthalpy of vaporization model as an extension of the GTD-model for vapor pressure as proposed by Ceriani *et al.* (2010) is, as for the rest of the properties, analyzed in terms of the average relative deviation (ARD) (see Table 3.16). Fatty acids have the largest deviation in Eqs. (3.11)-(3.12) 3.96% and 4.33% respectively. The smallest ARD (1.66 and 1.88%) is found for the fatty alcohols. Figure 3.16 and Figure 3.17 shows the comparison between the predicted and the experimental values for different carbon chain length of methyl esters at a given temperature and in a given range of temperature respectively.

As discussed by Su *et al.* (2011), the model proposed by Ceriani *et al.* (2010) has good agreement between the collected experimental data and the predicted values. However, the model has a limitation as the predictions show an unexpected increase of the heat of vaporization with increasing temperature (see Figure 3. 18). As the temperature increases, the heat of vaporization should decrease.

Table 3.16 ARD for the enthalpy of vaporization of fatty compounds using the extended version of the GTD-model

Chemical Specie	Number of Data Points	Carbon Length	ARD(%)	
			Eq. (3.11)	Eq. (3.12)
Triglycerides	9	5-20	3.00	3.00
Fatty Alcohols	37		1.66	1.82
Fatty Acids	120		3.96	4.33
Fatty Esters	38		2.98	2.99
Total	**204**		**3.24**	**3.43**

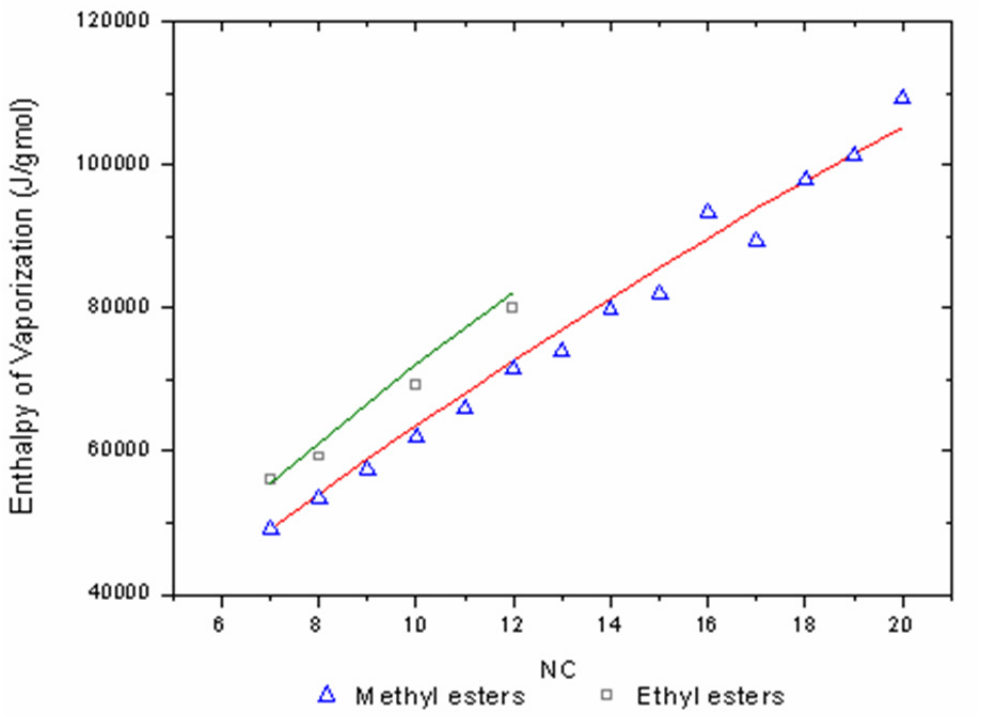


Figure 3.16 Comparison between predicted and experimental values for different carbon chain length of methyl and ethyl esters at 298K.

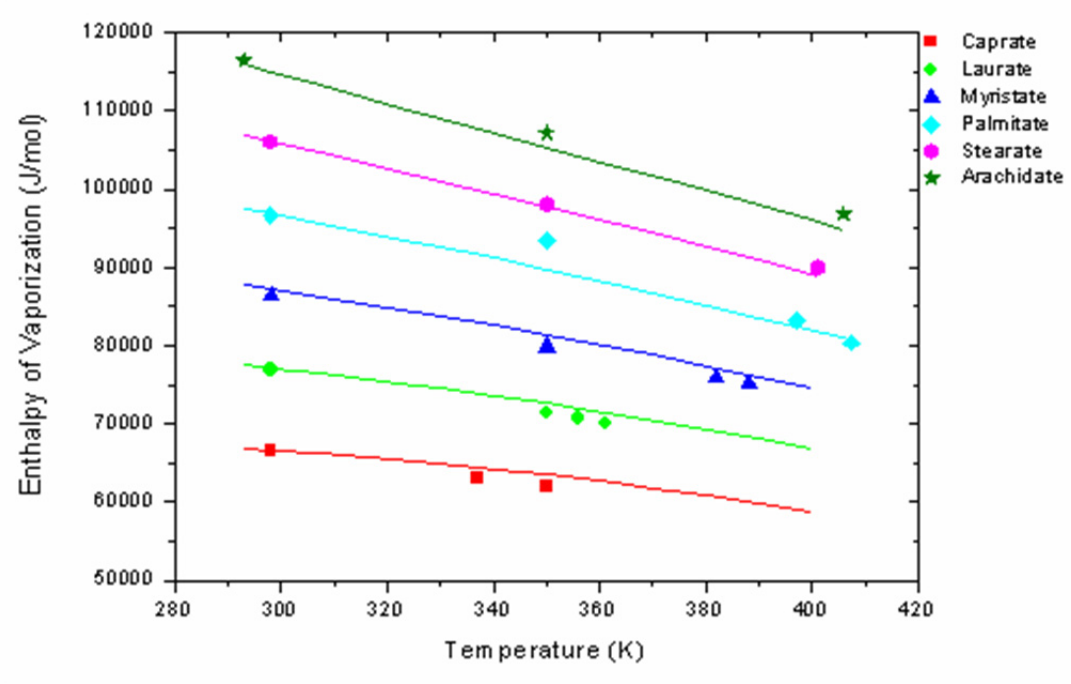


Figure 3.17 Experimental and predicted enthalpies of vaporization for different methyl esters

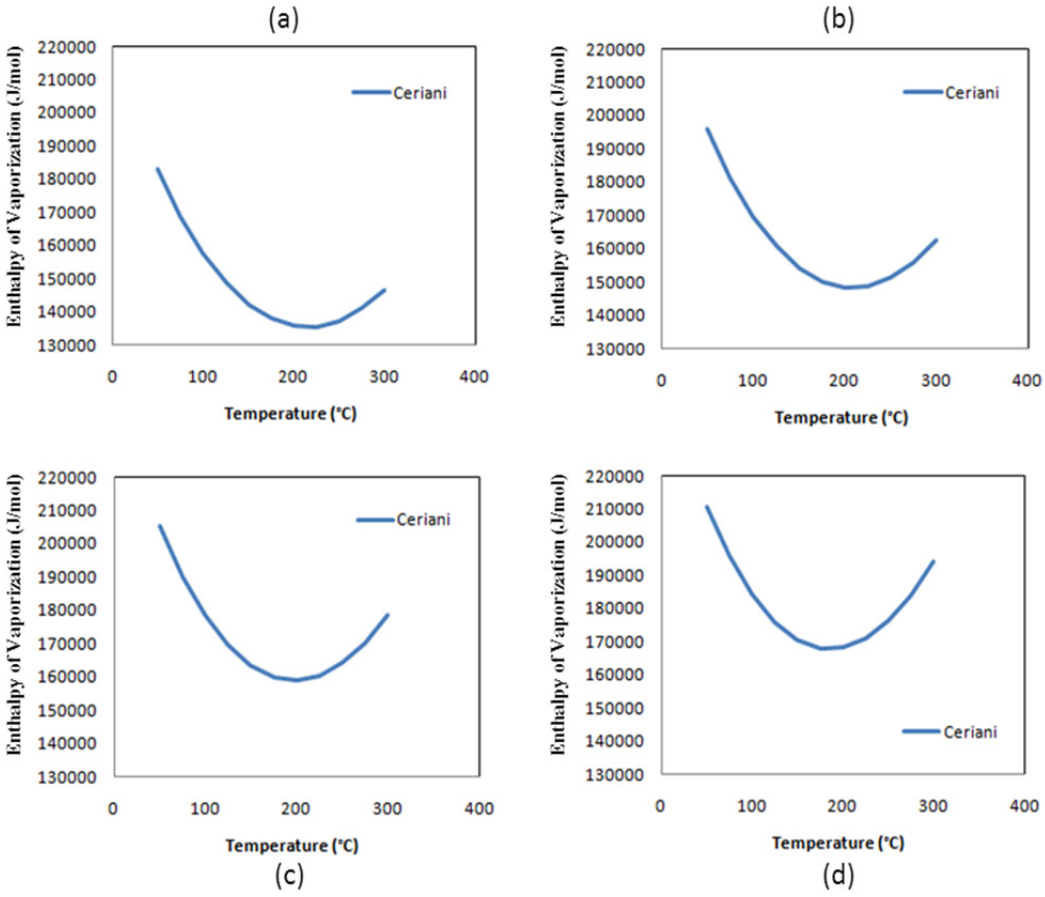


Figure 3. 18 Comparison of predicted heat of vaporization by Ceriani *et al.* (2010) from 50 to 300°C. (a) trilaurin, (b) trimyristin, (c) tripalmitin, and (d) tristearin. (adapted from Su *et al,.*2010).

d. Liquid Density

The accuracy of Eq. (3.13) for the prediction of liquid densities of oils, fatty acids, and fatty esters has been found to be <1% (see Table 3.17). Figure 3.19 shows a comparison between experimental values and the predicted values (with this model) of the liquid densities of Brazil Nut oil (composition given in Table 3.18), caproic acid, and erucic acid. Very good performance of the model can be noted.

In Figure 3.20, the predicted densities of mono- and di- glycerides formed with the same fatty acid fragment present the expected behavior with respect to the temperature. Zong *et al.* (2010b) showed that the density of partial glycerides decline in turn at the same temperature. The difference between the diglyceride and the triglyceride has no obvious change with the increment of carbon number of the constituent fatty acid. However, the gap between the monoglyceride and the triglyceride decreases for the components with the longer fatty acid fragments, contrary to vapor pressure and heat capacity.

Table 3.17 ARD(%) for liquid density of fatty compounds using the modified Rackett equation

Family	Number of Data Points	Carbon Length	ARD(%)
Triglycerides	76	39-57	0.164
Fatty Acids	49	9-22	0.079
Fatty Esters	41	2-23	0.120
Total	**166**	**2-57**	**0.363**

Table 3.18 Brazil nut oil fatty acid composition and their modified Rackett equation parameters

Fatty Acid	Composition (%)	Tc (K)	Pc(bar)	Mw (gr/grmol)	Zr
Myristic	0.11	765.00	16.44	228.38	0.23517
Palmitic	17.23	785.22	14.68	256.43	0.23379
Palmitoleic	0.38	800.34	14.71	254.41	0.23120
Stearic	10.11	804.00	13.60	284.48	0.23518
Oleic	37.08	781.00	13.90	282.47	0.23849
Linoleic	34.56	775.00	14.10	280.45	0.23800
Linoleninc	0.05	780.00	14.40	278.44	0.23718
Arachidic	0.36	821.00	12.40	312.54	0.23288
Gadoleic	0.05	837.03	11.18	310.51	0.21788
Behenic	0.07	855.00	11.00	340.59	0.22588

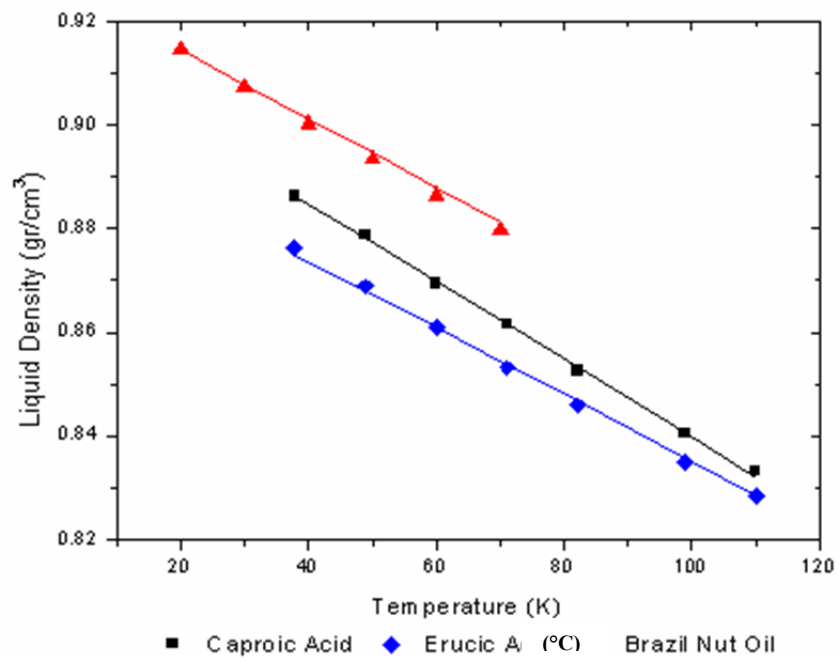


Figure 3.19 Comparison of experimental and predicted densities of two free fatty acids and edible commercial vegetable oil

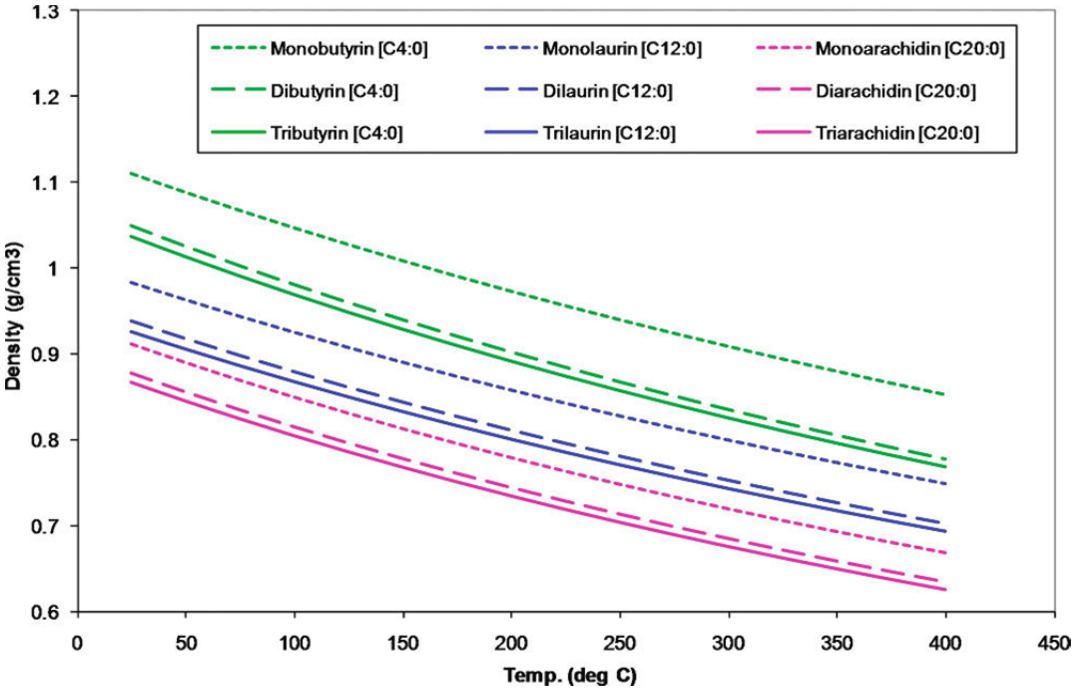


Figure 3.20 Comparison of predicted densities of mono-, simple di-, and triglycerides (Adapted from Zong *et al*, 2010b).

IV. Summary

In this section the thermophysical pure component properties of the identified most representative lipid compounds (see Table 3.1), that are needed for the design/analysis of processes involving lipid technology, have been studied. A total

of 15 properties have been selected. Among them, 9 correspond to single value properties, while the other 6 correspond to temperature dependent properties (see Table 3.3).

Four different types of methods/approaches have been used to model the selected thermophysical properties: Group contribution, modified Rackett equation, chemical constituent fragment approach, and the PC-SAFT EoS. The first method was used to model single value pure component properties, through the Marrero and Gani (2001) method, and temperature dependent properties such as vapor pressure, enthalpy of vaporization, liquid viscosity, and surface tension, through the GTD GC-based model. The modified Rackett equation and the Chemical Constituent Fragment Approach were used to compute the density of lipid compounds. Finally, the PC-SAFT EoS was used to predict temperature dependent properties (vapor pressure, enthalpy of vaporization, and liquid density) of minor compounds. The performance of each selected model was analyzed by comparing their predictions to the available experimental data.

Validated models are then used to generate, for each lipid compound, the model parameters for the selected thermophysical properties.

3.1.2.2. Database Thermophysical Model Parameters

As previously discussed, in this section of the database two different sets of data are contained: i) the computed single value pure component property database (see Appendix D) and ii) the computed temperature dependent pure component model parameters (see Appendix D).

At this point, the computed single value pure component properties can be directly stored into the database; however this is not the case of the computed temperature dependent parameters. Their implementation in other commercial computer-aided tools for the design/analysis of processes involving lipid technology, such as commercial process simulators has two main limitations:

i. The selected temperature dependent model forms (equations) are “tailor-made” and aimed to describe the thermophysical behavior of this particular set of

chemical species. Hence, their availability as mathematical correlations in any commercial process simulator is inexistent.

ii. The lack of an appropriate platform (*e.g.* database) that can be linked to the desired external computer-aided tools.

Fortunately, latest versions of commercial process simulators (PRO/II ®, ASPEN®, etc.) provide friendly user-interfaces to define user-added compounds. However, in order to have reliable performance of them it is necessary to fill out all the necessary physical property model parameters.

In the upcoming section, the proposed suitable model forms are disclosed for each one of the selected temperature dependent properties.

I. Suitable Model Form

a. Logarithmic Model.

The logarithmic behavior of the thermophysical properties vapor pressure, enthalpy of vaporization (when computed through PC-SAFT), and liquid viscosity with respect to temperature (see Figures 3.2, 3.5, and 3.6) has been correlated using different equation forms (*e.g.* the Antoine equation or a modified version of it). However, for the set of selected lipid compounds, the three parameters used by the Antoine equation are not enough to accurately describe the behavior of the identified properties. The selected model is given below:

$$\ln\left(\text{Prop}\right) = C_1 + \frac{C_2}{T} + C_2 \cdot \ln\left(T\right) + C_4 \cdot T^{C_5} \tag{3.23}$$

where: - Prop is the physical property to be estimated..
- T is the temperature in (K).
- C_1, C_2, C_3, C_4, C_5 are the new regressed property model parameters.

b. Polynomial Model

b.1 Surface Tension, Enthalpy of Vaporization, and Liquid Density

Figures 3.15, 3.17, and 3.19 show the behavior of the above-mentioned properties, respectively. Even though the trend of the properties in the applicable range of temperature could be considered to be linear, a polynomial model (see Eq.(3.24))

has been selected in order to account for the non-linearity of the original models (Eqs. 3.12, 3.13, and 3.19).

$$\text{Prop} = \sum_i C_i \cdot T^{i-1} \tag{3.24}$$

where: - Prop is the physical property to be estimated (Enthalpy of vaporization, surface tension or liquid density).
- T is the temperature in (K).
- C_i are the new regressed property model parameters.

b.2 Liquid Heat Capacity

This thermophysical property is a special case because by substituting the model coefficients given in Table 3.7 for the liquid heat capacity in Eq. 3.2, the GDT adopts the form of a linear equation (see Eq.(3.25)). Unfortunately, the selected commercial process simulator (PRO/II ®) does not have correlations for estimating the liquid heat capacity of a given compound; however, it does for liquid enthalpy.

$$c_{Pi}^{l} = \sum_k A_k + \sum_k B_k T \tag{3.25}$$

For a process that occurs at constant pressure and volume, the liquid enthalpy of any given chemical specie is defined by:

$$dH_i^l = c_P(T)\,dT \tag{3.26}$$

Substituting Eq. (3.25) in Eq. (3.26) and setting the reference temperature at 273.15K.

$$\int_{T_{ref}}^{T} dH_i^l = \int_{T_{ref}}^{T} \left(\sum_k A_k + \sum_k B_k T \right) dT$$

$$\text{Prop} = \Delta H_i^l = C_1 + C_2 T + C_3 T^2 \tag{3.27}$$

where: $C_1 = 273.15\left(\sum_k A_k + 136.575 \sum_k B_k \right)$

$$C_2 = \sum_k A_k T$$

$$C_3 = \frac{1}{2} \sum_k B_k$$

Feature 3: The User-Interface

This last feature consists of a two-section user-interface (see Figure 3.21):

i. In the first section (Data Input), the interface allows the selection of the desired lipid compound and the set of the temperature at which the properties should be estimated.

ii. In the second section (Results), the interface gives the predicted values of the listed physical properties, the mathematical models used to predict them, the closest experimental data point (available in the first feature of the database) for each property, and the reference from which experimental value was retrieved.

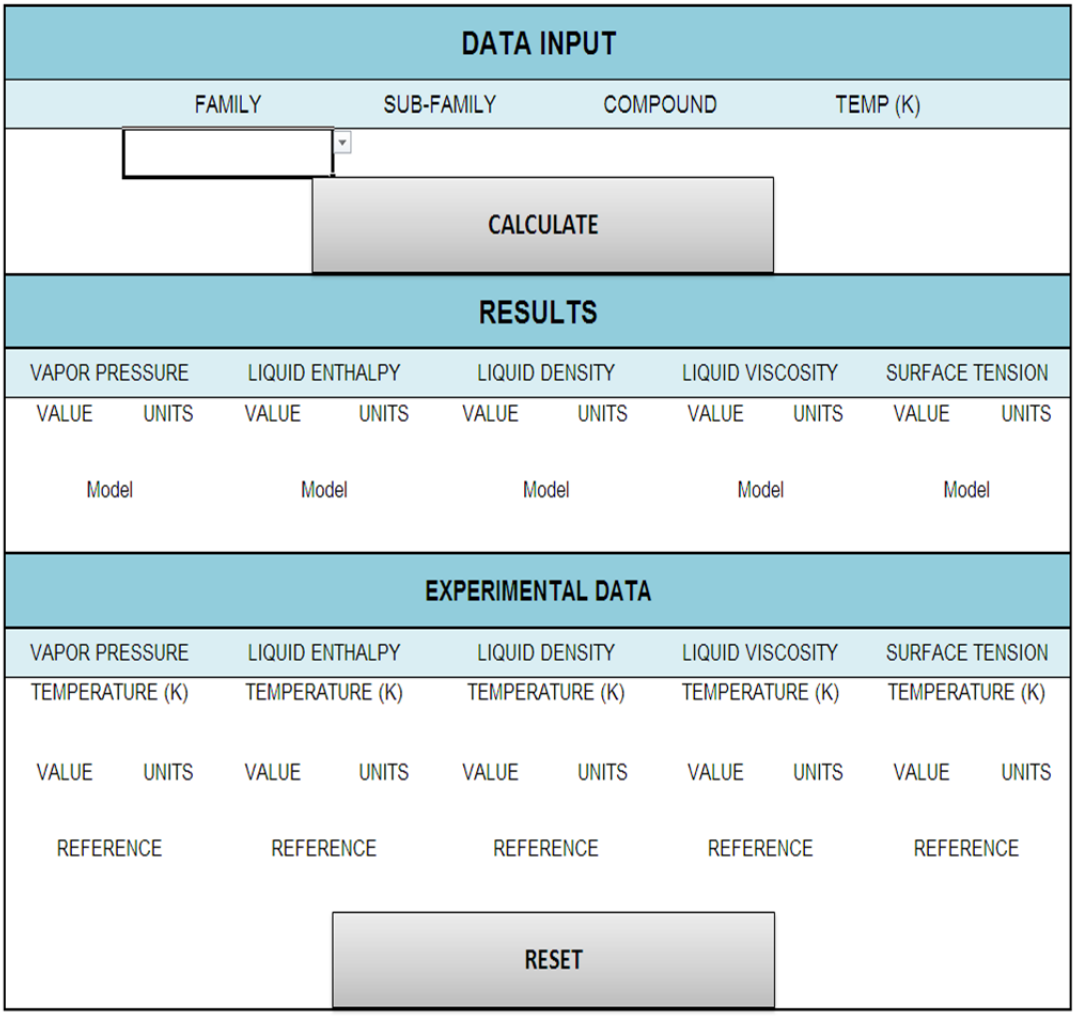


Figure 3.21 CAPEC_Lipids_Database user-interface

In order to illustrate the use of the interface, two lipid compounds have been selected: 1) tripalmitin (P-P-P) and 2) octadecanoic, methyl ester. Figure 3.22 and Figure 3.23 show the results as seen in the CAPEC_Lipids_Database user-interface.

DATA INPUT

FAMILY	SUB-FAMILY	COMPOUND	TEMP (K)
ACYLGLYCERIDES	TRIACYLGLYCERIDES	P-P-P	420

CALCULATE

RESULTS

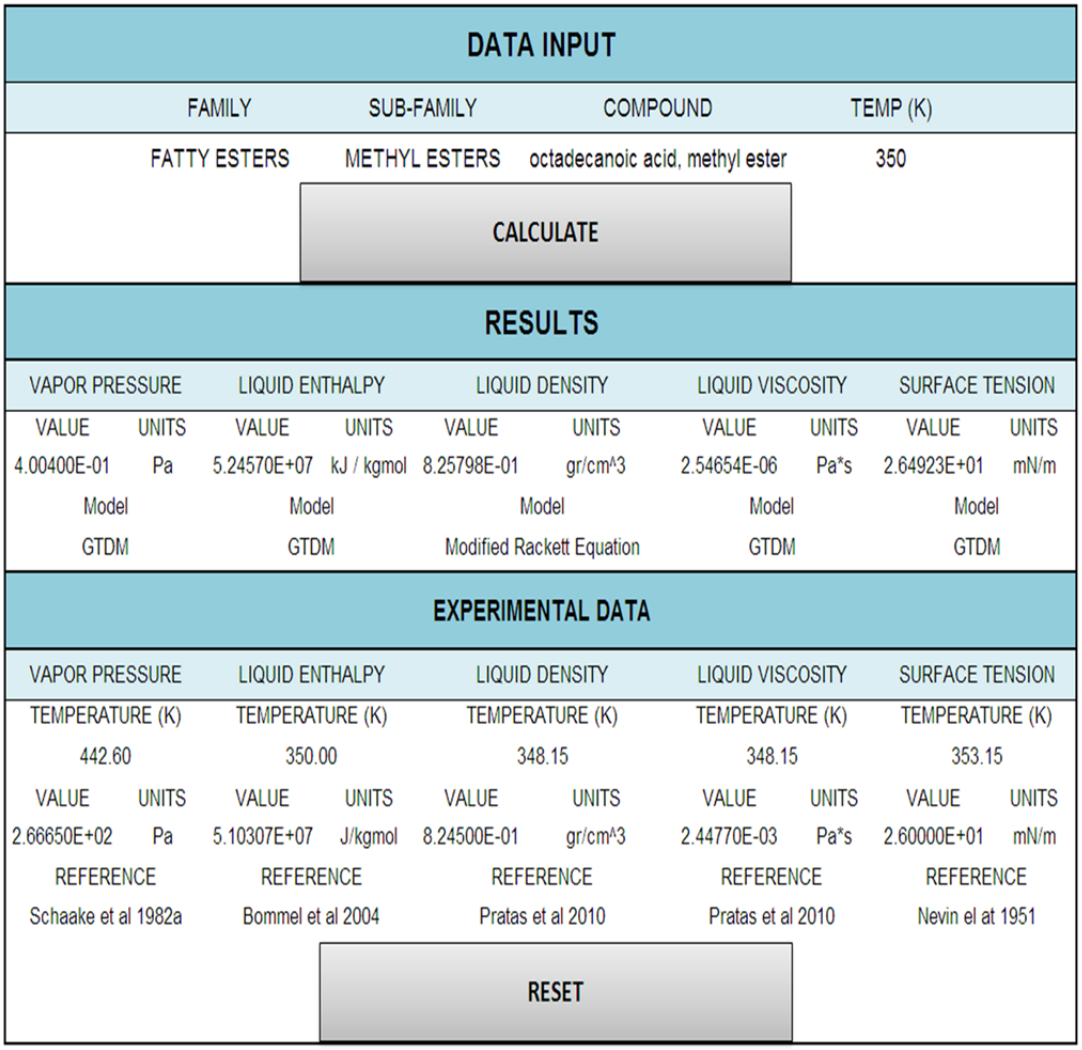
VAPOR PRESSURE		LIQUID ENTHALPY		LIQUID DENSITY		LIQUID VISCOSITY		SURFACE TENSION	
VALUE	UNITS	VALUE	UNITS	VALUE	UNITS	VALUE	UNITS	VALUE	UNITS
7.83824E-04	Pa	2.54767E+05	kJ / kgmol	8.23384E-01	gr/cm^3	3.59907E-03	Pa*s	2.28103E+01	mN / m
Model		Model		Model		Model		Model	
GTDM		GTDM		Modified Rackett Equation		GTDM		GTDM	

EXPERIMENTAL DATA

VAPOR PRESSURE		LIQUID ENTHALPY		LIQUID DENSITY		LIQUID VISCOSITY		SURFACE TENSION	
TEMPERATURE (K)		TEMPERATURE (K)		TEMPERATURE (K)		TEMPERATURE (K)		TEMPERATURE (K)	
571.15		418.15		N/A		423.15		403.15	
VALUE	UNITS	VALUE	UNITS	VALUE	UNITS	VALUE	UNITS	VALUE	UNITS
6.66612E+00	Pa	2.74403E+08	J/kgmol	N/A	gr/cm^3	3.33819E-03	Pa*s	2.35200E+01	mN/m
REFERENCE		REFERENCE		REFERENCE		REFERENCE		REFERENCE	
Goodrum & Geller 2002		Phillips & Mattamal 1976				Noor Azian et al 2001		Jasper 1972	

RESET

Figure 3.22 Predicted and experimental values for tripalmitin as seen in the CAPEC_Lipids_Database user interface



DATA INPUT

FAMILY	SUB-FAMILY	COMPOUND	TEMP (K)
FATTY ESTERS	METHYL ESTERS	octadecanoic acid, methyl ester	350

CALCULATE

RESULTS

VAPOR PRESSURE		LIQUID ENTHALPY		LIQUID DENSITY		LIQUID VISCOSITY		SURFACE TENSION	
VALUE	UNITS	VALUE	UNITS	VALUE	UNITS	VALUE	UNITS	VALUE	UNITS
4.00400E-01	Pa	5.24570E+07	kJ / kgmol	8.25798E-01	gr/cm^3	2.54654E-06	Pa*s	2.64923E+01	mN/m
Model		Model		Model		Model		Model	
GTDM		GTDM		Modified Rackett Equation		GTDM		GTDM	

EXPERIMENTAL DATA

VAPOR PRESSURE		LIQUID ENTHALPY		LIQUID DENSITY		LIQUID VISCOSITY		SURFACE TENSION	
TEMPERATURE (K)		TEMPERATURE (K)		TEMPERATURE (K)		TEMPERATURE (K)		TEMPERATURE (K)	
442.60		350.00		348.15		348.15		353.15	
VALUE	UNITS	VALUE	UNITS	VALUE	UNITS	VALUE	UNITS	VALUE	UNITS
2.66650E+02	Pa	5.10307E+07	J/kgmol	8.24500E-01	gr/cm^3	2.44770E-03	Pa*s	2.60000E+01	mN/m
REFERENCE		REFERENCE		REFERENCE		REFERENCE		REFERENCE	
Schaake et al 1982a		Bommel et al 2004		Pratas et al 2010		Pratas et al 2010		Nevin el at 1951	

RESET

Figure 3.23 Predicted and experimental values for methyl stearate as seen in the CAPEC_Lipids_Database user interface

3.2. Tools

ICAS

The Integrated Computer Aided System (ICAS) is a set of toolboxes oriented to solve a wide range of academic and industrial problems. Some of the main features of the ICAS suite are: the CAPEC DataBase, the Computer Aided Molecular Design tool (ProCAMD), the Property Prediction tool (ProPred), the Modeling Tool (MoT), among others.

Two are the main features of the ICAS software that were used in the development of this work. The first one is ICAS ProPred® which is a tool mainly used for two tasks:

1) The first task is the calculation of the single value pure component properties (see Section 3.1.2.1.II.a).
2) The second task is the molecular description of any compound in terms of the MG and CG functional groups. This is achieved by introducing the correspondent compound SMILES.

Another relevant Moreover, the software provides a feature that allows the user to export the generated data to other computer-aided tools, for example to the commercial process simulator PRO/II®.

The second feature is the Model Test-bed (MoT) toolbox. ICAS MoT® is a mathematical modeling solver designed to minimize the amount of effort to specify, solve, and visualize the solution of a system of Algebraic equations (AEs), Ordinary and Partial Differential equations (ODEs or PDEs) without sacrificing power and flexibility. In addition, it is possible to use this computer-aided tool to solve optimization problems as well as to perform the parameter regression of a given model from (pseudo) experimental data. These last characteristics play a significant role in this work, as they are used to regress the parameters of the second order model obtained through the Central Composite Design method (see Section 4.1.4.1) as well as to optimize it in terms of the significant process design variables.

3.3. "Add New Compound" Algorithm

In this section, the proposed algorithm (see Figure 3.24) for including any desired lipid compound into the database. The algorithm consists of the following steps:

Step 1: Selection.

a. Identify the desired lipid compound

b. Provide the available compound specifics (Name, molecular formula, SMILES, CAS Nr., *etc.)*

Step 2: Molecular Description.

In this step of the algorithm, the compound molecular structure is described through four different methods:

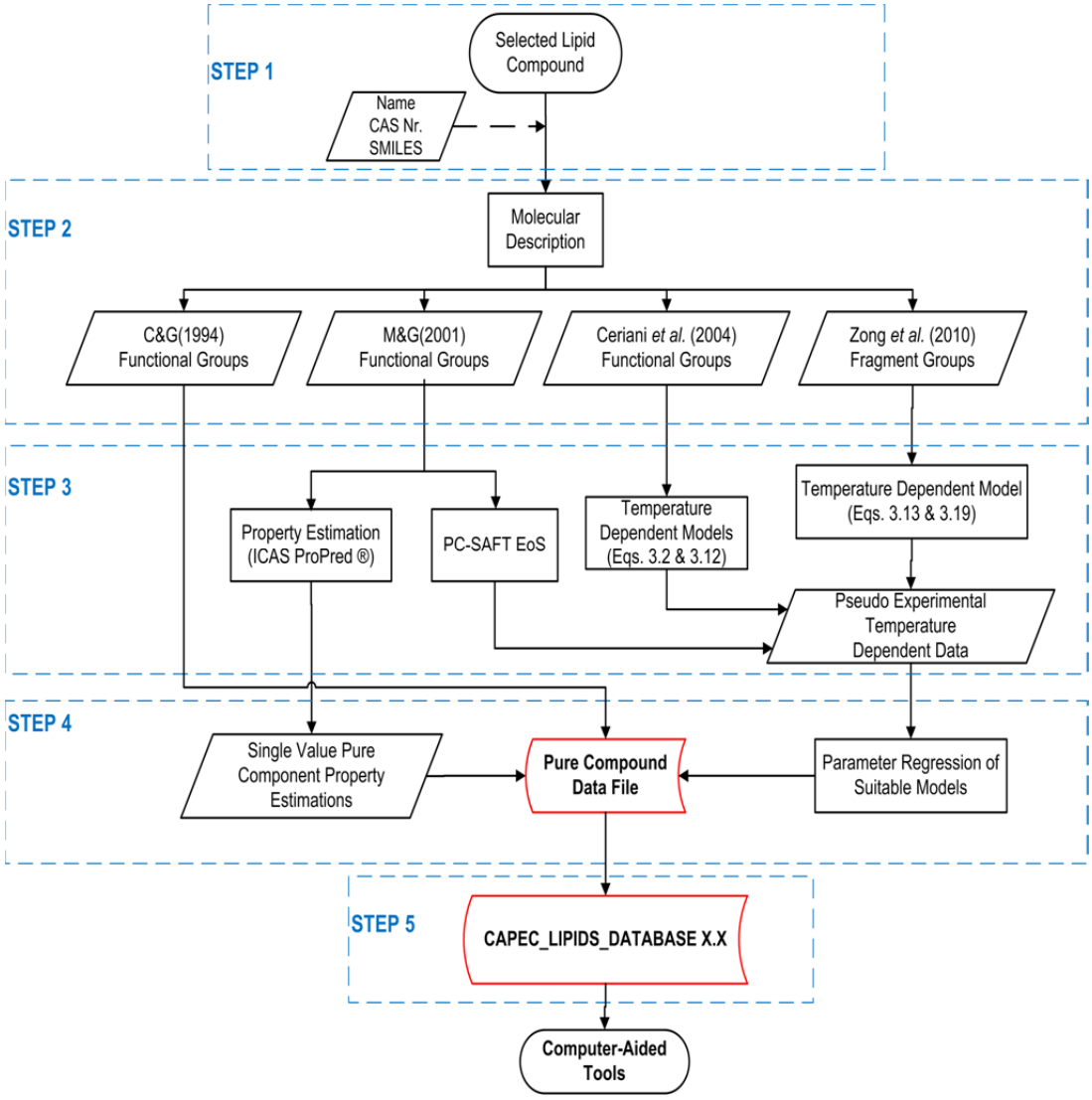


Figure 3.24 Flow diagram for adding a lipid compound into the CAPEC_Lipids_Database.

a. Constantinou and Gani (1994): Although this method can be considered as the predecessor of the Marrero and Gani (2001) method. The main contribution of this method to this work is not the estimation of single value pure component properties, but the molecular description of the selected lipid compounds in terms of functional groups that are equivalent to the original UNIFAC (Fredenslund *et al.,* 1975) GC-based EoS.

b. Marrero and Gani (2001): The functional groups defined by this method are used, as mentioned in Chapter 3, primarily for the computation of the single value pure compound properties. In addition, this method is used to compute the three parameters needed by the PC-SAFT EoS. This last feature is mainly used for minor compounds for which no experimental data is available.

c. Ceriani *et al.* (2004). The functional groups proposed in this method are almost entirely existent in the Marrero and Gani (2001) method. The significant difference consists in the proposal of the CH_2-CH-CH_2 functional group to account for the contribution of the glycerol backbone existent in all the glycerides and that has proved to improve the accuracy of the temperature dependent models.

   The functional groups defined with this method are used for the prediction of temperature dependent properties such as vapor pressure, enthalpy of vaporization, liquid heat capacity, liquid viscosity, and surface tension.

d. Zong *et al.* (2010): As discussed in Section 3.1.2.1, in this method the thermophysical behavior of glycerides is considered to be fragment (and not functional group as in the GC methods) dependent. This means that glycerides are lipid compounds composed of a free fatty acid fragment (*e.g.* lauric acid, paltmitic acid, oleic acid, *etc.*) attached to a (*tri-, di-, mono-*) glyceride fragment. The fragments groups defined in these methods are used mainly for the prediction of liquid density of glycerides, fatty acids, and fatty esters.

Step 3: Pure Component Property Estimation.

In this step of the algorithm, the set of molecular descriptions of the selected lipid compounds is used as an input to the correspondent method for estimating the selected thermophysical properties.

In the case of the single value pure component properties, the estimation of the properties is performed through the software ICAS ProPred® (Nielsen et *al.*, 2001; ICAS Documentation, 2001). A detailed depiction of the software and the advantages of it as a computer-aided tool are disclosed in Section 3.2.

For temperature dependent properties, as shown in Figure 3.24, the selected models are used to generate pseudo experimental data. These new data sets are used in a further step to regress the parameters of commonly used commercial process simulator models.

Step 4: Pure Component File Creation.

In this step of the algorithm, two main tasks are performed. In the first tasks, the functional groups generated through the Constantinou and Gani (1994) method and the estimated single value pure component properties are included into the correspondent compound file created by means of the software ICAS ProPred®.

In the second task, the pseudo experimental data generated in the previous step is used to regress the parameters of suitable models for commercial process simulators as described in Section 3.1.2.2.I. After the new model parameters are obtained, the information is sent to the same pure component file where the molecular description and the single value property estimations are stored.

Step 5: Database Storage

In this final step of the algorithm, the information of the recently created single compound generated in the previous steps and the file that contains this information are included into the main database (CAPEC_Lipids_Database x.x) and into the version that is linked to the process simulator PRO/II®, respectively.

3.3.1 Application of the "Add New Compound" Algorithm

To exemplify the applicability of the "add new compound" algorithm proposed in the previous section of this chapter, let us consider the following three lipid compounds: A) Glyceride (P-O-Li), B) Fatty acid (Stearic Acid), and C) Minor compound (α-carotene)

Step 1: Selection

Compound A	
Family	Glycerides
Sub-family	Triglycerides
Name:	1-hexadecanoyl-2-octadecenoyl-3-octadecadienoyl-sn-glycerol
Formula	C55H98O6
MW(gr/gmol)	857.37
Code Name	P-O-Li
CAS Nr.	N/A
SMILES	CCCCCCCCC=CCCCCCCCC(=O)OCC(COC(=O)CCCCCCCCCCCCCCC C)OC(=O)CCCCCCCC=CCC=CCCCCC

Compound B	
Family	Fatty Acid
Sub-family	N/A
Name:	Octadecanoic Acid
Formula	$C_{18}H_{36}O_2$
MW(gr/gmol)	284.48
Code Name	Stearic
CAS Nr.	57-11-4
SMILES	CCCCCCCCCCCCCCCCCC(=O)OC
Compound C	
Family	Minor Compounds
Sub-family	Carotenes
Name:	α-carotene
Formula	C40H56
MW(gr/gmol)	536.873
Code Name	A-CAROTN
CAS Nr.	7488-99-5
SMILES	CC(=CC=CC=C(C)C=CC=C(C)C=CC1C(C)=CCCC1(C)C)C=CC=C(C)C=CC2=C(C)CCCC2(C)C

Step 2: Molecular Description

Table 3.19 shows the molecular description of the selected lipid compounds through the four previously discussed methods.

Table 3.19a Molecular description of the selected lipid compounds

			COMPOUND		
			A	**B**	**C**
		Group	**Frequency**		
Constantinou and Gani (1994)	First Order	CH_3	3	1	10
		CH_2	39	16	5
		CH	1	0	1
		CH=CH	3	0	5
		CH=C	0	0	5
		CH_2COO	3	0	0
		COOH	0	1	0
		C=C(cyc)	0	0	1
	Second Order	CH_2-CHm=CHn	6	0	0
		CHn=CHm-CHp=CHk	0	0	8
		CH_3-CHm=CHn	0	0	4
		6 memb. ring	0	0	2

Table 3.19b Molecular description of the selected lipid compounds (continuation)

			COMPOUND		
			A	B	C
		Group/Fragment	Frequency		
Marrero and Gani (2001)	First Order	CH_3	3	1	10
		CH_2	39	16	0
		CH	1	0	0
		CH=CH	3	0	5
		CH=C	0	0	4
		CH_2COO	3	0	0
		COOH	0	1	0
		CH_2(cyc)	0	0	5
		CH(cyc)	0	0	1
		C(cyc)	0	0	2
		CH=C(cyc)	0	0	1
		C=C(cyc)	0	0	1
	Second Order	CH_2-CHm=CHn	6	0	0
		COO-CHn=CHm-OOC	2	0	0
		CHn=CHm-CHp=CHk	0	0	8
		CH_3-CHm=CHn	0	0	4
		(CHn=C)cyc-CH_3	0	0	3
		CHcyc-CH=CHn	0	0	1
		Ccyc-CH_3	0	0	4
	Third Order	No Groups Ocurring			
Ceriani *et al.* (2004)		CH_2-CH-CH_2	1	0	N/A
		CH_3	3	2	
		CH_2	43	16	
		CH=CH	3	0	
		COOH	0	1	
		COO	3	0	
Zong *et al.* (2010)		Triglyceride	1	0	N/A
		Palmitic	1	0	
		Stearic	0	1	
		Oleic	1	0	
		Linoleic	1	0	

Step 3: Pure Component Property Estimations

Table 3.20 shows the estimated single value pure component properties for the selected lipid compounds.

Table 3.20 Single value pure component property estimations through the MG method.

Property	COMPOUNDS		
	A	B	C
Tm (K)	432.50	364.43	430.30
Tb (K)	841.16	633.99	757.56
Tc (K)	1035.79	839.18	903.09
Pc (bar)	7.37	13.95	5.01
Vc (cm^3/mol)	3160.59	1074.21	1980.52
Hf[298K] (KJ/mol)	-1802.36	-760.5	260.09
Hfus (KJ/mol)	146.99	51.77	69.36
Hcom (KJ/mol)	-269.08	-222.97	1035.07
Gf[298K] (KJ/mol)	432.50	364.43	430.30

Table 3.21 shows the original model parameters used to compute the surface tension of compound A, liquid density of compound B, and the vapor pressure of compound C. Finally, Figure 3.25 shows the temperature dependent profiles of the pseudo experimental data generated through Eq. 3.2, Eq. 3.13, and the PC-SAFT EoS respectively.

Table 3.21 GTD- model, modified Rackett Equation, and PC-SAFT model parameters

	COMPOUND					
	A		B		C	
Model	Eq. 3.2		Eq. 3.13		PC-SAFT	
Parameters	A_{1k}	-493.3080	*Mw (g/gmol)*	284.483	m	11.826
	B_{1k}	15.5969	*Tc (K)*	804.000	σ	4.155
	A_{2k}	547.7368	*Pc (bar)*	13.600	ε/k	304.060
	B_{2k}	-12.3405	*R(bar cm^3/mol K)*	83.144		
	f_0	2.4227	*Spec. Grav.*	0.8804		
	f_1	-0.1843	Z_{RA}	0.2352		
	s_0, s_1	0.0000				
	α	1.7810				
	β	0.4289				
	γ, δ	0.0000				
Property	Surface Tension		Liquid Density		Vapor Pressure	

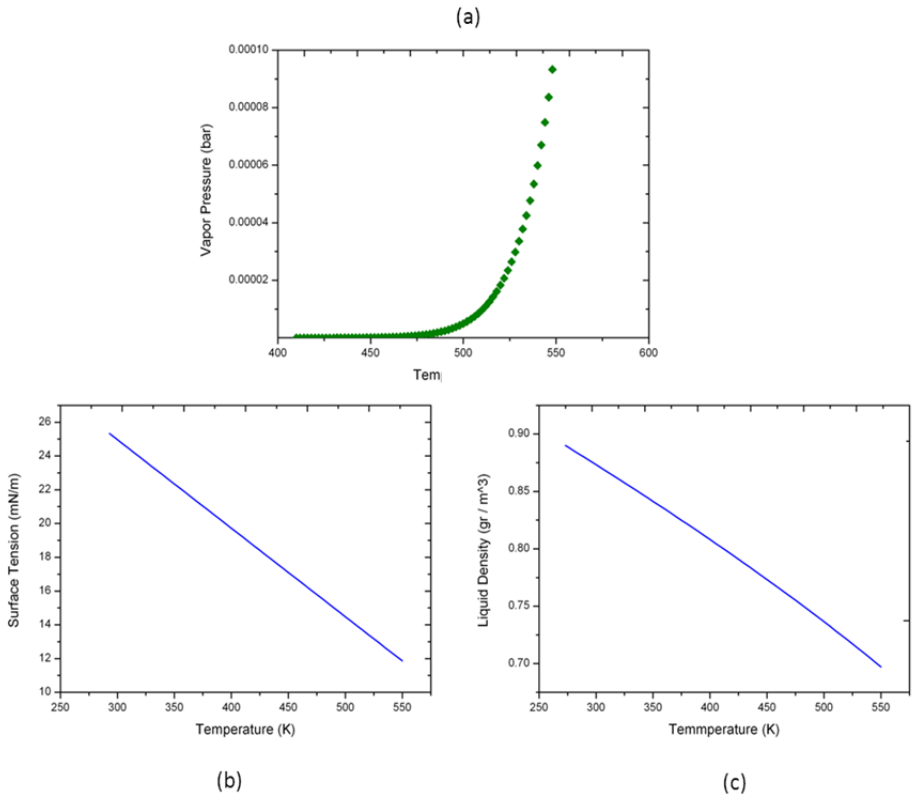


Figure 3.25 Pseudo experimental data profiles as a function of temperature for vapor pressure, surface tension, liquid density

Finally, the new suitable model form parameters that are included into the CAPEC_Lipids_Database are shown in Table 3.22. Figure 3.26 shows the comparison between the experimental values and the estimated values computed with the new model parameters for the liquid density of stearic acid.

Table 3.22 New model parameters for the selected compounds

	COMPOUND					
	A		B		C	
Model	Eq. 4.2		Eq. 4.2		Eq. 4.1	
Parameters	C_1	40.6880	C_1	1.06580	C_1	8.2880E+01
	C_2	-5.24157E-02	C_2	- 7.07212E-4	C_2	-2.7349E+04
	C_3	0.0000	C_3	4.00342E-7	C_3	-2.0178E+01
	C_4	0.0000	C_4	-6.0593E-10	C_4	0.0000
	C_5	0.0000	C_5	0.0000	C_5	0.0000
Property	Surface Tension		Liquid Density		Vapor Pressure	

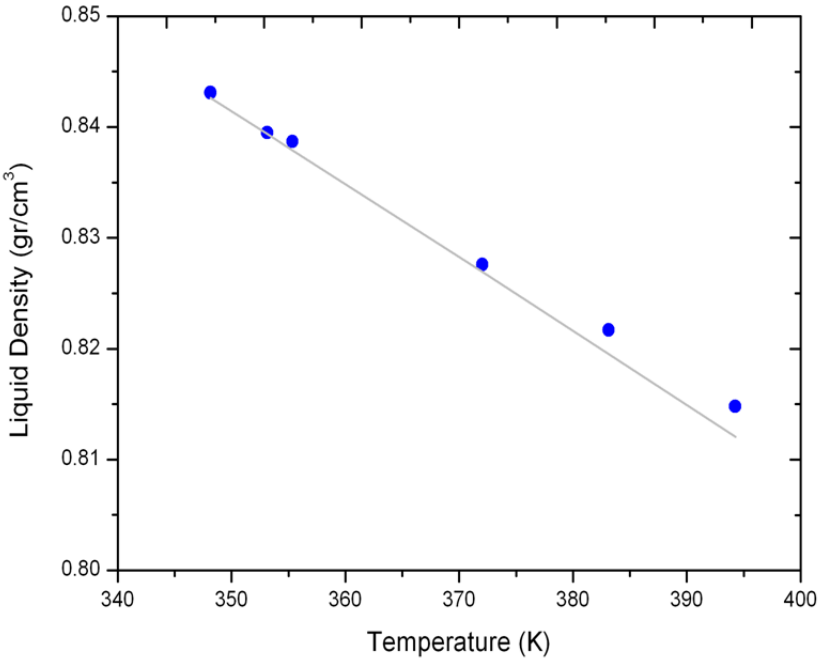


Figure 3.26 Predicted and experimental values comparison for the liquid density of stearic acid

4.

Design/Analysis Methodology & Application of the Design/Analysis Methodology

In this chapter, the proposed methodology for the design/analysis of industrial processes involving lipid technology and its application through the study of three processes (the solvent recovery section of the crude oil extraction process, the palm oil deodorization process, and the soybean oil deacidification process) that have significant impact on the final quality of edible oil are considered.

The design/analysis methodology consists of a step-wise approach for the analysis, simulation, and validation of any given lipid process and its optimization in terms of their design variables.

The simulation models used to describe the three selected processes were validated with the available plant data provided by the company Alfa Laval Copenhagen A/S. These validated models were used to perform the optimization of the processes in terms of their selected design variables. For this purpose, the fractional/full factorial designs were employed to identify the single and combined effects that the design variables have on the selected response variable and, therefore, on the process performance.

4.1. Design/Analysis Methodology

When a given chemical process is designed or analyzed, the aim of the project is usually well known and established at the start. However, the large amount of variables (process conditions, appropriate unit operations, property prediction methods, *etc.*) that needs to be considered is, in most of the times, constraining the processes to operate outside the earlier established optimal conditions.

In this section, the proposed methodology for the design/analysis of processes involving lipid technology is presented. This D/A methodology (see Figure 4.1) consists of four main steps: process analysis, simulation model development, model validation, and process optimization. These steps are discussed in the subsequent sections of this chapter.

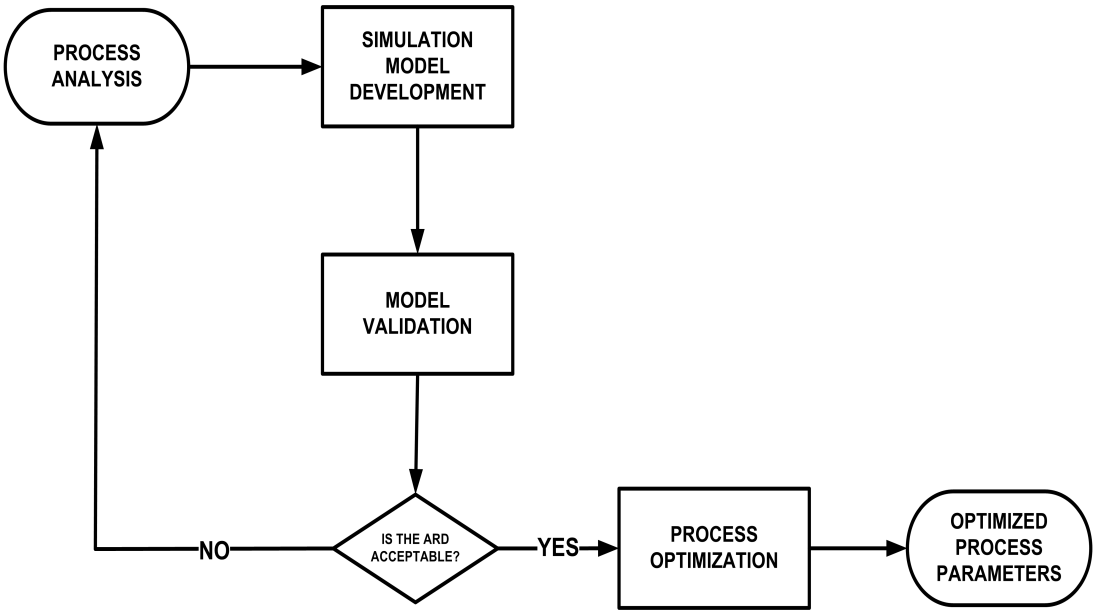


Figure 4.1 Proposed methodology for the design/analysis of any process involving lipid technology (Diaz-Tovar *et al.*, 2010)

4.1.1. Process Analysis

In this first step of the methodology, all the information regarding the lipid process is gathered. This information (see Figure 4.2) contains details about the chemical compounds, unit operations, process conditions, thermophysical properties, and the assumptions that can be used in the next step of the methodology.

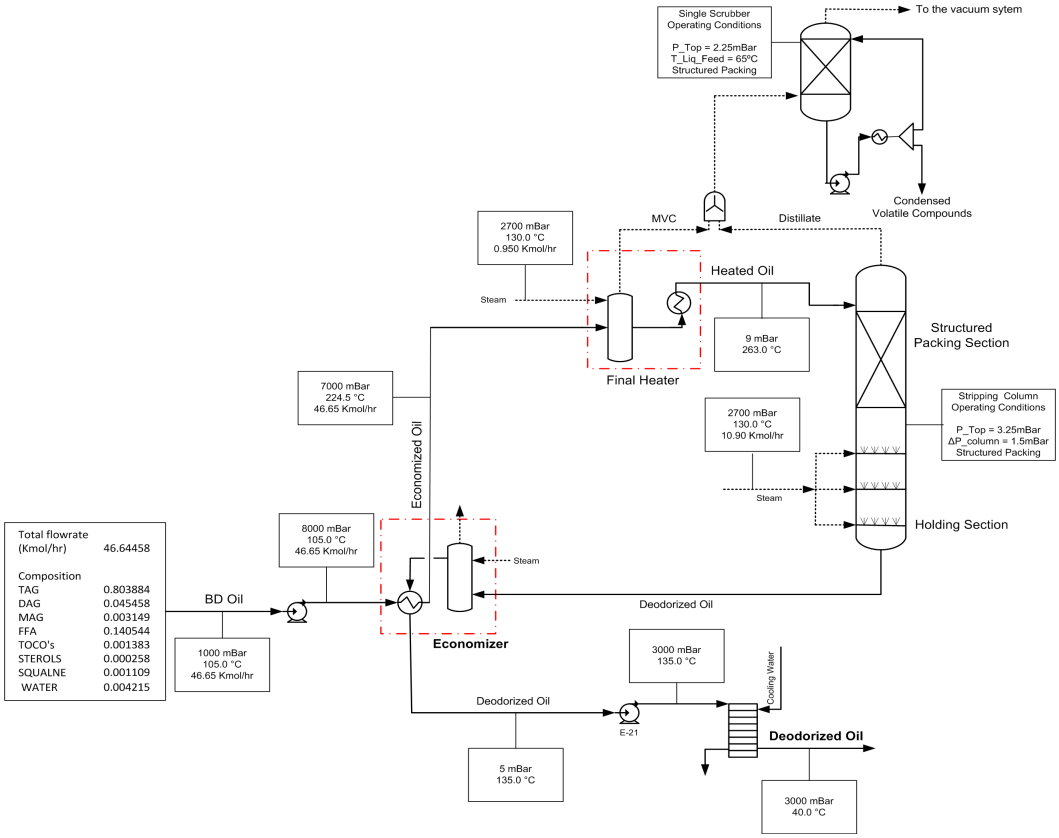


Figure 4.2 Deodorization process analysis

4.1.2. Simulation Model Development

Once the information regarding the selected lipid process is gathered, it is transferred to the desired commercial process simulator, where the simulation model is developed. This means that the identified chemical species as well as the unit operations and the process conditions are set to represent the blueprint of the real plant. Figure 4.3 illustrated a simulation model developed for the physical refining of fats and oils process.

All simulation results to be highlighted in this PhD-Thesis have been obtained with the commercial simulator PRO II. This commercial simulator was selected for two main reasons: i) because it has built-in models for the unit operations present in the

process and ii) because, it is possible to retrieve the necessary property data of the lipid chemical compounds from an external user-added database; that is, the CAPEC_Lipids_Database.

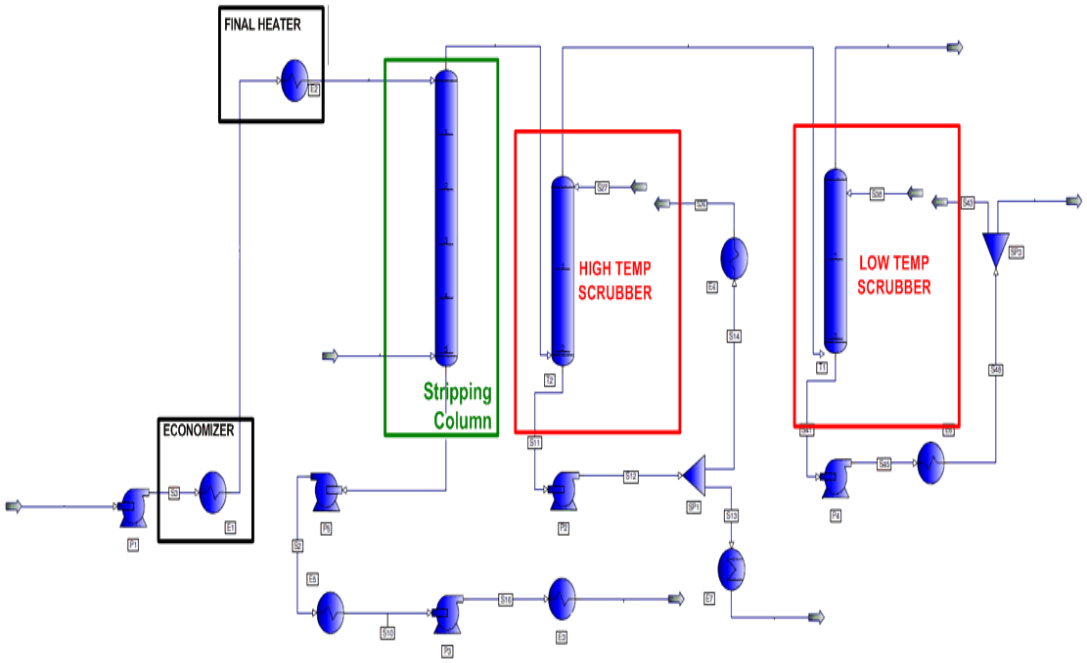


Figure 4.3 Physical refining process with a double scrubber system as represented by PRO II.

4.1.3. Model Validation

In this step, the results obtained through the process simulator are compared with the available experimental/plant data. Deviations of the simulation results with respect to the experimental/plant data are analyzed by means of the average relative deviation (ARD) as given in Eq. (4.1)

$$ARD(\%) = \frac{1}{n}\sum_{i=1}^{n}\frac{\left|x_i^{\exp} - x_i^{\sim}\right|}{x_i^{\exp}} * 100 \qquad (4.1)$$

where:

n is the number of experimental/plant data points

x_i^{exp} is the experimental/plant value;

x_i^{sim} is the value obtained through the simulation;

The desired accuracy of the developed simulation model is determined depending on the information available (plant or experimental data). If the selected accuracy is not achieved, a revision and improvement of the simulation model is to be performed.

4.1.4. Process Optimization

In this step of the methodology the setup of the optimization problem definition is performed. This includes:

- Definition of the objective function, this is, the aim of the optimization problem.
- Identification of the process design variables that are to be manipulated within a range of values commonly found in the oleochemical industry.
- Selection of the process parameters that will remain unchanged during the analysis of the behavior of the response variable(s).
- Selection of the response variables. This is done in order to follow the behavior of the system as the design variables are manipulated.

After defining the optimization problem it is necessary to establish the correlation between the selected response variables and the design variables. Montogomery (2007) suggests that single and combined effects of design variables on the selected response variable(s) can be determined by means of full factorial designs (*i.e.* Central Composite Designs).

In this case, every single simulation is considered to be equivalent to an experiment. Consequently, the validated simulation model is used as the base case experiment and from it, the different scenarios (simulations) are generated and the effect on the response variable(s) is analyzed.

The advantage of techniques such as the Central Composite Design is that it is possible to generate second-order models (providing a maximum or a minimum), that correlate the selected design variables to response variables, and that are then used in the optimization problem.

However, if the selected number of design variables leads to a high number of experiments (simulation runs), a sensitivity analysis (*i.e.* Plackett Burman design)

can be performed. The aim of this analysis is to screen out and determine the minimum number design variables needed to fully represent the system under study.

Once the design variables are correlated to the response variable(s), and the constraints defined by their known upper and lower limits of the identified response variables, the optimization problem can be solved as a NLP.

A more detailed description of the methods used in each one of the steps and methods employed in the process optimization algorithm is given bellow.

4.1.4.1. Process Optimization Algorithm

In this section, the proposed algorithm for the selected lipid processes is considered. As shown in Figure 4.4, different methods are employed in the step-wise algorithm in order to ensure the optimization of the process. In the upcoming sections, the theoretical background of the methods is given.

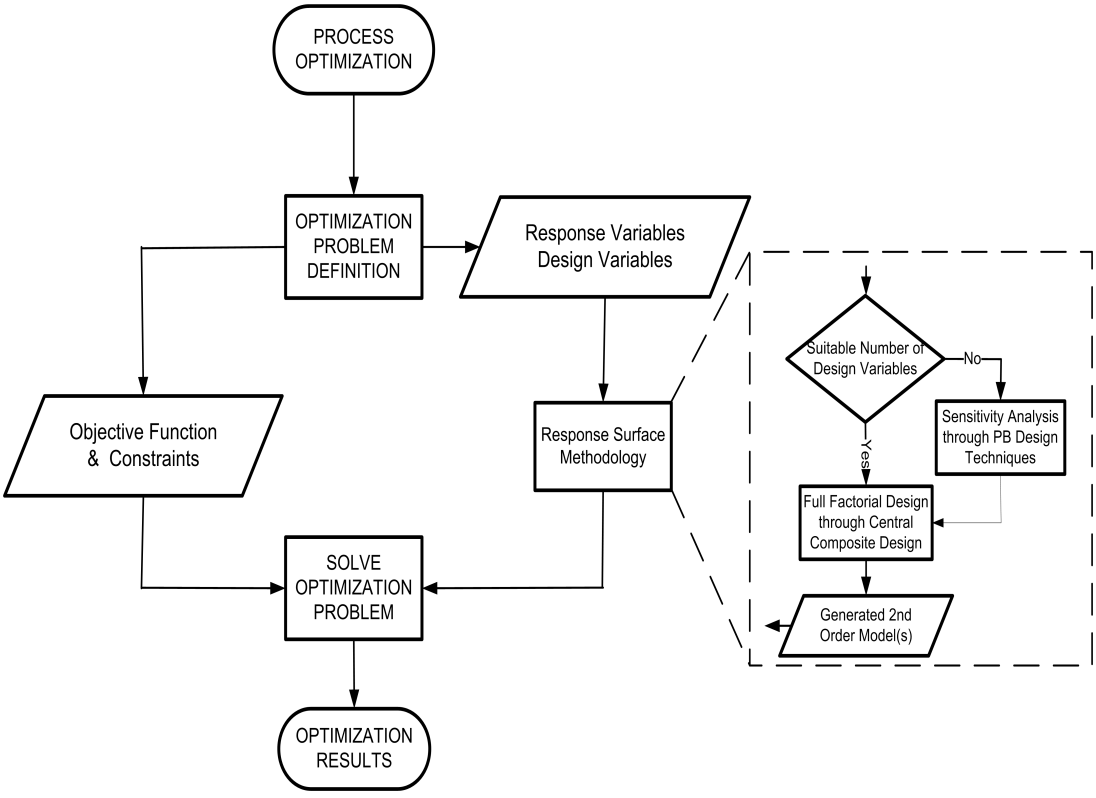


Figure 4.4 Flow diagram for the optimization of a selected lipid process.

The Optimization Problem

The basic concept of optimization is to find the best possible solution to a given model/problem. Every engineering system or process is designed with an intended purpose (Castillo, 2007). The purpose frequently entails a desired performance of the operation of the product being manufactured or of the process that manufactures it. In many cases, engineering design activities involve tests or experimentation, since the product or process is not well understood, and the desired performance cannot be guaranteed. Experimental design and analysis has been used to improve the performance of processes given the inherent noise in the various responses of interest.

Factorial Designs

The main objective here is not to use process simulator but to use a simple input-output model. To do this, it is necessary to have data on the behavior of the system (process) to be analyzed, which is generated through the simulator. Factorial designs helps to identify the simulation runs and the process conditions to use.

The observed changes in a response variable may be correlated with, but not only caused by, observed changes in individual process variables. Simultaneous changes in multiple factors may produce interactions that are difficult to separate into individual effects (Montogomery, 2007).. To analyze the effects that two or more factors in have in response variable, different types of experiments have been proposed. Among these experiments, factorial designs have proven to be the most efficient type.

In factorial designs, each complete trial or replication of the experiment considers all possible combinations of the levels of the factors that are investigated (Montogomery, 2007). The effect of a factor is defined to be the change in response produced by a change in the level of the factor. This is frequently called a main effect because it refers to the primary factors of interest in the experiment.

Sensitivity Analysis Through Fractional Factorial Designs

Regardless of the fact that two-level (upper and lower limits) designs are sufficient for evaluating many production processes, experiments with many factors (variables) can lead to large amounts of data. Fractional factorial designs have been

proposed as an alternative to analyze the effects because they only use a fraction of the runs required by full factorial designs to determine the model parameters.

The use of methods for screening design alternatives is interesting in the early stage of an experiment or simulation based design studies because they allow to identify the most sensitive set of independent variables that the process responses of interest. One of the most common fractional factorial designs is the Plackett-Burman (PB) method (Montgomery, 2005), which is a technique where only the main effects are considered to be significant, achieving thereby a reduction in the number of design variables. The advantage of this technique is that it only requires a number of experimental runs that are a multiple of 4 instead of a power of 2 (Montgomery, 2005). Table 4.1 shows the PB design for eight runs (rows) manipulating seven two-level factors (the last seven columns), in this case defined as design variables. The +1 and -1 represent the upper and lower limits that the factor can adopt. The number of runs is a fraction $\frac{8}{2^7} = 0.0625$ of the runs required by a full factorial design. Economy is achieved at the expense of confounding main effects with any two-way interactions.

Table 4.1 PB Design for 8 runs and 7 two-level factors (adapted from Matlab Documentation, 2011)

RUN	FACTOR						
	X_1	X_2	X_3	X_4	X_5	X_6	X_7
1	1	1	1	1	1	1	1
2	-1	1	-1	1	-1	1	-1
3	1	-1	-1	1	1	-1	-1
4	-1	-1	1	1	-1	-1	1
5	1	1	1	-1	-1	-1	-1
6	-1	1	-1	-1	1	-1	1
7	1	-1	-1	-1	-1	1	1
8	-1	-1	1	-1	1	1	-1

Response Surface Methodology

Response Surface Methodology (RSM) is a series of experimental design, analysis, and optimization techniques that originated in the work by Box and Wilson in 1951 (Castillo, 2007). In order to optimize an industrial process (see Figure 4.5), RSM methods suggest building a parametric model for the expected response using designed experiments. These models should be local approximations, valid in a

small experimental region. A response surface model is a multivariate polynomial model that arises from a factorial designed experiment, in which the data-producing process is manipulated to improve the quality of information.

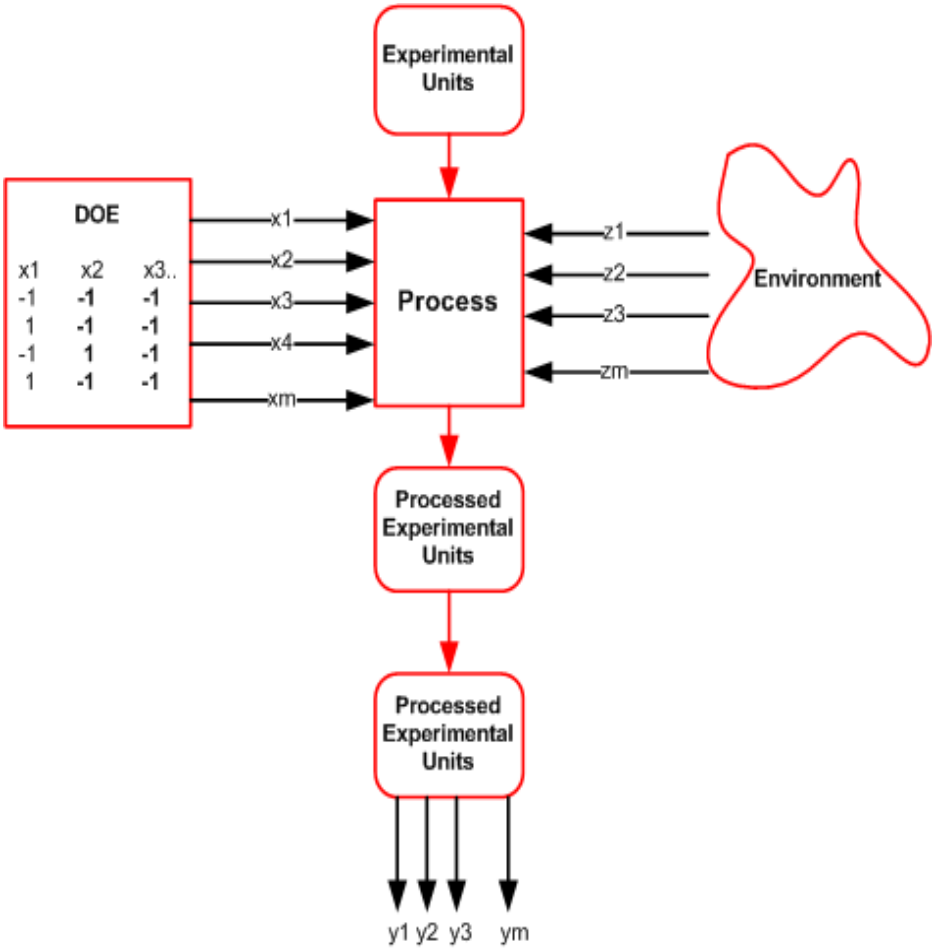


Figure 4.5 A process seen as a black box (adapted from Castillo, 2007)

Central composite design (Montgomery, 2005) is widely used for estimating second order response parameters to produce response surfaces with a maximum or a minimum. This factorial design can be seen as the union of (see Figure 4.6):

- (a) eight corners of a cube, which form a two level full factorial design (-1 & +1),
- (b) six points in the centers of each face, known as star points (-α and + α), and
- (c) the center point (0).

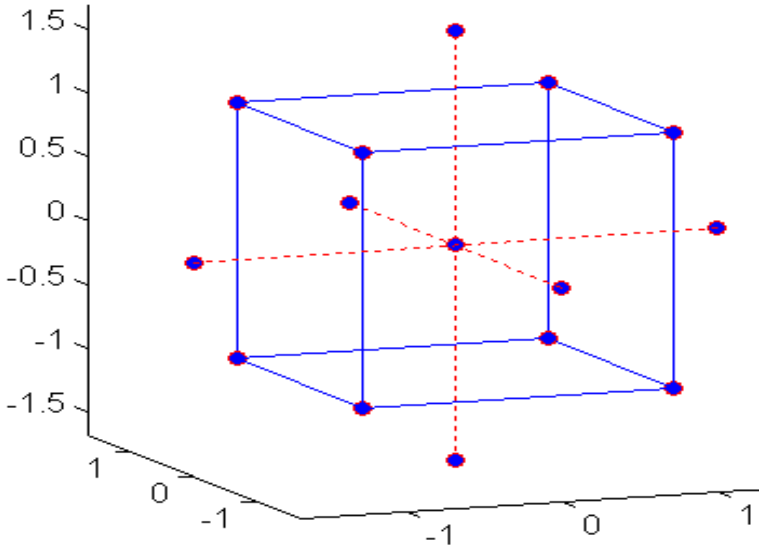


Figure 4.6 Central composite design, also known as Box-Wilson designs (source Matlab Documentation, 2011)

A resolution of at least the factorial part allows clear estimates of all main effects and 2-factor interactions (Castillo, 2007). The axial points allow the estimation of the pure quadratic effects. Some center points can be designed to be run together with the factorial points and some more can be run together with the axial points.

Table 4.2 shows a central composite design table. The axial distance is α. The total number of runs N is thus $F + n_0 + 2k$, where F is the number of factorial points. Notice the structure of the experimental design is fixed; the tuning parameters of this experimental design are α and n_0.

Table 4.2 The D matrix for a central composite design

x_1	x_2	x_3	…	x_k
	± 1 from a 2k design			
0	0	0	0	0
0	0	0	0	0
⋮	⋮	⋮	⋮	⋮
0	0	0	0	0
-α	0	0	…	0
α	0	0	…	0
0	-α	0	…	0
0	α	0	0	0
0	0	-α	0	0
0	0	α	0	0
⋮	⋮	⋮	⋮	⋮
0	0	0	0	-α
0	0	0	0	α

4.2. Application of the Design/Analysis Methodology

In this section, the applicability of the developed methods and tools that were implemented into the design/analysis methodology is illustrated through the analysis of three lipid-based processes:

- The solvent recovery section of the crude soybean oil extraction process,
- The crude palm oil deodorization process, and
- The crude soybean oil deacidification process.

The simulation models used to describe the process behavior were validated with the available plant data. These validated models were then used to perform the optimization of the processes in terms of a selected set of design variables. To observe the impact that the selected design variables have in the overall process performance, the design of experiments theory (Montgormery, 2005) was employed.

4.2.1. Case Study 1: Solvent Recovery Section

4.2.1.1. Process Description

Nowadays, the production of soybean oil by means of mechanical unit operations (*e.g.* hydraulic presses) is not much used because it is expensive and gives lower yields. As a consequence, soybean oil is almost exclusively produced by solvent based extraction. The solvent used in the majority of oilseed solvent extraction plants around the world is commercial hexane (Shahidi, 2005). As stated by the American Oil Chemists' Association (O'Brien, 2004), the term hexane is merely a common name for a mixture of liquid hydrocarbon molecules with a six-carbon chain, 14-16 hydrogen atoms, and a boiling temperature range of 65–69°C. This hydrocarbon mixture is considered to be a good solvent because it has unique physical properties such as excellent oil selectivity, low boiling point, low latent heat of vaporization, low specific heat, and low solubility in water (see Table 4.3). Also, the solvent can be recovered at low temperature and its low solubility in water leads to a nearly total recovery (Shahidi, 2005; Martinho *et al*., 2008). However, it also has properties (toxicity, high flammability, high heat of combustion, and high vapor pressure) that can cause safety concerns if not effectively addressed in process design and operation. For reasons of operating economics, environmental

responsibility and general safety, the solvent must be recovered to the greatest extent possible.

Table 4.3 Physical properties of Hexane

PROPERTY	
Molecular formula	C6H14
Molecular weight	86.178
Normal melting point (K)	177.8
Normal boiling point (K)	341.89
Solubility in water (mg/L)	13 @ 20°C
Density (gr/cm^3)	0.659 @ 20°C
Viscosity (cP)	0.31 @ 20°C
Enthalpy of vaporization (KJ/mol)	31859.90 @ 20°C
Liquid heat capacity (J/mol*K)	197.66 @ 20°C

Consequently, the analysis of the solvent (hexane) recovery section of the soybean oil production process is crucial. Plant data of this section was made available by the company Alfa Laval, therefore the analysis of the section performance is studied in terms of the identified set of design variables and process parameters, and not in terms of the impact that different solvents could have in the overall performance of the process section.

Although the aim of this study is the analysis of the solvent recovery section, it is also necessary to describe the crude oil extraction process. In summary, the two processes are composed as follows:

- The crude soybean oil extraction is a four-stage process composed by two steps: the seed preparation and the crude oil extraction (see Figure 4.7).
- The hexane recovery section (see Figure 4.7) includes four parts: An oil recovery, a condensation system, a mineral oil system and a water-solvent separation.

After the preparation of the oil seeds, the flakes are “washed” and both the miscella (mixture of oil and solvent) and the white flakes (extracted flakes wet with solvent) are heated separately to remove the solvent. The flakes go to a desolventiser–toaster–drier–cooler (DTDC) unit and the miscella enters the first part of the solvent recovery section, the oil recovery system, where the oil is concentrated. In the oil recovery part, the oil is concentrated by removing the solvent from the oil, which is

subsequently concentrated to nearly 100% (crude oil). All the recovered solvent vapors mixed with steam, including those coming from the DTDC facility, are retrieved by means of three sub-systems that are part of the solvent recovery system: the condensation, the MOS (mineral oil system), and the water–solvent separation. Therefore, vapors are condensed and the residual vapors are captured in the mineral oil system. The condensates from the condensation system enter a water–solvent separation section, where the solvent is recovered and, after mixing with a make-up stream, is redirected to the extractor.

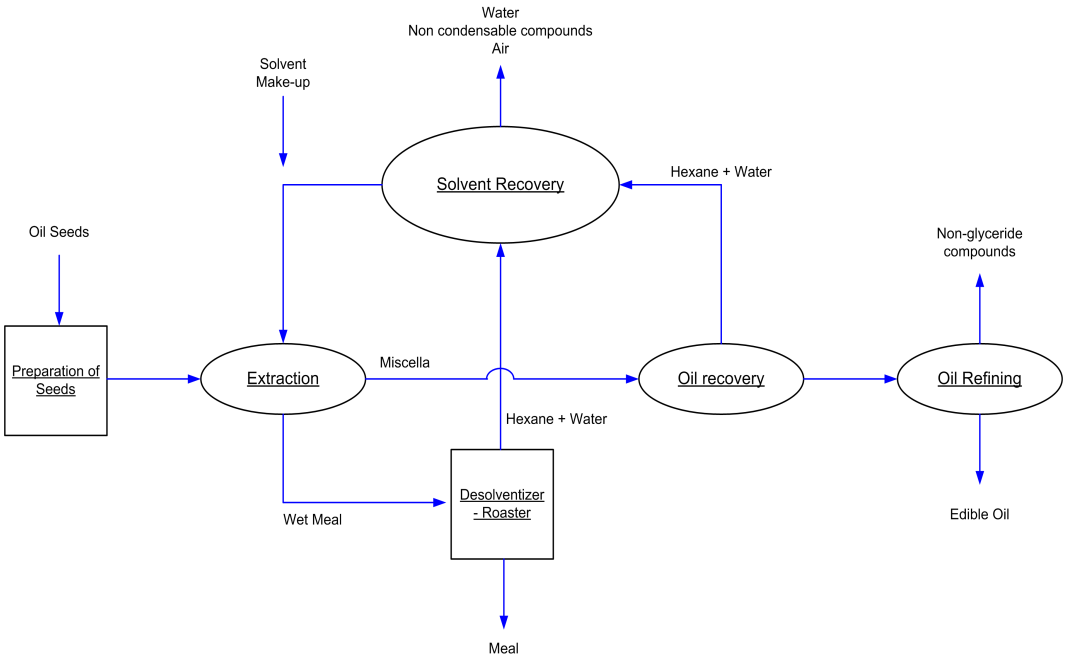


Figure 4.7 Flow diagram of soybean oil production through a solvent-based extraction process.

4.2.1.2. Solvent Recovery Process Simulation Model

Process Unit Operations Sequence

The process model the solvent recovery section hves been widely discussed in the open literature (O'Brien, 2004; Shahidi, 2005; Martinho *et al*., 2008). The solvent recovery section consists of several unit operations: flash, heat exchange, mixing, splitting, stripping, and absorption. In this case study, the oil-containing seeds fed to the process contain: 19% oil, 11% moisture, and 70% hulls. An average composition of the soybean oil reported in the literature, together with the

composition used as the feed in the simulation flowsheet, is given in Table 4.4. As discussed in Chapter 2, the composition of any crude oil depends on the raw material used and on the way the raw material is handled.

Table 4.4 Soybean oil crude composition (wt %)

COMPONENT	LITERATURE (Shahidi, 2005)	CASE STUDY 1*
Triacylglycerides	94.4	95.8
Free Fatty Acids	0.3-0.7	1.3
Phospholipids	3.7	-
Plant Sterols	0.236	1.5**
Tocopherols	0.123	1.4***
Hydrocarbons	0.38	-
Trace metals	ppm	ppm
Iron	1-3	-
Copper	0.03-0.05	-

*Based on available data **Expressed as cholesterol ***Expressed as α-tocopherol

Oilseed Preparation

In a first stage, the soybean seeds (FEED_SEEDS) are cracked and dehulled to concentrate the available oil and protein in the oil seeds and to increase the capacity of the plant (O'Brien, 2004). A second stage comprises the conditioning and flaking of the cracked and dehulled seeds (meats). The conditioning process cooks the meats in the presence of elevated moisture. The heat of this process softens the meats, reduces the viscosity of the oil, and coagulates the proteins. The flaking is the final process in the preparation of the seeds for the extraction and its purpose is to reduce the granular meats into thin flakes, increasing with this the surface area per unit of mass.

Crude Oil Extraction

In a third stage, the flakes (EXTCT_FEED) are introduced into completely closed vessels (extractors) designed to convey flakes through a wash of solvent until the majority of the oil has been extracted. Finally, the miscella (MISCELLA) enters the final stage of the soybean oil production process, the solvent recovery section. On the other hand, wet flakes (MEAL) enter a desolventiser–toaster–drier–cooler (DTDC) unit to remove the residual hexane present in them and to enhance the digestibility of the proteins in animal feeds. The gases produced in the DTDC

process (HEX_REC_MEAL) are condensed and directed to the solvent –water separator.

Oil Recovery

The oil recovery process is used to produce commercially acceptable solvent free oil. Miscella from the extractors enters the bottom of the first effect evaporator (1ST_EVAP), where it is concentrated to about 65%, and then sent to the second effect evaporator (2ND_EVAP), where the oil is further concentrated to almost 90%. Concentrated miscella is fed on the top of a stripping column (STP1), which has been modeled as a distillation column without re-boiler and condenser, to remove the final traces of hexane from the oil. The crude oil leaves the bottom of the stripping column as a stream named CRUDE_OIL and is directed to the subsequent refining processes.

Condensation System

This section consists of a sequence of chilled water condensers, where almost all the hexane vapor mixed with the steam is condensed. In this model, the vapor streams rich in hexane from the two evaporators (HEX_REC and HEX_REC_2) are mixed (M1) and sent to two condensers in series.

The water-hexane vapor stream of the stripping column (HEX_REC_3) is partially condensed. The condensed streams of the flash separators are mixed (HEX_REC_MIX2) and sent to the solvent-water separator. On the other hand, non-condensed vapors of the condensed section are also mixed (HEX_REC_MIX3) and sent to the mineral scrubbing oil system.

Mineral Oil System

This system consists of an adsorption column (ABSPC) followed by a stripping column (STP2) with a network of heat exchangers (E7, E8, E9, and E10) between them that controls the temperature of the mineral oil. The mineral oil has been modeled as an alkane with a linear chain of 15 carbon atoms (NC15). The absorption column (ABSPC) receives at the bottom the non-condensed vapors of the condensation section (HEX_REC_MIX3), which include the air leaking from the vacuum system and, at the top, the mineral oil. Two streams leave the absorption

column: at the top, the non-absorbed compounds (AIR_OUT) and, at the bottom, the mineral oil containing hexane (T1_REC_OUT).

The mineral oil is then heated by means of the heat exchanger network and the feed to the stripping column (STP2). Steam (T2_STEAM_FEE) is used to strip out the hexane from the mineral oil. Steam rich in hexane leaves the column at the top (HEX_REC_DEST) and is sent to the water solvent separation section; hexane-free mineral oil leaves the column at the bottom (T2_REC_OUT) and enters the heat exchangers, where it is cooled down and sent back to the absorption column.

Water-Solvent Separation

The condensate hexane-water from the MOS System (HEX_REC_DEST) and the mixed hexane condensed streams from the previous processes (COND_HEX) are mixed and the resulting stream (WET_HEX_REC) is sent to a decanter tank (DECANT). As a result of the immiscibility and density difference of the two-liquid phases, hexane separation from the aqueous solution is achieved. Two liquid streams leave the decanter tank: the water waste (WS_WATER) and the recovered hexane (DRY_HEX_REC).

Simulation Model

The simulation flowsheet of the solvent recovery section as shown in Figure 4.8 was developed as follows:

- The identified lipid compounds used to represent a typical soybean crude oil (Table 4.5) and the thermophysical pure component property models are retrieved from the CAPEC_Lipids_Database (Diaz-Tovar *et al.*, 2011) (see Table 4.5).
- VLE equilibria of lipid systems has been model through the original UNIFAC (Ceriani & Meirelles, 2004) as the compounds involved can be represented with an already available set of functional groups as discussed in Chapter 3.
- The *Oil Recovery Section* is modeled with two flash vessels that represent the double-evaporator system (1ST_EVAP & 2ND_EVAP). The stripping column (STP1) is modeled, based on industrial information, as a 5-stage distillation column with no condenser and no re-boiler.
- The *Condensation System Section* is divided into two sub-sections:

i. The first sub-section is a double-condenser system modeled each one as a heat exchanger (E3 and E4) followed by an adiabatic flash vessel (COND1 and COND2).
ii. The second sub-section is also modeled as a heat exchanger (E2) followed by an adiabatic flash vessel (COND3).

- The *Mineral Oil System Section* is represented by an adsorption and a stripping column. The columns are modeled, also based on industrial information, as a 5-stage and 3-stage distillation columns, respectively, without re-boiler and condenser.
- The *Water-Solvent Separation Section* was modeled by means of a two-liquid phase adiabatic flash vessel to represent the water/hexane decanter.

Finally, the process operation conditions of each unit operation are given in Table 4.8.

Table 4.5 Lipid compound and thermophysical property data retrieved from the CAPEC_Lipids_Database

Family	Compound	Thermophysical Property Data
TAGs	Li-Li-Li	
FFAs	LINOLEIC (LI)	Single value properties,
Minor Compounds	B-TOCOPH	Vapor pressure,
	STIGSTRL	Enthalpy of vaporization
	SQUALNE	

4.2.1.3. Model Validation

In this section, the aim is to compare the simulation results with the available plant data. In this case study, the accuracy of the solvent recovery section simulation has been determined by comparing the simulated results of the base simulation model (see Table 4.6) with data from a full-scale industrial plant under the same operational conditions. To be highlighted that the industrial data is assumed to be correct and that it has already been reconciled. The average relative deviation (ARD) between the industrial data and the simulated data for the crude oil and the overall loss of hexane was analyzed according to Eq. (4.1).

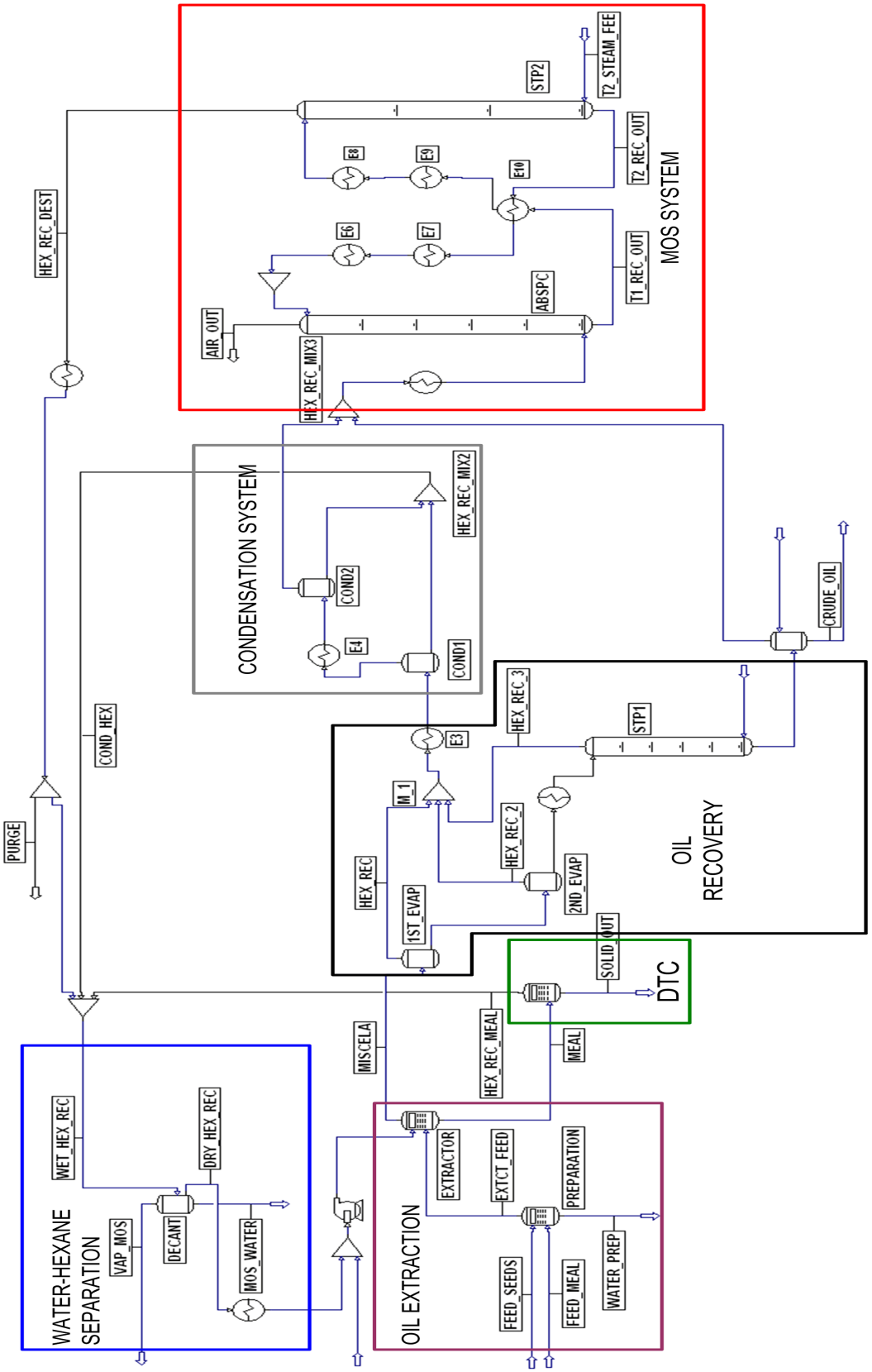


Figure 4.8 Solvent recovery process flow sheet (Martinho *et al*., 2008), as represented by PRO II.

Table 4.6 Result of the base case simulation model

	STREAM							
	FEED_SEEDS	MISCELA	SOLID_OUT	CRUDE_OIL	T1_FEED	T1_VAP_OUT	T2_OUT	DRY_HEX_REC
T (°C)	20	23	23	124	20	25	93	29
P (Bar)	1	1	1	0.7	0.30	0.03	0.3	0.3
Mass Rate (kg/hr)	67230	93093.58	48082.92	65121.59	39.70587	5.431	491.8754	49675.91
Water	0.00000	0.00000	0.05437	0.00346	0.90496	0.99861	0.99241	0.00016
Hexane	0.00000	0.30289	0.00000	0.00000	0.09418	0.00139	0.00759	0.99984
Glutamic	0.00000	0.00000	0.89710	0.00000	0.00000	0.00000	0.00000	0.00000
Li-Li-Li	0.95783	0.66795	0.04603	0.95485	0.00000	0.00000	0.00000	0.00000
Linoleic Acid	0.01506	0.01051	0.00070	0.01503	0.00000	0.00000	0.00000	0.00000
Cholesterol	0.01406	0.00953	0.00120	0.01363	0.00000	0.00000	0.00000	0.00000
A-Tocoph	0.01305	0.00911	0.00061	0.01303	0.00086	0.00000	0.00000	0.00000

Plant data was available for the overall mass balance of the oil composition in the crude oil stream and the total process hexane loss. The ARD for the oil composition in the crude oil stream is 0.31%, while the ARD for the loss of hexane in the process is 4.71%. This comparison confirmed that the proposed simulation model for hexane and oil gives an acceptable match of the observed data in the industrial process. It should be noted that the simulated hexane concentration in the crude oil stream was indeed the main loss of hexane.

4.2.1.4. Optimization Problem Definition

The validated solvent recovery section simulation model was used to generate data through the two-level factorial design. The generated data was then used to obtain a model that was used in the optimization problem definition. The aim is to optimize the performance of the solvent recovery section in terms of vegetable oil and hexane loss by manipulating the selected design variables. The goal of the optimization problem is to minimize the loss of hexane solvent and vegetable oil (product).

The Optimization Problem

The optimization problem is defined by determining, according to the flow diagram; the streams where both the hexane solvent and vegetable oil can be lost (see Table 4.7). From the available plant data it was possible to set the process parameters and the design variables that were manipulated during the performance analysis of the process.

Table 4.7 Process streams from were hexane or vegetable oil can be lost

PROCESS SECTION	DESCRIPTION	CODE NAME
DTDC	Solid (flakes) output stream	Solid_Out
Oil Recovery	Crude oil output stream	Crude_Oil
MOS System	Absorption column vapor output stream	Vap_Out
N/A	Purge	Purge
Water-Hexane Separation	Water output stream	WS_Water
Water-Hexane Separation	Vapor phase output stream	WS_Vap

The selected design variables were perturbed in the range of 5-30% with respect to their nominal value, since this is an acceptable range within the usual industrial practice (Martinho *et al.*, 2008). Table 4.8 shows the design variables (DV) and the process parameters (PP) with their nominal values and the perturbation applied during the performance analysis.

Table 4.8 Selected design variables (DV) and process parameters(PP)for the performance analysis

PROCESS SECTION	DESCRIPTION	CODE NAME	TYPE	NOMINAL VALUE	VARIATION
Oil Recovery	Temperature in evaporator 1	TEVAP1	DV	62.75°C	±15%
Oil Recovery	Pressure in evaporator 1	PEVAP1	DV	0.56bar	±30%
Oil Recovery	Temperature in evaporator 2	TEVAP2	DV	110.00°C	±20%
Oil Recovery	Feed temperature in stripping column 1	TSTP1	DV	110.00°C	±5%
Oil Recovery	Number of stages in stripping column 1	NSTP1	DV	5	±20%
Condensation	Pressure in condenser 1	PCOND1	DV	0.30bar	±15%
Condensation	Temperature in condenser 2	TCOND2	DV	31.00°C	±15%
Water-Hexane Separation	Temperature in decanter	TDECANT	DV	26.85°C	±5%
Water-Hexane Separation	Pressure in decanter	PDECANT	DV	0.30bar	±40%
Oil Recovery	Press. evaporator 2	PEVAP2	PP		N/A
Oil Recovery	Pressure in stripping column 1	PSTP1	PP	0.70bar	N/A
Condensation	Temp. condenser 1	TCOND1	PP	35.00°C	N/A
Condensation	Pressure in condenser 2	PCOND2	PP	0.31bar	N/A
MOS System	Feed temperature in stripping column 2	TSTP2	PP	75.00°C	N/A
MOS System	Number of stages in stripping column 2	NSTP2	PP	3	N/A
MOS System	Pressure in stripping column 2	PSTP2	PP	0.30bar	N/A
MOS System	Feed temperature in absorption column	TABSPC	PP	20.00°C	N/A
MOS System	Number of stages in absorption column	NABSPC	PP	5	N/A
MOS System	Pressure in absorption column	PABSPC	PP	0.03bar	N/A

Eq. (4.2) is the objective function that is to be minimized; while equations (4.3)-(4.11) are the constraints that the objective function is subject to.

Objective Function

$$OF = Crude\_Oil(Hex) + Vap\_Out(Hex) + Solid\_Out(Hex) + Purge(Hex) + Vap\_Mos(Hex) + Mos\_Water(Hex) + WS\_Vap(Oil) + WS\_Water(Oil) \quad (4.2)$$

Constraints

$$26.46 \le TCOND2(°C) \le 35.80 \quad (4.3)$$

$$25.51 \le TDECANT(°C) \le 28.19 \quad (4.4)$$

$$53.34 \le TEVAP1(°C) \le 72.16 \quad (4.5)$$

$$88.00 \le TEVAP2(°C) \le 132.00 \quad (4.6)$$

$$104.50 \le TSP1(°C) \le 115.50 \quad (4.7)$$

$$0.26 \le PCOND1(bar) \le 0.36 \quad (4.8)$$

$$0.18 \le PDECANT(bar) \le 0.42 \quad (4.9)$$

$$0.39 \le PEVAP1(bar) \le 0.73 \quad (4.10)$$

$$\text{Number of Stages} \ge 1 \quad (4.11)$$

Analysis of the Objective Function

The validated simulation model from PRO II was used to determine which terms of the objective function (see Eq. (4.2)) could be disregarded from further analysis. By means of the steady state simulation results, it was possible to establish the following observations:

- Presence of hexane in the stream Solid_Out can be neglected because, according to the plant data, the DTDC process is capable of removing all hexane and water from the white flakes.
- The major loss of vegetable oil in the process is located in the solvent extraction process, where some oil may remain in the waste solid. Since a predictive model to calculate this variable was not available, the stream Solid_Out was not considered in the model reduction step. Since the emphasis in this study is on the recovery of the extracted oil, this loss of non-extracted oil can be neglected.

- The amount of oil in the streams Purge and WS_Water can be neglected as these values were found to be on the order of 10-7 kgmol/hr. This means that under the current operating conditions there is no vaporization of the oil and, therefore, the amount of it compared to that of the water or hexane is minimum.
- Two liquid phases (water and hexane) are present in the vessel equipment named DECANTER. Therefore, the stream tagged as WS_Vap, which is in the gaseous state in the flow diagram, was neglected in the further solution steps.

Based on the above observations, the corresponding terms correlating the above streams (where hexane and / or oil could be lost) to the response variables have no influence on the performance of the process. As a consequence, by neglecting these terms, Equation (4.2) is reduced to:

$$OF = Crude\_Oil(Hex) + Vap\_Out(Hex) + Purge(Hex) \quad (4.12)$$

Eq. (4.12) actually corresponds to the amount of hexane recovered in the process, which will now be maximized.

$$\text{Objective Function} = \text{Recovery of Hexane} \quad (4.13)$$

Model Reduction

As mentioned in Section 4.1.4.1, the observed changes in a response variable maybe correlated with, but not caused by, observed changes in individual process variables. Simultaneous changes in multiple factors may produce interactions that are difficult to separate into individual effects (Ceriani *et al.* 2008).

According to the Central Composite Design theory (Montgomery, 2005), the number of experiments (simulation runs) needed to observe the effect of the individual and interaction effects on the selected design variables:

$$\text{Simulation runs} = 2^9 + 2*9 + 1 = 531$$

Among them 2^9 simulation runs are factorial points, 2*9 are the star points, and 1 is the central point. According to the factorial design theory, the central point should be performed three times; however, due to the fact that the central point is obtained through simulation, this point is only performed once.

While the individual simulation runs do not take too much time, the off-simulation time related to simulation problem set-up, data analysis and data-flow could be quite substantial. Fractional factorial designs (*e.g.* Plackett-Burman (PB) designs) are commonly employed tools used to perform a screening procedure in order to discard design variables that do not affect significantly the overall performance of the process.

Plackett-Burman Design (PB)

In order to give more flexibility to the experimental design and, therefore, not utilize all the degrees of freedom to estimate the main effects, a PB design with 16 runs was employed (see Table 4.9). In each one of the runs, the selected design variables have to adopt one of the upper (+1) or lower (-1) values (perturbed values) so that the statistical analysis of the simulation results can identify the main effects.

Table 4.9 Plackett-Burman design for 9 design variables and response variable values in the16 simulations

RUN	VARIABLE									
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**Hexane Recovery (%)**
1	1	-1	-1	-1	1	-1	-1	1	1	99.921
2	1	1	-1	-1	-1	1	-1	-1	1	99.886
3	1	1	1	-1	-1	-1	1	-1	-1	99.626
4	1	1	1	1	-1	-1	-1	1	-1	99.879
5	-1	1	1	1	1	-1	-1	-1	1	99.842
6	1	-1	1	1	1	1	-1	-1	-1	99.826
7	-1	1	-1	1	1	1	1	-1	-1	99.824
8	1	-1	1	-1	1	1	1	1	-1	99.888
9	1	1	-1	1	-1	1	1	1	1	99.845
10	-1	1	1	-1	1	-1	1	1	1	99.661
11	-1	-1	1	1	-1	1	-1	1	1	99.896
12	1	-1	-1	1	1	-1	1	-1	1	99.567
13	-1	1	-1	-1	1	1	-1	1	-1	99.896
14	-1	-1	1	-1	-1	1	1	-1	1	99.825
15	-1	-1	-1	1	-1	-1	1	1	-1	99.661
16	-1	-1	-1	-1	-1	-1	-1	-1	-1	99.842

According to the range of values that can be found within the usual industrial practice, ±1 levels for each one of the design variables used in the 16 simulations are listed in Table 4.10. Statistical analyses of the 16 simulation results showed that only five of the original nine design variables were found to affect significantly the performance of the solvent recovery section of the soybean oil extraction process

(see Table 4.11). This is reasonable since the small variation of the response variable (see Table 4.9) is more to be a consequence of the interaction of a smaller set of design variables rather than a consequence of all nine of them.

Table 4.10 Perturbed values of the design variables for the Plackett-Burman design

DESIGN VARIABLE	LEVELS	
	-1	+1
TCOND2(°C)	26.46	35.8
PCOND1(bar)	0.26	0.36
TDECANT(°C)	25.51	28.19
PDECANT(bar)	0.18	0.42
TEVAP1(°C)	53.34	72.16
TEVAP2(°C)	88.00	132.00
TSTP1(bar)	104.50	115.50
NSTP1	4.00	6.00
PEVAP1(bar)	0.39	0.73

Table 4.11 Plackett-Burman design technique results

PROCESS STREAMS	SIGNIFICANT DESIGN VARIABLES
Vap_Out	TCOND2, PCOND1, TEVAP1
Crude_Oil	TCOND2, TEVAP2, TEVAP1
Purge	TCOND2, TSTP1

Full Factorial Design

Based on the results of the PB design, a second set of 43 simulations, 25 trials plus a star configuration (2*5) and one central point, was performed using the central composite design. Table 4.12 shows the values for each one of the levels (-1, +1, -α, + α, and c) of the five design variables employed in the performance analysis of the solvent recovery section.

Table 4.12 Perturbed values of the design variables for the Central Composite design

DESIGN VARIABLES	LEVELS				
	-α	-1	0	1	+ α
TCOND2	26.46	29.17	31.13	33.09	35.80
PEVAP1	0.3900	0.4989	0.5600	0.6315	0.7300
TEVAP1	53.34	58.79	62.75	66.71	72.16
TEVAP2	88.00	100.75	110.00	119.25	132.00
TSP1	104.50	107.69	110.00	112.31	115.50

The second-order model proposed by the central composite design theory is given by Eq. (4.14).

$$\text{Recovery of Hexane} = a_0 + \sum_{i=1}^{N} b_i X_i + \sum_{i=1}^{N} \sum_{j>i}^{N} c_{ij} X_i X_j + \sum_{i=1}^{N} d_i X_i^2 \qquad (4.14)$$

The statistical analysis of the results given in Table 4.9 is shown in Table 4.13. It is to be highlighted that from the original 21 terms of Eq. (4.14), only 6 terms are significant.

Table 4.13 Statistical analysis of the regressed model coefficients

Term	Regressed Coefficients	p
a_0	9.9963E+01	0.0000E+00
T_{EVAP2} (b_4)	1.3017E-02	1.4889E-08
T_{EVAP2}^2 (d_4)	-5.0000E-03	4.3341E-03
T_{SP1} (b_5)	-1.7800E-02	6.4121E-12
$T_{SP1}T_{COND2}$ (c_{14})	4.6500E-03	3.3073E-02
$T_{EVAP2}T_{SP1}$ (c_{45})	5.4000E-03	1.4614E-02

Consequently, the model correlating the hexane recovery with the design variables is given in terms of 3 design variables (TCOND2, TEVAP2, and TSP1) since these variables are the only ones that affect the hexane content in the output stream Crude_Oil (see Table 4.14 and Eq. (4.15)).

Table 4.14 Optimal values for the design and response variables

VARIABLE	VALUE
Design	
TCOND2	26.46°C
TEVAP2	110.14°C
TSTP1	115.50°C
Response	
Objective Function (Hexane Recovery)	99.98%

The ARD value for the reduced model is 0.008%. The response surface indicates the performance of the process in terms of the design variables with respect to the response variables. Surface responses were generated from the reduced model (see

Eq. (4.15)). Figure 4.9 is generated by setting the value of the variable TCOND2 (see Table 4.12) to its nominal value (0) and by modifying the value of the variables TEVAP2 and TSP1 within their respective range of values (see Table 4.12) in Eq.(4.15).

Figure 4.9 shows the expected behavior. As the temperature in the EVAP2 increases, the amount of solvent loaded in to the stripping column is lower and the amount of stripping steam is enough to remove the solvent from the crude oil.

Figure 4.10 and Figure 4.11 were generated by setting the value of the variable TSP1 and TEVAP2 (see Table 4.12) to its nominal value (0) and by modifying the other two variables within their respective range of values (see Table 4.12) in Eq. (4.15) respectively. As it can be seen in Figure 4.10 and Figure 4.11 the amount of solvent recovered almost remain constant as both variables are perturbed within their range of values, indicating that TEVAP2 is clearly the variable with more influence in the process performance.

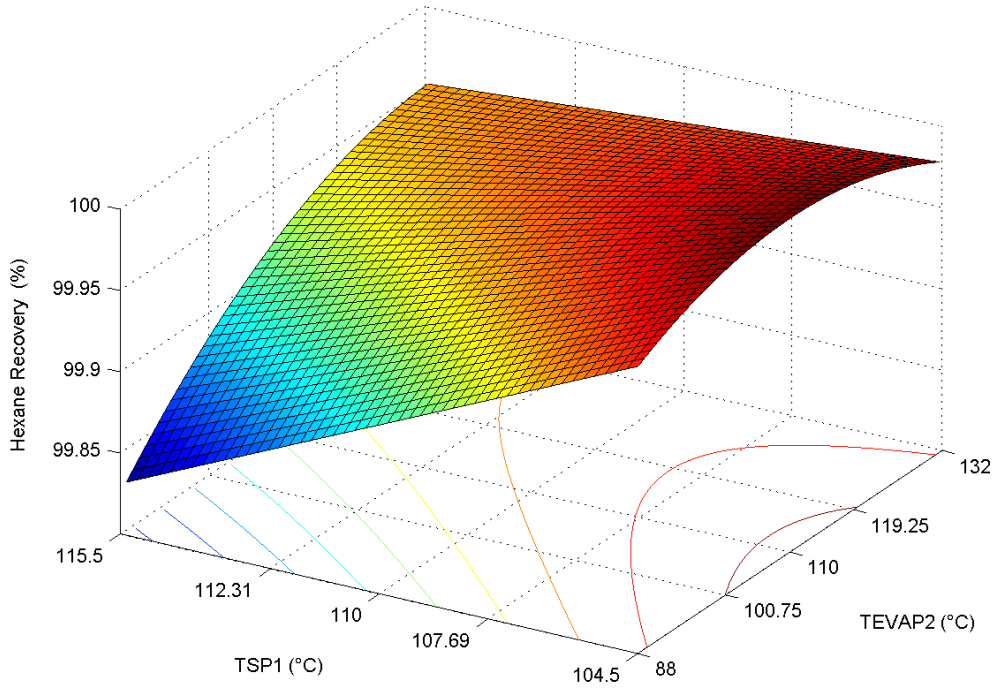


Figure 4.9 Hexane recovery surface response (TCOND2 fixed to its nominal value)

$$\text{Hexane Recovery} = -0.005T_{\text{EVAP2}}^2 + 0.013T_{\text{EVAP2}} + 0.0054\left(T_{\text{EVAP2}}\right)\left(T_{\text{SP1}}\right) - 0.0178T_{\text{SP1}} - 0.0047\left(T_{\text{SP1}}\right)\left(T_{\text{COND2}}\right) + 99.963 \quad (4.15)$$

The objective of obtaining a reduced second order model is to observe where the process is currently operating and if further improvements in the process performance can be achieved.

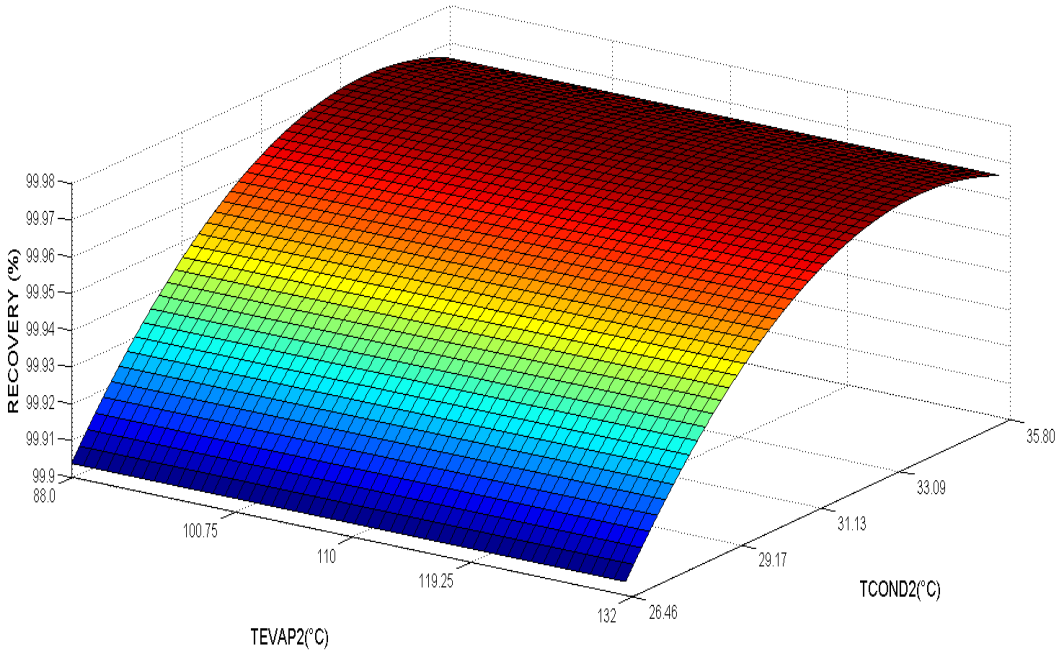


Figure 4.10 Hexane recovery surface response (TSTP1 fixed to its nominal value)

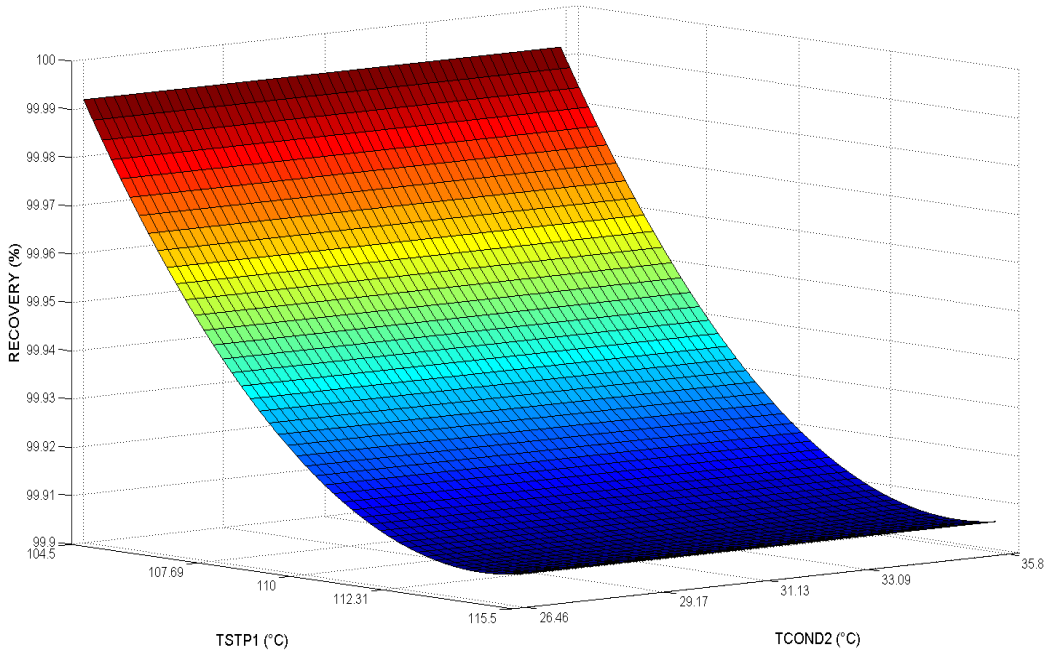


Figure 4.11 Hexane recovery surface response (TEVAP2 fixed to its nominal value)

The reduced second order model that correlates the response variable to the selected design variables is represented by Eq. (4.16)-(4.19). As the objective function (see Eq.(4.15)) is non-linear, the optimization problem has the form of a Non-linear Programming problem (NLP). This NLP problem was solved by means of the software ICAS™ MoT and optimum operational points where Eq. (4.16) is maximized were found (see Table 4.14).

Max Objective Function = Hexane Recovery (4.16)

s.t.

$$26.46 \leq T_{COND2}\left(^{\circ}C\right) \leq 35.80 \quad (4.17)$$

$$88.00 \leq T_{EVAP2}\left(^{\circ}C\right) \leq 132.00 \quad (4.18)$$

$$104.50 \leq T_{STP1}\left(^{\circ}C\right) \leq 115.50 \quad (4.19)$$

According to the results obtained from the optimization of the reduced model, the temperatures in the feed of the stripping column and in the second condenser have to be modified to operate at the lower boundary (–α) and at the higher boundary (α), respectively (see Table 4.12). However, the nominal temperature of the second evaporator (see Table 4.8) should be kept at the current operation value to achieve the best performance of the solvent recovery section.

Finally, Figure 4.12 shows both, the current and optimal operating conditions, with respect to the design variables TSP1 and TEVAP2. Notice that even the process is currently working close to the optimal zone, improvements could be achieved if the selected design variables are modified.

4.2.1.5. Conclusions

The model that describes the soybean oil extraction process, with special emphasis on the solvent recovery section, has been studied in this work. The good comparison between the available data plant and the results obtained from the model simulation validated the proposed unit operations used to describe the process, as well as the model proposed to predict the physical properties of the chemical species involved in the soybean oil extraction process.

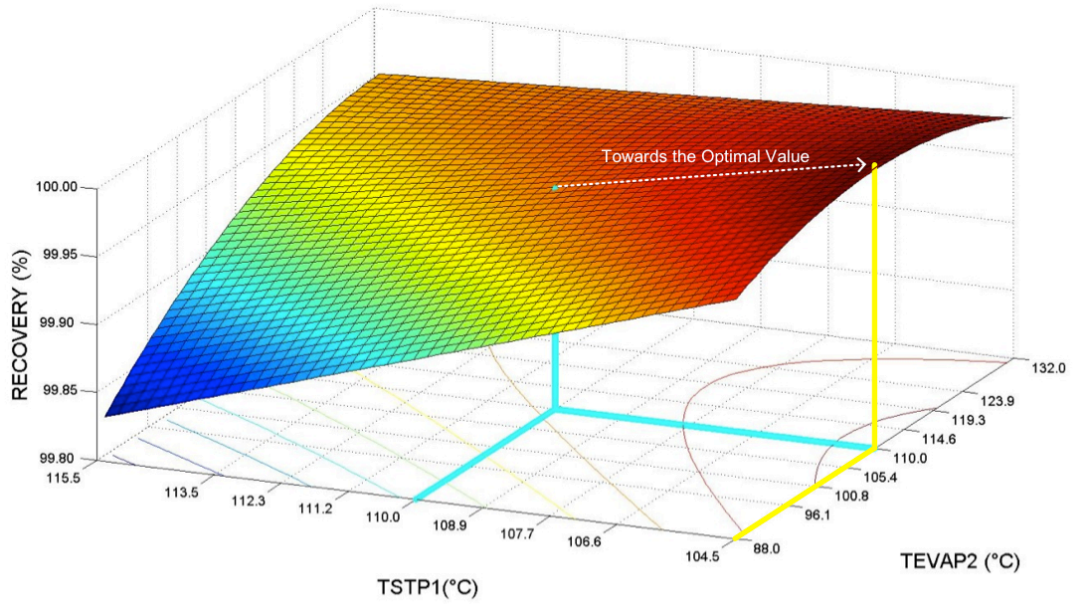


Figure 4.12 Hexane recovery surface response generated with the reduced second order process model

The accuracy of the proposed models provided the basis for further analysis of the solvent recovery section performance in terms of the selected design variables. Although, the optimization of validated simulation models by means of the process simulator PRO II can be performed, this is not the case. By perturbing the design variables within their range of values, inconsistencies (*e.g.* one-product-stream flashes) and unit operation convergence problems (*e.g.* adsorption and stripping columns in the MOS system) are present in the simulation model. Consequently, alternative methods were used to optimize the solvent recovery section, for example the design of experiments theory.

From the design of experiment theory it is to be concluded that: The original nine operational variables considered in the formulation of optimization problem could potentially require more than 500 simulations if the full factorial technique were used without any pre-analysis. Therefore, the Plackett-Burman method was employed to reduce significantly the total number of simulations that needed to be performed. With the reduced set of design variables, the full factorial technique was applied following the central composite design and a reduced model correlating the selected design variables and response variable was obtained. The response surface generated through the reduced model showed that the process is within the optimal

zone, although improvements are possible. Therefore, optimal values of design variables where hexane recovery is maximum were found. The results are consistent with the expected behavior of the system. This is that by setting the temperature of the feed of the STP1 column to its upper limit, a higher reduction on the amount of hexane in the crude oil can be achieved and also by reducing the temperature on the COND2 the load/duty of the MOS system can also be reduced.

4.2.2. Case Study 2: Physical Refining (Deodorization) Process of Palm Oil

In this case study, the aim is to analyze the impact that the design variables have in the overall performance of the deodorization process. Unlike the first case study, industrial know-how was employed to validate the results given by the simulation model.

4.2.2.1. Process Description

Physical Refining (Deodorization) of Fats and Oils

Vegetable oil and fats are a complex matrix of different families of chemical species where variable amounts of nonglyceride impurities, such as fatty acids, non-fatty materials generally classified as “gums”, and color pigments (Carr, 1978). Most of these impurities are detrimental to end product fresh and aged quality characteristics, hence must be eliminated by purification process. Consequently, deodorization process (steam distillation) and its parameters have a great relevance in lipid processing technology since they have significant impact on the quality of the finished oil as it stripes from the relatively nonvolatile oil, volatile odor- and color-causing substances (Maza *et al.* 1992; Bailey, 1941). Table 4.15 shows a comparison between a typical composition of crude and refined soybean oil.

For lauric oils and palm oil physical refining is preferred in terms of both operating cost and refining loss (Shahidi, 2005). In the case of soybean and rapeseed oils, physical refining is suitable only for crude oils of a high quality, i.e., with a low degree of oxidation and a sufficiently low. Another important factor is the free fatty acid content of the crude oil. In general, physical refining only becomes advantageous when the acidity of the crude oil is sufficiently high. For relatively

cheap oils, like soybean oil, the higher oil yield with the physical refining is less important than the higher bleaching earth consumption, making chemical refining more attractive. For other unsaturated oils with a higher value, such as peanut oil and sunflower seed oil, physical refining will be more attractive.

The physical refining of vegetable oils is a distillation process in which, under low absolute pressure of 2 to 10torr and high temperatures of 240 to 270°C, the accompanying lower boiling compounds are distilled off from the triacylglycerides by using unsaturated open steam as the effective stripping agent (Stage, 1985). The deodorization of fats and oils is a complex process that involves many different unit operations (flash, heat exchange, steam stripping, *etc.*) playing each one of them an important role in every single step of the process (see Figure 4.13). Hence, due to the significance of the steam stripping unit operation, in this work state of the art thin-film deodorizer is used to model this key unit operation (Ahrens, 1999).

Table 4.15 Typical chemical analysis of crude oil and RBD canola oil. (Adapted from Gunstone, 2002)

Parameter	Crude Oil	RBD
Free Fatty Acids	0.3-1.2	0.03
Phosphorus (mg/kg)	300-500	< 2
Water Degummed	120-200	-
Acid-water degummed	10-40	-
Chlorophyl (mg/kg)	4-30	< 0.025
Sulfur (mg/kg)	2-15	< 1
Iron (mg/kg)	0.5-1.5	< 0.2
Copper (mg/kg)	< 0.2	< 0.02
Nickel (mg/kg)	-	< 0.3
Peroxide Value (mg/kg)	0.5-3.0	0 (freshly deodorized)
Anisidine value	1-3	< 2
Colour, Lovibond	-	< 1.5 red/10 yellow
Moisture (%)	< 0.3	-
Flavour	-	bland

Thin-film deodorizer

In the open literature it is possible to find the information needed to model state of the art thin-film deodorization process. For decades, thin-film technology has been well known and widely used for gas/liquid mass transfer operations such as distillation, absorption, and extraction (Shahidi, 2005). During the 1980ies, worldwide consolidation and specialization of the oil industry took place and in 1996 a thin-film deodorizer for physical reefing of palm oil was introduced.

The main difference of these state of the art deodorizers with respect to the ones formerly used is the structured packing type instead of random packing. This new type of packing has, among others, the advantages of allowing an even distribution of oil and to avoid local overheating. This is achieved because the structured packing creates a surface between the liquid (oil) and gas (steam) phases, which allows one ton of oil is spread over the surface.

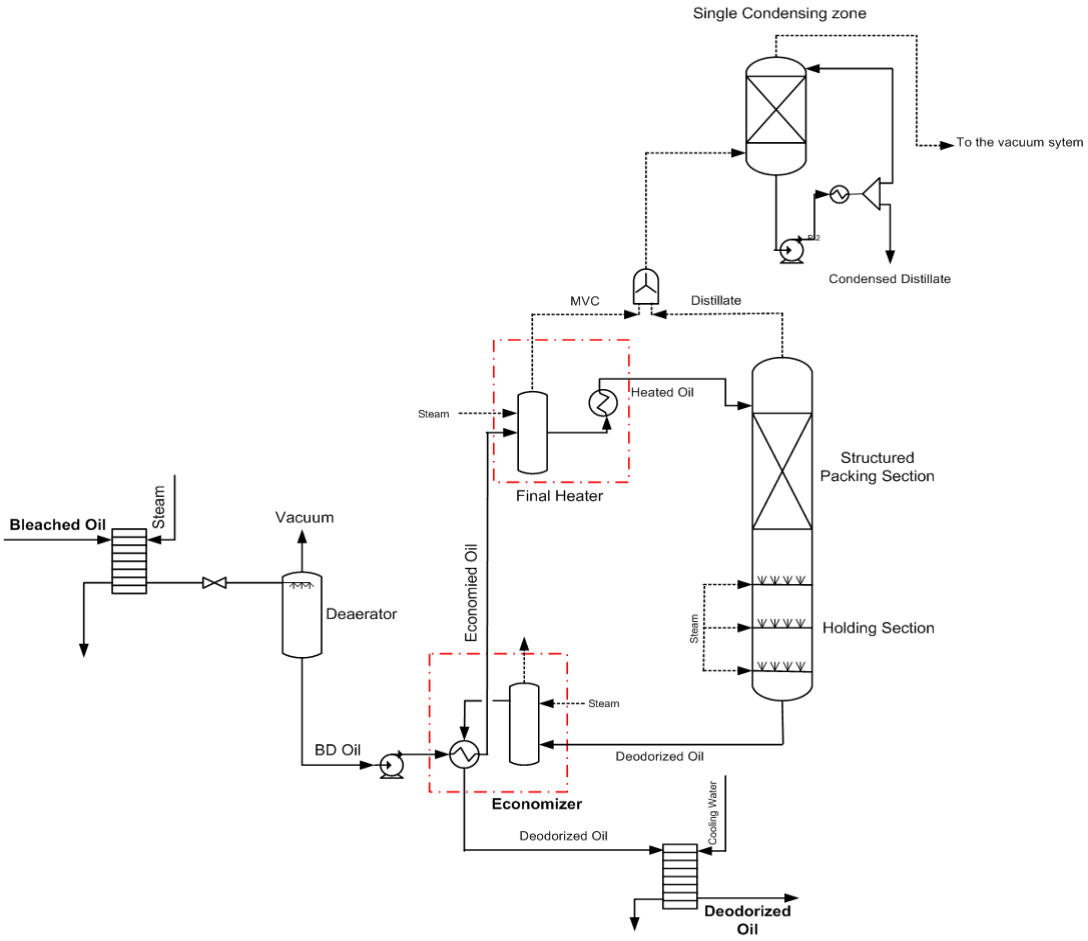


Figure 4.13 Typical deodorization and distillate treatment processes of edible oil and fats

The thin-film deodorizer unit operation is divided into a continuous stage for fast removal of free fatty acids and other volatile compounds from the oil in structured packing, and a discontinuous holding stage for heat bleaching and deodorization. As mentioned above, the large liquid surface in the structured packing permits a mass transfer rate high enough to de-acidify the oil in less than five minutes. However, this time in the packed column is not enough for thermal breakdown of pigments

and deodorization; however, an additional time has to be added. The holding section consists of three open, baffle free trays each one equipped with sparge steam pipes. This section operates according to the sequenced batch principle and retention time can be adjusted, according to quality requirements, by setting the oil level in the trays.

As stated before, the deodorization process targets only the undesirable compounds; however, simultaneous loss of valuable oil components (acylglycerides or natural antioxidants) in unavoidable. Besides, during the steam stripping, complex chemical and physical phenomena are taking place. The chemistry involved includes thermal decomposition, hydration of conjugated polyenic compounds, and hydrolysis of triacylglycerides generating free fatty acids. The main physical effects are vaporization of volatiles and the entrainment of neutral oil droplets in the stripping stream. Since the oil quality (absence of pesticides, low free fatty acid, acceptable flavor, and stability) depends on a large number of process variables, the aim of this work is to perform process optimization based on statistical design.

Fats and Oils Hydrolysis during Deodorization Process

Deviations of steam deodorization curves from theoretical calculations have been attributed to two main reasons (Copeland *et al.*, 2004): a) hydrolysis of the oil by steam stripping; b) a negative deviation of the oil/fatty acids system from ideality.

Szabo-Sarkadi (1959) proved that the extent to which the hydrolysis occurs may be sufficiently great to cause serious error when the vaporization efficiency is calculated on the basis of free fatty acid reduction. As fatty acids have catalytic action on hydrolysis, which may be attributed to the non-associated acid molecules, their initial content in the crude oil significantly affects the degree of hydrolysis.

The study concluded that: a) as a result of catalytic action, the rate of hydrolysis is a function of the free fatty acids content and moreover increases in direct proportion with the absolute pressure; b) only monomeric acid has catalytic action. Concluding that when the vaporization efficiency is based upon the reduction in free fatty acid content, hydrolysis may give rise to serious errors.

4.2.2.2. Process Simulation Model Development

Process Unit Operations Sequence

The bleached oil (composition given in Table 4.16) is first dearated and pumped through a heat exchanger (economizer) with a counter current flow pattern (ECON_OIL). The final heater heats up the oil to the deodorizer temperature. From the final heater (FIN_HEAT_OIL) the oil flows by gravity through the deodorizer. The deodorizer is divided up into a continuous stage for fast FFA removal in a structured packing, and a holding discontinuous holding stage for heat bleaching and deodorization.

Table 4.16 Typical composition of crude palm oil (Ceriani *et al.*, 2010)

Family	Compound	Mass Composition
TAGs	P-P-P	5.51
	P-P-O	36.39
	P-S-O	6.10
	P-P-LI	9.92
	P-O-O	20.84
	P-O-LI	9.55
DAGs	P-P-OH	2.25
	P-O-OH	4.47
	P-LI-OH	1.04
MAGs	P-OH-OH	0.30
	O-OH-OH	0.17
	LI-OH-OH	0.04
FFAs	PALMITIC (P)	1.75
	STEARIC (S)	0.00
	OLEIC (O)	1.14
	LINOLEIC (LI)	0.34
Minor Compounds	B-TOCOPH	0.10
	STIGSTRL	0.01
	SQUALNE	0.06
Other	WATER	0.01

Simulation Model

The simulation flowsheet of the deodorization process as shown in Figure 4.13 was developed as follows:

- The identified lipid compounds used to represent a typical palm oil (see Table 4.16) and the thermophysical pure component property models are retrieved from the CAPEC_Lipids_Database (Diaz-Tovar *et al.*, 2011) (see Table 4.17).
- The selected thermodynamic model is the original UNIFAC.

- Crude oil flowrate is equal to 10000 kg/hr and the composition is defined as presented in Table 4.16. The amount stripping steam (for the base simulation) to be 1% of the total feed flowrate.

Table 4.17 Thermophysical property data retrieved from the CAPEC_Lipids_Database

Family	Thermophysical Property Data
TAGs, DAGs, MAGs & FFA	Single value pure component properties. Vapor Pressure Enthalpy of vaporization Liquid enthalpy Liquid density Liquid viscosity & surface tension UNIFAC functional groups
Minor compounds	Single value pure component properties. Vapor Pressure Enthalpy of vaporization Liquid density UNIFAC functional groups

- The economizer and the final heater are modeled as a heat exchanger plus a flash (Ceriani *et al.*, 2010). The configuration of each one of them is defined as follows: a) In the economizer, the crude oil flows in the tube side while stripping steam flows in the shell side of the heat, and b) in the final heater, the oil flashes in contact with stripping steam in the shell side of the heat exchanger.
- The thin-film deodorizer modeled as a distillation column with no reboiler and no condenser (Ahrens, 1999). The inner arrangement of the first section is commercial structured packing produced by the company Sulzer Ltd; while the second section is modeled with a two flashes and a reactor.
- The hydrolysis reactor is modeled as a conversion reactor. The reaction is defined as follows:

$$TAG + H_2O \rightarrow DAG + FFA$$

The reaction kinetics is defined as a first-order-type reaction and the model parameters (energy of activation and pre-exponential factor) were fine-tuned based on heuristic rules. As these parameters were calculated based on the know-how of the company Alfa Laval Copenhagen A/S, it is not possible to disclose their final values.

The process parameters used in the development of the simulation model are given in Table 4.18.

Table 4.18 Process parameters of the deodorization process.

Process Parameter	Economizer	Final Heater	Stripper
Temp. Feed (°C)	105	230	250
Temperature (°C)	-	-	250
Pressure Top(mbar)	-	-	3.5
ΔP(mbar)	1000	10	1.5
NTS*	-	-	4

*Number of theoretical stages

4.2.2.3. Model Validation

As pointed out at the beginning of Section 4.2.2, the simulation results were validated based on the industrial know-how and confidential information provided by the company Alfa Laval Copenhagen A/S. Consequently, a description of the results obtained through Simulation 15 is given in this section. Table 4.19 shows the composition, temperature, and pressure profiles of the most significant streams involved in the deodorization process of crude palm oil at the defined (Table 4.18) process conditions.

Table 4.19 Results for the base case simulation

	STREAM					
	BD_OIL	**ECON_OIL**	**MVC**	**DEOD_DIST**	**FEED_DEOD**	**FINAL_OIL**
T (°C)	105	214.05	210	244.8	250	40
P (mBar)	1000	7000	4.66	4.66	4.66	2006.692
Mass Rate (kg/hr)	10000	10000	37.67507	540.4969	9972.324	9594.504
TAGs	0.8814	0.8814	0.000268	0.003365	0.883845	0.917296
DAGs	0.0775	0.0775	0.003435	0.037187	0.077702	0.079483
MAGs	0.0051	0.0051	0.015407	0.068271	0.005056	0.00147
FFAs	0.03415	0.03415	0.692627	0.63239	0.031628	0.000356
TOCOs	0.001	0.001	0.001525	0.007913	0.000997	0.000596
SITOs	0.000125	0.000125	0.000112	0.000649	0.000125	9.37E-05
SQUAL	0.0006	0.0006	0.000581	0.003057	0.000599	0.000453
WATER	1.00E-04	1.00E-04	0.286045	0.247168	2.24E-05	0.000226

In the economizer the crude oil stream (BD_Oil) is heated from 105°C to 214°C (ECON_OIL). Even though free fatty acids are aimed to be removed in the deodorizer, by injecting steam into the final heater, the crude oil is flashed. The generated vapor steam (MVC) carries ca. 1.2% and 8% of the incoming mass of MAGs and FFAs respectively.

Removal of the free fatty acids in the deodorizer is achieved to a final composition in the de final product of 0.036%. Under these process conditions, the tocopherol content is also maintained within the product specification (600ppm). And finally, the Neutral Oil Loss (NOL) that considers the loss of glycerides due to vaporization and hydrolysis is ca. 1%.

4.2.2.4. Optimization

Different authors have identified the main deodorization process parameters and their effect on finished oil quality (Maza *et al.*, 1992; Shahidi, 2005; Ahrens, 1999). As discussed in section 2.1, the composition of the crude oil to be deodorized depends on the source of the raw material; hence, process operation conditions have to be adjusted to meet the final product requirements.

Table 4.20 shows the identified key process parameters and their respective range of values used in the physical refining of different vegetable oils and fats.

Table 4.20 Upper and lower limits for the identified design variables

Design Variable	Literature Values		Reference
	Lower Limit	Upper Limit	
Temperature (°C)	230.00	270.00	Maza *et al*. (1992), Shahidi (2005)
Pressure (mmHg)	1.00	6.00	Maza *et al*. (1992), Ahrens (1999)
Steam (%)	0.50	2.00	Shahidi (2005), Ahrens (1999)

The Optimization Problem

A variable that needs to be considered in any refining process is the amount of oil that can be lost due to the process operating conditions. The neutral oil loss is a key factor in the refining edible oils/fats as it affects directly the overall yield of the process.

Eq. (4.20) is the objective function, while Eqs. (4.21)-(4.23) are the design variables constraint, and Eqs. (4.24)-(4.25) are related to the product specifications.

Objective Function

$$\mathrm{OF} = \mathrm{NOL}\left(T - STRIP, P - STRIP, STEAM\right) \tag{4.20}$$

Constraints

Design Variables

$$230.0 \le T-STRIP(°C) \le 270.0 \tag{4.21}$$

$$1.0 \le P-STRIP(mmHg) \le 6.0 \tag{4.22}$$

$$0.5 \le STEAM(\%) \le 2.0 \tag{4.23}$$

Product Specifications

$$FFA\_Content(T-STRIP, P-STRIP, STEAM) \le 0.03\% \tag{4.24}$$

$$Toco\_Content(T-STRIP, P-STRIP, STEAM) \ge 600\,ppm \tag{4.25}$$

Full Factorial Design

The second-order model proposed by the central composite design theory is given in Eq.(4.26).

$$2nd\text{-}Order\_Model = a_0 + \sum_{i=1}^{N} b_i X_i + \sum_{i=1}^{N}\sum_{j>i}^{N} c_{ij} X_i X_j + \sum_{i=1}^{N} d_i X_i^2 \tag{4.26}$$

To determine the parameters that have an effect on the selected design variables, a set of 15 simulations was performed in order to establish the effect of the design variables on the response variables according to the central composite design theory. Among these 15 simulations, 2^3 correspond to the full factorial design, 2*3 correspond to the star points, and 1 corresponding to the central point. The perturbed values of the design variables to be used in the simulations are given in Table 4.21. Table 4.22 shows the arrangement of the central composite design as well as the results obtained for each one of the design variables in each simulation. In Table 4.22, the ±1 values correspond to the factorial levels of the design variables, ±α to the lower and upper values of the design variables, while 0 correspond to the nominal values of the design variables. The second-order regressed model parameters corresponding to each one of the design variables are presented in Tables 4.20 - 4.22.

Table 4.21 Perturbed values of the design variables of the deodorization process

Design Variable	**-α**	**-1**	**0**	**1**	**α**
T-STRIP (°C)	230.00	238.10	250.00	261.90	270.00
P-STRIP (mmHg)	1.00	2.01	3.50	4.99	6.00
STEAM (%)	0.50	0.80	1.25	1.70	2.00

Table 4.22 Central composite design problem and the response variables results

	Sim	X1	X2	X3	FFA_CONT(%)	TOC_CONT(ppm)	NOL(%)
					Sim	Sim	Sim
Factorial Design	1	-1	-1	-1	0.0786949	704.6295	0.4354562
	2	1	-1	-1	0.0252374	364.4968	1.1985402
	3	-1	1	-1	0.4414550	882.9410	0.2234604
	4	1	1	-1	0.0521795	692.5229	0.6532856
	5	-1	-1	1	0.0307721	510.4522	0.6536743
	6	1	-1	1	0.0180316	150.7019	1.7484649
	7	-1	1	1	0.0922576	766.7790	0.3659775
	8	1	1	1	0.0244401	451.0688	0.9799633
Star Points	9	-α	0	0	0.2058781	831.4621	0.2690435
	10	α	0	0	0.0211968	303.1846	1.4619762
	11	0	-α	0	0.0221714	206.3718	1.3845072
	12	0	α	0	0.0813597	755.3219	0.4460300
	13	0	0	-α	0.1728003	0.0800	0.3818523
	14	0	0	α	0.0245754	441.7482	0.8288271
	15	0	0	0	0.0356405	596.4853	0.6463001

Table 4.23 Statistics of the regressed model parameters for the design variable TOC_CONT

Term	Regressed Coefficients	p
Intercept	594.2814	< 0.0001
T_STRIP (°C)	-153.3636	< 0.0001
P_STRIP (bar)	145.4399	< 0.0001
STEAM (Kg/hr)	-100.2098	< 0.0001
T_STRIP * P_STRIP	24.2193	0.0912
T_STRIP^2	-37.8344	0.0364

Table 4.24 Statistics of the regressed model parameters for the design variable FFA_CONT

Term	Regressed Coefficients	p
Intercept	8.84460E-02	0.0033
T_STRIP (°C)	-6.10599E-02	0.0030
P_STRIP (bar)	4.07955E-02	0.0229
STEAM (Kg/hr)	-4.98906E-02	0.0089
T_STRIP * P_STRIP	-4.88619E-02	0.0330
T_STRIP *STEAM	4.52719E-02	0.0443
P_STRIP*STEAM	-4.02260E-02	0.0670

Table 4.25 Statistics of the regressed model parameters for the design variable NOL

Term	Regressed Coefficients	p
Intercept	0.650533	< 0.0001
T_STRIP (°C)	0.359376	< 0.0001
P_STRIP (bar)	-0.248357	< 0.0001
STEAM (Kg/hr)	0.145645	0.0002
T_STRIP * P_STRIP	-0.101758	0.0034
T_STRIP *STEAM	0.064483	0.0211
T_STRIP^2	0.071645	0.0239
P_STRIP^2	0.089237	0.0104

$$FFA\_Cont(\%) = 8.845*10^{-2} - 6.106*10^{-2}X_1 + 4.080X_2*10^{-2} - 4.989*10^{-2}X_3 - 4.886*10^{-2}X_1X_2 + 4.527*10^{-2}X_1X_3 - 4.023*10X_2X_3 \quad (4.27)$$

$$TOC\_CONT(ppm) = 608.5262 + 12.2039X_1 - 102.3211X_2 + 4.4546X_3 + 1.0236X_1X_2 - 9.5698X_2^2 \quad (4.28)$$

$$NOL(\%) = 23.7402 - 2.178*10^{-1}X_1 + 7.920*10^{-1}X_2 - 2.241*10^{-2}X_3 - 4.301*10^{-3}X_1X_2 + 1.204*10^{-4}X_1X_3 + 5.059*10^{-4}X_1^2 + 2.257*10^{-2}X_2^2 \quad (4.29)$$

From these second-order models given in (4.27) - (4.29), surface response were generated by fixing one of the variables to its correspondent nominal value and by manipulating the two variables left within their range of values (see Figures 4.14-4.16).

Although, it could be expected that the FFA content in the final product could be at the lowest value when the amount of stripping steam and the temperature in the stripping column are in their highest values, the combined effects that the design variables have on the response variable affects the surface response shape.

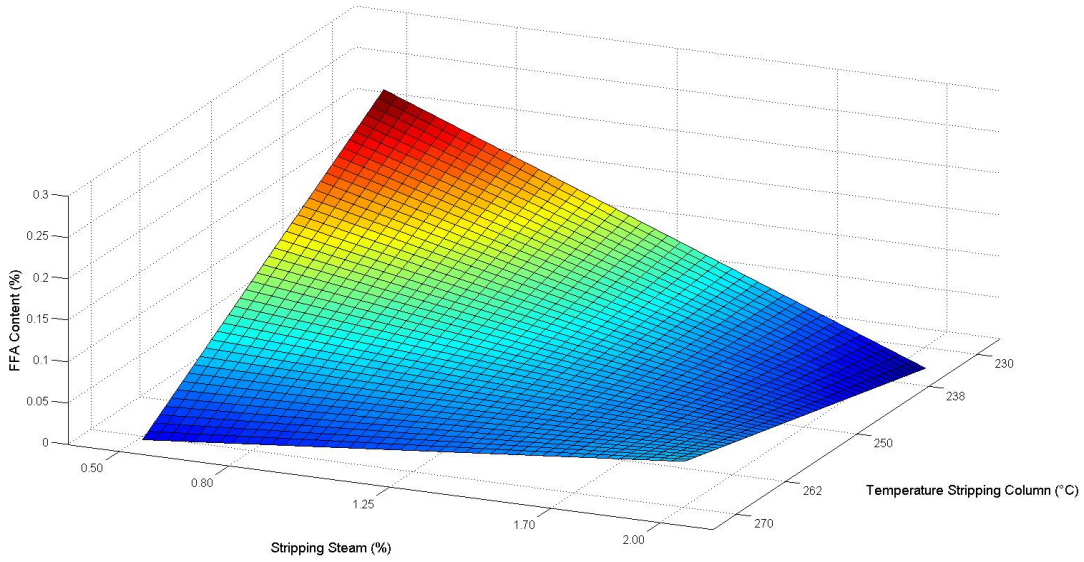


Figure 4.14 Surface response for free fatty acid content in the final product

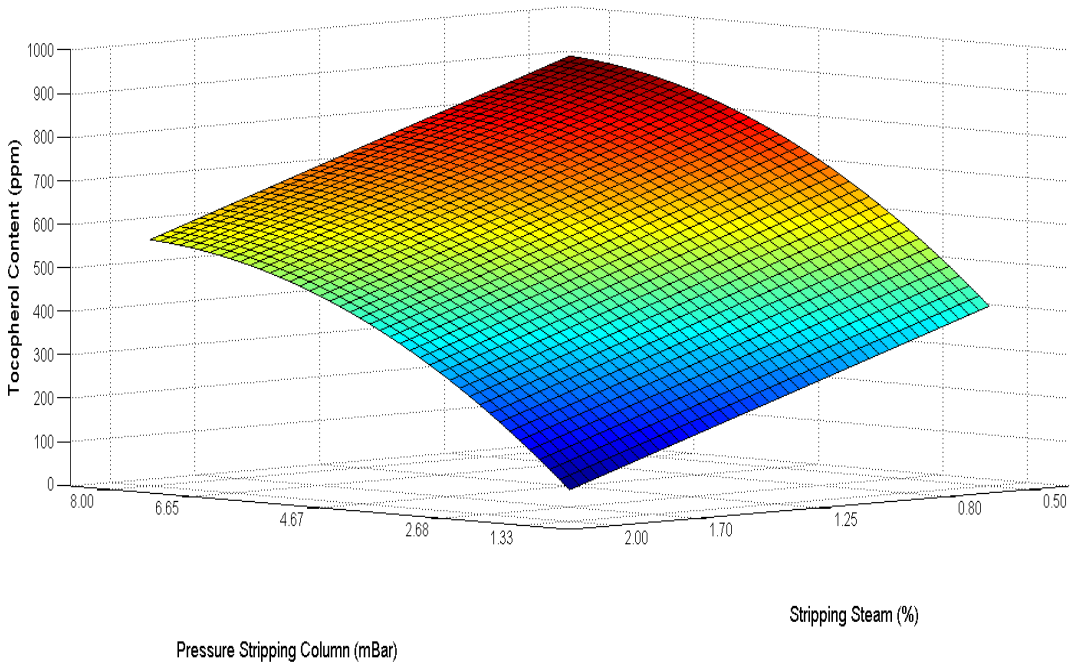


Figure 4.15 Surface response for the tocopherol content in the final product

The amount of tocopherols in the final product shows the expected behavior (see Figure 4.15), as the amount of stripping steam increases and the pressure in the stripping column decreases the retention of these compounds in the final product is reduced.

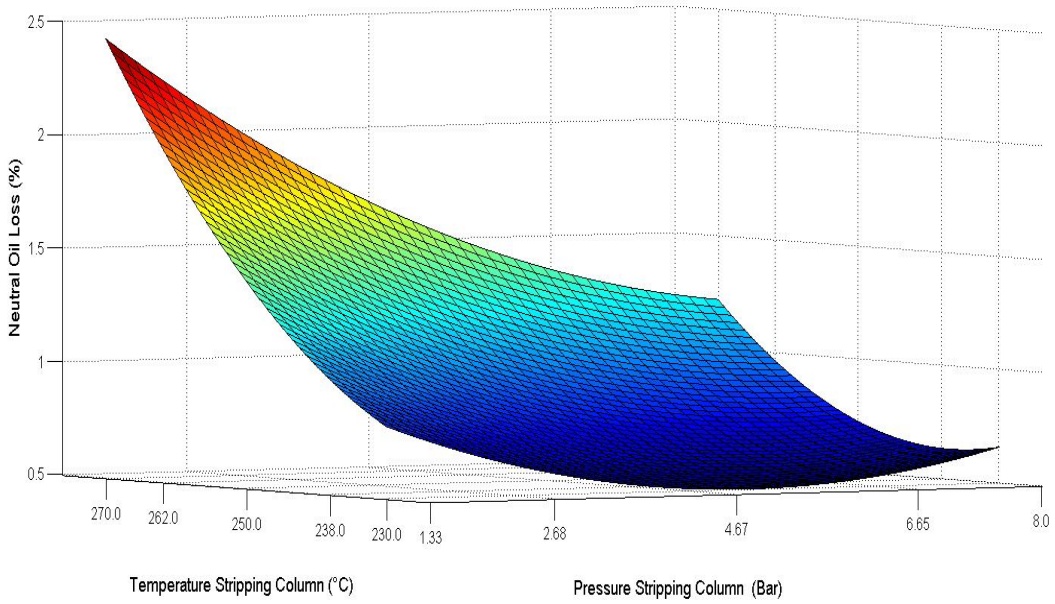


Figure 4.16 Surface response for the neutral oil loss

Finally, Figure 4.16 shows that as the temperature and the pressure in the stripping column increases and decreases, respectively, the neutral oil loss increases. This is, to some extent, due to the temperature dependence of the hydrolysis reaction of fats.

Incorporating the second-order models (Eqs. (4.27)-(4.29)) to the original optimization problem defined by Eqs. (4.20)-(4.25), the final set of equations is given by:

$$\begin{aligned} OF = {} & 26.70853 - 0.23554X_1 + 0.71827X_2 - 6.7346E^{-3}X_3 \\ & - 3.94981E^{-3}X_1X_2 + 3.4533E^{-3}X_1X_3 + 5.3159E^{-4}X_1^2 + 0.0394X_2^2 \end{aligned} \tag{4.30}$$

Constraints

Design Variables

$$230.0 \le T - STRIP(°C) \le 270.0 \tag{4.31}$$

$$1.0 \le P - STRIP(mmHg) \le 6.0 \tag{4.32}$$

$$0.5 \le STEAM(\%) \le 2.0 \tag{4.33}$$

Product Specifications

$$\begin{aligned} 0.03\% \ge {} & 0.87854 - 3.82884E-3X_1 + 0.31212X_2 - 3.4303E-3X_3 \\ & - 1.0741E-3X_1X_2 + 1.4586E-5X_1X_3 - 7.6308E-5X_2X_3 \end{aligned} \tag{4.34}$$

$$600\,ppm \le 2585.4282 - 3.6059X_1 + 3.1692X_2 + 0.7409X_3 + 0.5867X_1X_2 - 0.0077X_1X_3 - 8.1456X_2^2 + 0.00057X_3^2 \quad (4.35)$$

The optimization problem is solved as a NLP by means of the free trial version of the software GAMS. Results (see Table 4.26) show that for the given typical composition of palm oil, a reduction in the neutral loss oil can be achieved while keeping the level of FFA and tocopherols within the product specifications.

Table 4.26 Optimized values of the design variables

Design Variable	Value
T-STRIP (°C)	245.5
P-STRIP (mbar)	1.33
STEAM (%)	0.5

4.2.2.5. Conclusions

The simulation model of the deodorization of crude palm oil was developed based on the information available in the open literature. The simulation model performance was fine-tuned based on heuristic rules and the typical behavior observed in the industry.

The relationship between the selected design variables and the overall performance of the processes has been established by means of a full factorial design. Central composite design was used to generate second–order models in order to find the optimized values of the design variables that can reduce the neutral oil loss.

Results showed that for the given composition of the crude palm oil and the process configuration it is possible to manipulate the design variables within their known upper and lower values in order to minimize the loss of neutral oil.

It is important to be highlighted that as more information on the complex physicochemical phenomena taking place in the deodorizer (*i.e.* trans-fatty acids formation or color reduction, also called “heat bleaching”) and on the resulting variations in investment, operating costs or product values (resulting from the different design/operating scenarios) become available, current limitations of the model could be overcome.

4.2.3. Case Study 3: Physical Deacidification of Vegetable Oils as Used in Biodiesel Pretreatment and Distillate Treatment Processes

In this case study, the physical deacidification of soybean oil and the distillate treatment processes are addressed (see Figure 4.17). The objective here is to determine the effect that the selected design variables have in the final product quality and in the by-product stream. For the validation of the simulation model, plant data was available and used to validate the simulation model. This validated model was further used to perform the process optimization in terms of the selected design variables.

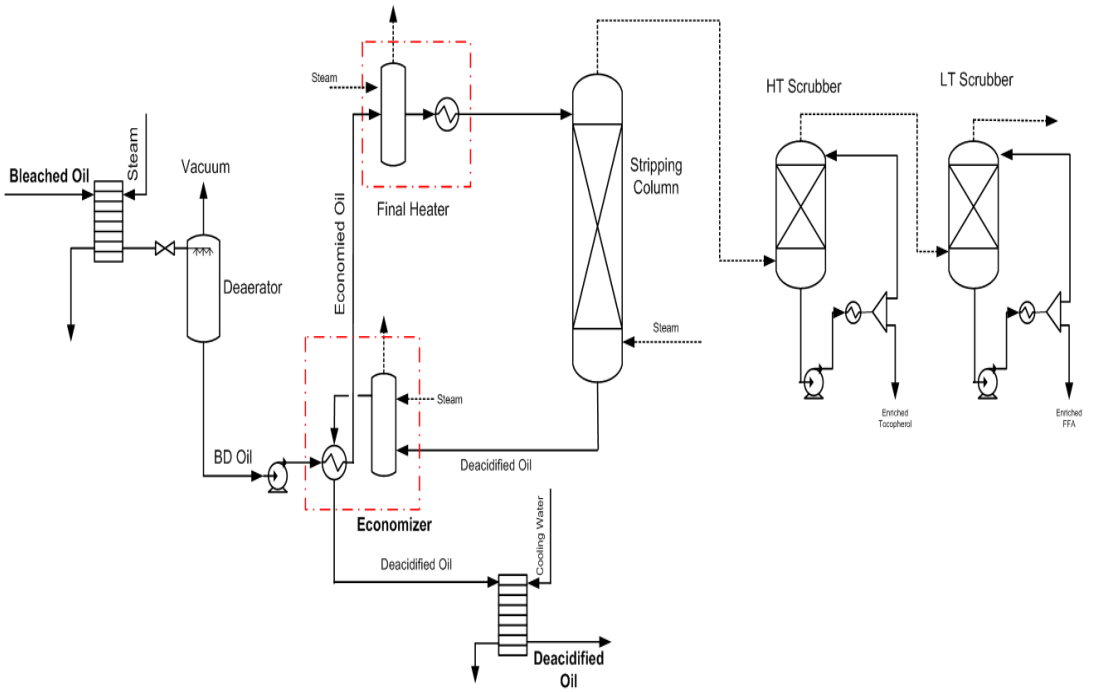


Figure 4.17 Physical deacidification process of soybean oil

4.2.3.1. Process Description

Deacidification of Vegetable Oils and Fats

As previously discussed, triglycerides are the major constituents of crude oils and fats; however due to the action of an enzyme (lipase) free fatty acids (FFA) can be formed, after the oilseed has been harvested, or the animal has been slaughtered (Bhosle & Subramanian, 2005). Hydrolysis of ester bonds in lipids (lipolysis) resulting in the liberation of FFA, may be caused by enzyme action or by heat and

moisture. The release of short-chain fatty acids by hydrolysis is responsible for the development of an undesirable rancid flavor (hydrolytic rancidity).

The deacidification process has the maximum economic impact on oil production (Bhosle & Subramanian, 2005). Any inefficiency in this process has a great bearing on the subsequent process operations. Physical deacidification uses steam stripping under vacuum, a procedure that removes FFA, unsaponifiable substances, and pungent compounds, thus circumventing chemical neutralization with its environmentally objectionable soapstocks. As a consequence, oil losses are reduced, the quality of FFA is improved, and the operation is simplified. It consumes less steam, water, power, and, hence, requires less capital investment (Cvengros, 1995).

The principles and aim of this process step have been discussed extensively in Section 4.2.2.1. However, it is to be highlighted that in this case, there is no holding section present in the stripping column as it is present in the deodorizer. This allows the unit operation to be modeled as a two-stage stripper column and to disregard the hydrolysis reaction of triglycerides considered on the previous case study.

Distillate Treatment

Deodorization or deacidification processes are usually the final step in producing oils and fats from plant and animal sources. The combined steam and entrained distillation vapors are usually collected and condensed to form a distillate that can be disposed of or processed further to recover valuable materials. The major constituents of deodorizer distillates are fatty acids, tocopherols, and sterols, which are present un various relative amounts depending on the oil source and the refining steps the oil is subjected to prior to deodorization. The commercial value of the deodorizer distillate can be greater when it is split into a fatty acid-enriched fraction and a fraction enriched in sterols and tocopherols.

Fatty acids isolated from deodorized distillates are utilized in several nonfood applications and as precursors in a wide variety of molecular synthesis schemes. Meanwhile, the sterols and tocopherols obtained from the second fraction can be used as precursors in the production of hormones and in the production of Vitamin E, respectively.

The double condensation zone is a complex process comprised by a set of two structured packed scrubbers operating under low pressure and two heat exchangers, used to cool down the outgoing streams and then recycle a fraction of them to wash the incoming vapors on each one of the condensing zones (see Figure 4.18).

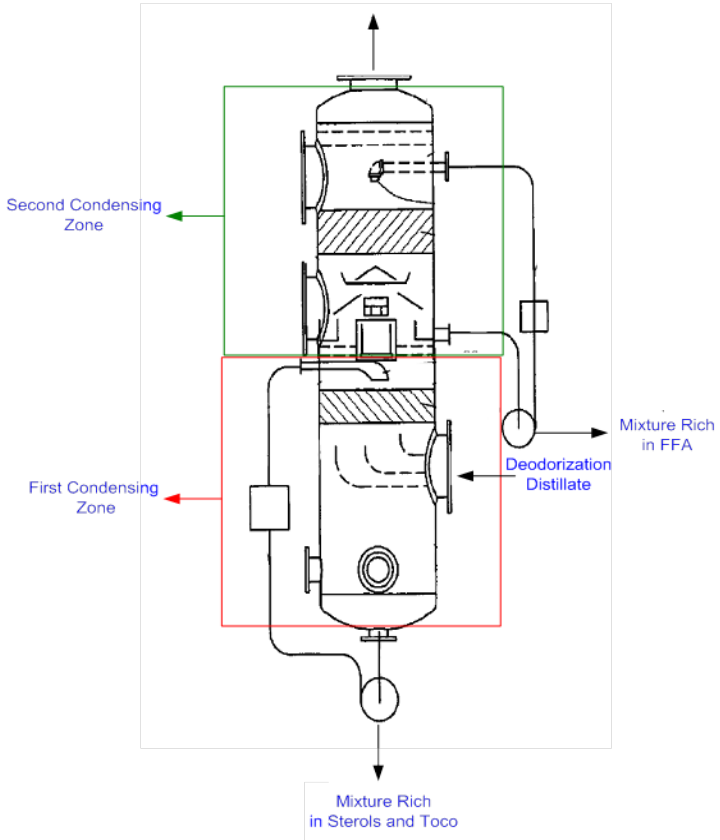


Figure 4.18 Condensing unit suitable for carrying out the separation of vaporized distillate

4.2.3.2. Process Simulation Model

Process Unit Operations Sequence

The economizer and the final heater section of the deacidification section of this process are modeled as described in the previous case study (section 4.2.2.1) and the stripping column is modeled as a distillation column with no reboiler and no condenser. Based on the plant information gathered from the open literature (Copeland *et al.*, 2004), it has been possible to model the deodorized distillate treatment process. The model comprises the steps for isolating the components of a vaporized distillated by introducing this stream (DEOD_DIST) to a first condensing zone of a condensing unit having at least two condensing zones and operating at a pressure of less than about 10mmHg, the first condensing zone operating at a

temperature of from about 165°C to about 180°C; condensing a first fraction of the vaporized distillate in the first condensing zone to form a first condensate enriched in sterols and tocopherols (ENRICHED_TOC) by passing the vaporized distillate through a first packing where it is contacted with recycled first, leaving a remaining fraction of vaporized distillate, introducing the remaining fraction of vaporized distillate into a second condensing zone of the condensing unit, the second condensing zone operating at a temperature of from about 35 to about 75°C; condensing a second distillate in the second condensing zone to produce a second condensate enriched in fatty acids (ENRICHED_FFA) by passing the remaining fraction of vaporized distillate through a second packing where it is contacted with recycled second condensate, leaving a waste vapor (WASTE_STEAM).; recovering the first condensate; and recovering the second condensate.

Simulation Model

The selected process (see Figure 4.17) has been modeled in the commercial process simulator PRO-II as follows:

- The identified lipid compounds used to represent a typical crude soybean (Table 4.27) and the thermophysical pure component property models are retrieved from the CAPEC_Lipids_Database (Diaz-Tovar *et al.*, 2011) (see Table 4.28).
- The selected thermodynamic model is the original UNIFAC.
- The total design capacity of the plant is 400 tons per day.
- The amount stripping steam (for the base simulation) to be 1% of the total feed flowrate.
- The economizer, final heater, and the stripping section are modeled as described in Section 4.2.2.2.
- The double scrubber system is modeled as a two 2-stage distillation columns with no re-boiler or heater. The inner arrangement of the both columns is commercial structured packing (Mellapack) produced by the company Sulzer Ltd.
- The process parameters used in the development of the simulation model are given in Table 4.31.

Table 4.27 Crude soybean oil composition

Family	Compound	Mass Composition
TAGs	OOO	45.000
	POS	42.250
	PPP	8.5930
DAGs	O-O-OH	2.4800
MAGs	O-OH-OH	0.1000
FFAs	OLEIC (O)	0.6500
Minor Compounds	B-TOCOPH	0.1200
	STIGSTRL/STRC18.1 (1:1)	0.8000
	SQUALNE	0.0020

Table 4.28 Thermophysical property data retrieved from the CAPEC_Lipids_Database

Family	Thermophysical Property Data
TAGs, DAGs, MAGs & FFA	Single value pure component properties. Vapor Pressure Enthalpy of vaporization Liquid enthalpy Liquid density Liquid viscosity & surface tension UNIFAC functional groups
Minor compounds	Single value pure component properties. Vapor Pressure Enthalpy of vaporization Liquid density UNIFAC functional groups

4.2.3.3. Model Validation

The accuracy of the proposed process simulation model that represents the deacidification and distillate treatment processes has been determined by comparing the simulation results with the available industrial data for the following operating conditions: Stripping column temperature and pressure equal to 260°C and 3.3mbar, and the amount of stripping steam set to 1% of the feed. Shows the simulation results for the above-mentioned operating conditions

In this case information about the composition of tocopherols in the degummed oil that is fed into the stripping column as well as in the deacidified oil was available for comparison. To be highlighted that:

a) The real values cannot be disclosed as they are protected by a confidentiality agreement.
b) The process is assumed to be operating under steady state conditions and, therefore, the experimental data is consistent.

Table 4.29 Results for the base case simulation

	STREAM					
	BD_OIL	ECON_OIL	DEOD_DIST	TOC_PROD	FFA_PROD	FINAL_OIL
T (°C)	16666.67	16666.67	342.49	63.88	111.72	16490.18
P (mBar)	90.00	260.00	259.31	170.00	65.00	40.00
Mass Rate (kg/hr)	1200.00	3700.00	3.30	1700.00	1200.00	1900.00
TAGs	95.8475	95.8475	1.6696	9.0635	0.0007	96.8387
DAGs	2.4800	2.4800	4.4818	24.1262	0.1137	2.4134
MAGs	0.1000	0.1000	3.7123	7.3315	7.1958	0.0240
FFAs	0.6500	0.6500	30.4404	7.9949	88.5300	0.0247
TOCOs	0.1200	0.1200	2.7606	12.0813	1.1729	0.0579
SITOs	0.8000	0.8000	8.1772	39.2389	2.8265	0.6387
SQUAL	0.0025	0.0025	0.0506	0.1596	0.0637	0.0015
WATER	0.0000	0.0000	48.7075	0.0039	0.0967	0.0011

The average relative deviation (ARD), as given in Eq. (4.1), for the tocopherol retention is 11.60%. This deviation could be considered to be within the acceptable range of error as the modeling of thermophysical properties of minor compounds complex as discussed in Chapter 3.

However, the accuracy of the model could be improved by taking into account that thermal break down of several minor compounds take place under the current process conditions. Fernholz (1938) reported that hydroquinone is a characteristic pyrolitic decompostion product of α-tocopherol (see Figure 4.19). Fernholz (1938) analytically determined that thermal decomposition of tocopherols occurs at temperatures close to 260 and a maximum of 5% of total tocopherols loss is present due to these phenomena.

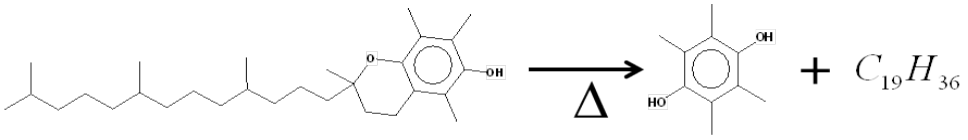


Figure 4.19 Thermal decomposition of α-tocopherol

After taking into consideration the thermal breakdown in the model simulation of the process, the average relative deviation (ARD) for the tocopherol retention is 6.0%. At this point, the simulation model performance is within the desired range of

accuracy. Hence, the model can be used to perform the optimization of the process in terms of the selected design variables.

4.2.3.4. Process Optimization

The aim of this optimization problem is to determine under which operating conditions the content and yield of tocopherol in the high-temperature-scrubber distillate could be maximized while keeping the deacidified oil within the product specifications (see Table 4.30).

Table 4.30 Typical product specification of commercial edible oils/fats

Product Specification	Code Name	Value	Reference
FFA Content (%)	FFA_Content	<0.03	Shahidi (2005)
Tocopherol Content (ppm)	Toco_Content	>600	Shahidi (2005)

Selected design variables, and their industrial range of values, remain the same as the ones chosen for the deodorization process. In addition, the temperature of the first condensing zone (HT_Scrubber) is included in the set of design variables (Table 4.31).

Table 4.31 Upper and lower limits of the selected design variables

Design Variable	Code Name	Literature Limits		Reference
		Lower	Upper	
Temperature (°C)	T-STRIP	230.00	270.00	Maza *el al*. (1992), Shahidi (2005)
Pressure (mmHg)	P-STRIP	1.00	6.00	Maza *el al.* (1992), Ahrens (1999)
Steam (%)	Steam	0.50	2.00	Shahidi (2005), Ahrens (1999)
Temperature HT-Scrubber (°C)	T-HT_SCRUB	165.00	180.00	Copeland *et al.* (2004)

The Optimization Problem

Eq. (4.36) is the objective function to be maximized; while Eqs.(4.37) - (4.42) are the constraints classified into two groups: design variables limits and product specifications.

Objective function

$$OF = TOC\_Flowrate \quad (4.36)$$

Constraints

Design Variables

$$230.0 \le T - STRIP(°C) \le 270.0 \quad (4.37)$$

$$1.0 \le P - STRIP(mmHg) \le 6.0 \quad (4.38)$$

$$0.5 \le STEAM(\%) \le 2.0 \quad (4.39)$$

$$165.0 \le T - HT\_SCRUB(°C) \le 180.0 \quad (4.40)$$

Product Specifications

$$FFA\_Content(\%) \le 0.03 \quad (4.41)$$

$$Toco\_Content(ppm) \ge 600 \quad (4.42)$$

To be highlighted that the product specifications are constraints that are function of the design variables. Hence, in order to establish the dependency of them to the design variables, they will be considered also as response variables.

Full Factorial Design

In order to establish the effect that individual and combined effects of the design variables have on the selected response variables, the central composite design has been selected. In this case the number of experimental runs (simulations) needed to perform this analysis is given by:

Simulation Runs = $2^4 + 2*4 + 1 = 25$

Among these 25 simulations, 16 correspond to the full factorial design, 8 correspond to the star configuration, and 1 to the central point. Table 4.32 shows the values of each level for each design variable. Table 4.33 shows the values of each one of the response variables obtained in each one of the 25 simulations performed. In Table 4.33, the ±1 values correspond to the factorial levels of the design variables, ±α to the lower and upper values of the design variables, while 0 correspond to the nominal values of the design variables.

The statistical analysis of the simulation results, in terms of coded variables, is shown in Tables 4.28 – 4.30. The resultant second-order models obtained from it are given in Eqs. (4.44)-(4.46).

Table 4.32 Perturbed values of the design variables for the Central Composite Design

Design Variable	-α	-1	0	1	α
T-STRIP (°C)	230.00	238.10	250.00	261.90	270.00
P-STRIP (mmHg)	1.00	2.01	3.50	4.99	6.00
STEAM (%)	0.50	0.80	1.25	1.70	2.00
T-HT_Scrubber (°C)	165.00	168.04	172.50	176.96	180.00

The second-order model proposed by the central composite design is given in Eq. (4.43).

$$2nd\text{-}Order\_Model = a_0 + \sum_{i=1}^{N} b_i X_i + \sum_{i=1}^{N}\sum_{j>i}^{N} c_{ij} X_i X_j + \sum_{i=1}^{N} d_i X_i^2 \quad (4.43)$$

Table 4.33 Central composite design and the response variables results

Simulation	X1	X2	X3	X4	TOC_Cont (ppm)	FFA_Cont (%)	TOC_HT (kg/hr)
1	-1	-1	-1	-1	798.30	0.06965	5.1342
2	1	-1	-1	-1	440.00	0.01624	10.6300
3	-1	1	-1	-1	1023.79	0.20045	1.5638
4	1	1	-1	-1	760.06	0.06217	5.0427
5	-1	-1	1	-1	555.90	0.02648	7.6563
6	1	-1	1	-1	229.86	0.00550	12.8624
7	-1	1	1	-1	859.75	0.08582	2.6276
8	1	1	1	-1	507.36	0.02043	7.9329
9	-1	-1	-1	1	798.30	0.06965	4.7734
10	1	-1	-1	1	440.00	0.01624	7.8094
11	-1	1	-1	1	1023.79	0.20045	0.0000
12	1	1	-1	1	760.06	0.06217	2.9297
13	-1	-1	1	1	555.90	0.02648	2.8904
14	1	-1	1	1	229.86	0.00550	9.1091
15	-1	1	1	1	859.75	0.08582	0.0000
16	1	1	1	1	507.36	0.02043	4.1048
17	-α	0	0	0	997.13	0.15075	1.2028
18	α	0	0	0	490.16	0.01468	9.1269
19	0	-α	0	0	331.70	0.00928	12.2588
20	0	α	0	0	855.92	0.08432	2.1837
21	0	0	-α	0	942.11	0.13100	2.6697
22	0	0	α	0	507.10	0.02031	5.9796
23	0	0	0	-α	765.80	0.04993	5.8542
24	0	0	0	α	765.80	0.04993	1.1580
25	0	0	0	0	765.80	0.04993	3.4956

Table 4.34 Statistical analysis results of the regressed parameters Eq. (4.36)

Term	Regressed Coefficients	p
a_0	0.053953	< 0.0001
T-STRIP	-0.03625	< 0.0001
P-STRIP	0.029018	< 0.0001
STEAM	-0.02802	< 0.0001
T-STRIP* P-STRIP	-0.01616	< 0.0001
T-STRIP* STEAM	0.013167	0.0003
P-STRIP* STEAM	-0.01281	0.0004
$(\text{T-STRIP})^2$	0.008536	0.0154

Table 4.35 Statistical analysis results of the regressed model parameters of Eq. (4.41)

Term	Regressed Coefficients	p
a_0	0.076876	< 0.0001
T-STRIP	-0.01595	< 0.0001
P-STRIP	0.014481	< 0.0001
STEAM	-0.01141	< 0.0001
$(\text{T-STRIP})^2$	-0.00177	0.0445
$(\text{P-STRIP})^2$	-0.00708	< 0.0001
$(\text{STEAM})^2$	-0.00245	0.0080

Table 4.36 Statistical analysis results of the regressed model parameters of Eq. (4.42)

Term	Regressed Coefficients	p
a_0	4.2315	< 0.0001
T-STRIP	2.2679	< 0.0001
P-STRIP	-2.4759	< 0.0001
STEAM	0.6866	0.0035
T-HT_SCRUBBER	-1.3732	< 0.0001
P_STRIP*T-HT_SCRUBBER	0.0980	0.6845
$(\text{T-HT\_SCRUBBER})^2$	1.0723	0.0007

$$FFA\_Content = 1.8089 - 0.0125\ X_1 + 0.0757 X_2 - 0.0014 X_3 - 0.0002 X_1 X_2 + 5.2666E^{-6} X_1 X_3 - 3.0723E^{-5} X_2 X_3 - 2.1341E^{-5} X_1^2 \quad (4.44)$$

$$TOC\_Content = -0.0229 + 0.0014\ \mathrm{X}_1 + 0.01028 \mathrm{X}_2 - 2.5968E^{-5} \mathrm{X}_3 - 4.4363E^{-6} X_1^2 - 6.3687E^{-4} X_2^2 - 1.5674E^{-6} X_1^2 \quad (4.45)$$

$$TOC\_Flowrate(kg/hr) = 15.0369 + 0.1134X_1 - 2.3179X_2 + 0.0055X_3 \\ -0.2014X_4 + 0.0039X_2X_4 + 0.0964 * X_2^2 \quad (4.46)$$

From the second-order models (see Eqs. (4.44) - (4.46)), surface responses were generated. Figure 4.20 was generated by fixing the variable P-STRIP to its nominal value and by modifying the values of the other two variables within their limits.

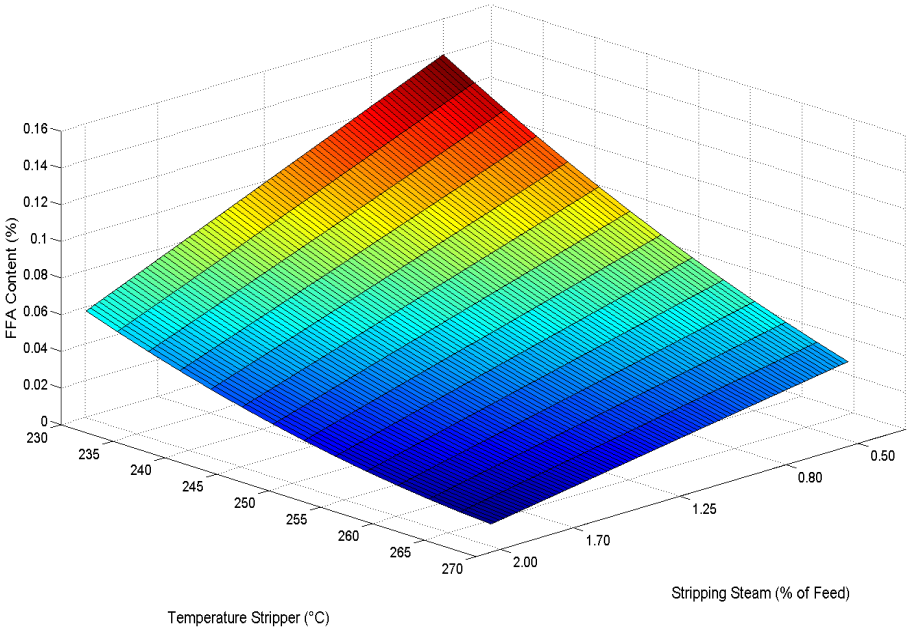


Figure 4.20 Surface response of the FFA content in the final product.

Figure 4.20 shows that the behavior of the variable FFA_Content is as expected. This means, that as the temperature in the stripper and the amount of stripping steam increase, the content of free fatty acids decline rapidly.

The response surface for the response variable Tocopherol Content is given in Figure 4.21. To highlight that to in order to create the response surface the design variables P-STRIP and T-STRIP were varied within their respective range of value, while the third design variable (STEAM) was set to its nominal value of 1.25.

A predictable behavior of the variable Tocopherol_Content is observed in Figure 4.21. The retention of tocopherols in the final product increases as the temperature and the pressure in the stripping column decreases and increases, respectively. Finally, in the case of the last response variable Tocopherol_Flowrate (see Figure 4.22), the correspondent surface response was generated by manipulating the design

variables T-HT_Scrubber and P-Stripper and by setting the design variables T-STRIP and STEAM to their nominal values, 250°C and 1.25% respectively.

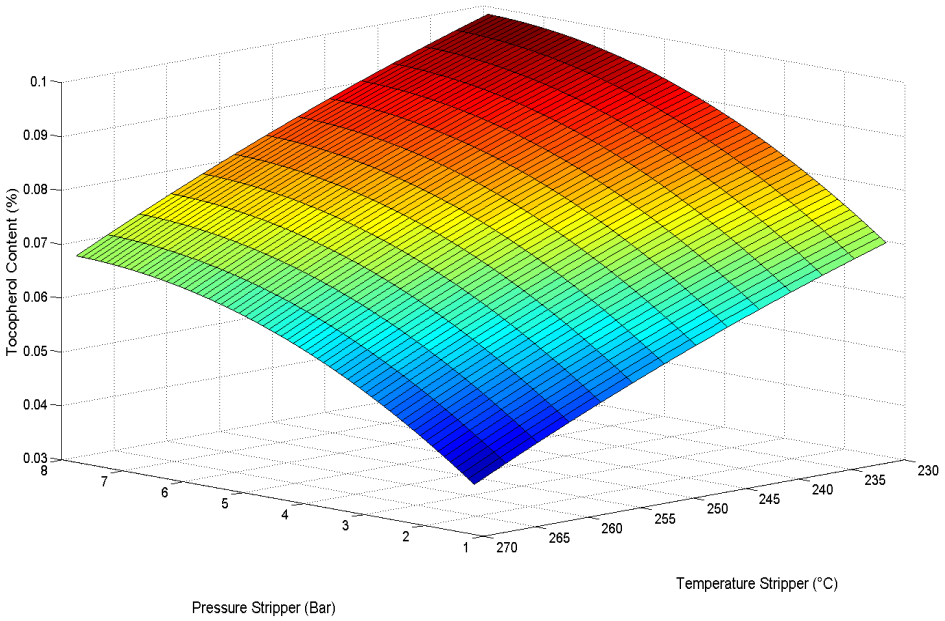


Figure 4.21 Surface response of the Tocopherol content in the final product.

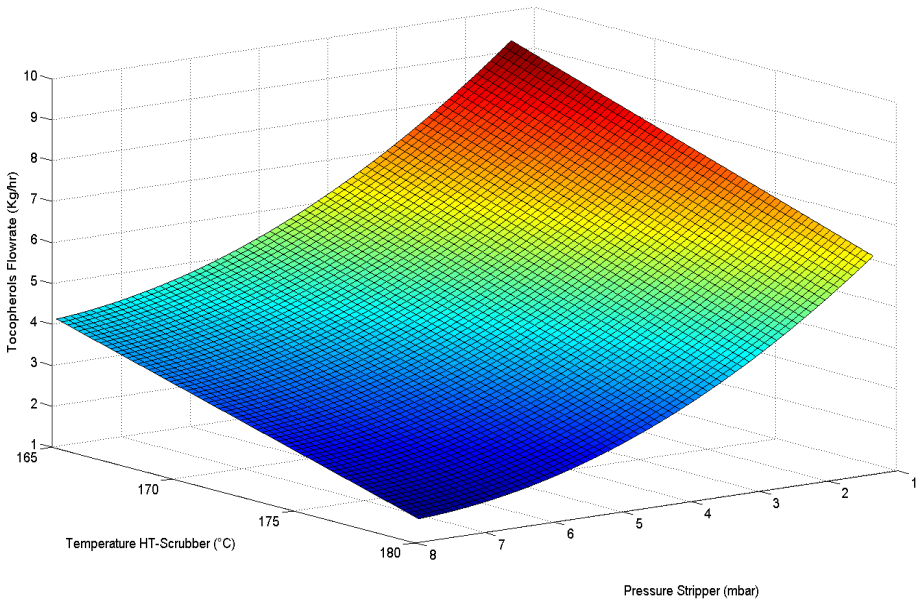


Figure 4.22 Surface response of the produced tocopherols

With the incorporation of the generated second order models (see Eqs. (4.44) - (4.46)), the optimization problem is then defined by Eqs. (4.47)-(4.53).

Objective function

$$\begin{aligned}\text{Max OF} = {} & 15.0369 + 0.1134\,X_1 - 2.3179\,X_2 + 0.0055\,X_3 \\ & -0.2014\,X_4 + 0.0039\,X_2X_4 + 0.0964 * X_2^2\end{aligned} \tag{4.47}$$

Constraints

Design Variables

$$230.0 \le T - STRIP(°C) \le 270.0 \tag{4.48}$$

$$1.0 \le P - STRIP(mmHg) \le 6.0 \tag{4.49}$$

$$0.5 \le STRIP\_STEAM(\%) \le 2.0 \tag{4.50}$$

$$165.0 \le T - HT\_SCRUB(°C) \le 180.0 \tag{4.51}$$

Product Specifications

$$\begin{aligned}0.03 \ge {} & 1.8089 - 0.0125\,X_1 + 0.0757\,X_2 - 0.0014\,X_3 - 0.0002\,X_1X_2 \\ & +5.2666E^{-6}\,X_1X_3 - 3.0723E^{-5}\,X_2X_3 - 2.1341E^{-5}\,X_1^2\end{aligned} \tag{4.52}$$

$$\begin{aligned}600 \le {} & 15.0369 + 0.1134\,X_1 - 2.3179\,X_2 + 0.0055\,X_3 - 0.2014\,X_4 \\ & + 0.0039\,X_2X_4 + 0.0964 * X_2^2\end{aligned} \tag{4.53}$$

The optimization model has been solved as a NLP problem by means of the software GAMS trial version 23.6.5. Table 4.37 shows the optimum values found for all the design variables.

Table 4.37 Optimized values of the design variables

Design Variable	Value
T-STRIP (°C)	263.5
P-STRIP (Bar)	2.26
STEAM (%)	0.52
T-HT_Scrubber (°C)	165.00

4.2.3.5. Conclusions

The deacidification process of soybean oil has been addressed in this case study. The process was analyzed according to the proposed methodology. From the identification of the representative families of chemical species that compose the soybean oil to the process operation conditions (process parameters and design

variables), the methods and tools developed for the design/analysis of lipid-related processes were used to setup the simulation model and validate it.

From the validated simulation model the correspondent optimization problem was defined. The central composite design methodology was used to obtained second order models that correlate the design variables to the selected response variables. From the resulting second-order models the optimization problem has been solved and the results showed that, if the same configuration of the unit operations is kept, by manipulating the design variables the process could reduce the amount of stripping steam used by almost 50% and, at the same time, increase the amount of tocopherols produced.

However, it is to be noted that a further improvement of this case study can be obtained as more information on the product streams of the double scrubber system. With this information a constraint for the composition of tocopherols in the Enriched_Tocopherols stream and another one for that considers the separation between the LT-Scrubber and the HT-Scrubber could be included.

5.
Conclusions and Future Work

The impact of vegetable oil and fats on human life has been significant for thousands of years (as a source of energy and fat-soluble vitamins). This significance along with the exponential growth of human population had converted the olechemical industry into a well-known traditional industry with well-established processes. However, consumer preferences for healthier food together with the overproduction of vegetable oils and fats, have led this industry to face major challenges in terms of product and process design.

Nowadays, state of the art in modeling of thermophysical behavior of the complex chemical systems present in lipid-related processes lags far behind that of the chemical or petrochemical industry. Currently, latest versions of commercial process simulators have included within their databases the most representative major lipid

compounds (tri-, di-, and mono-glycerides, fatty acids, and fatty esters). This has been driven mostly by the growing interest in biodiesel and, consequently, by the need to develop computer-aided methods and tools suitable for the design/analysis of these lipid-related processes. However, the chemical systems involved in the lipid-related processes include a second set of chemical families (minor compounds) that have major impact in the value chain of any vegetable oil or fat.

Consequently, the aim of this work was to develop computer-aided methods and tools for the systematic design/analysis of processes involving lipid technology, from the chemical species involved to the lipid-related processes. In the upcoming sections the achievements of this work and the future perspective are discussed in Sections 5.1 and 5.2, respectively.

5.1. Achievements

The two main contributions of this work are described as follows:

1. A filled-out database (CAPEC_Lipids_Database) that contains:
   a. The most representative families of lipid-related chemical species.
   b. Basic information of each lipid compound (name, molecular weight, SMILES, and CAS Nr).
   c. Molecular description of the lipid compounds.
   d. Available experimental data of the identified thermophysical properties (vapor pressure, enthalpy of vaporization, liquid heat capacity, liquid density, liquid viscosity, and surface tension).
   e. Validated property model parameters for the estimation/prediction of single value and temperature dependent pure compound properties.
   f. A user-interface for the fast adoption of the information contained in the database.
   g. The linkage of the database to the commercial process simulator PRO II ® as a user-added database.
2. The analysis in terms of their significant design variables of three lipid-related processes that are a key in the production of edible oils and fats: the solvent

recovery section of the crude soybean oil extraction process, the palm oil deodorization process, and the soybean oil deacidification process.

Regarding the first significant contribution of this PhD project, the following remarks are given:

- Even though lipid compounds are complex molecules, it is possible to describe this type of chemical species by a small set of already available Marrero and Gani (2001) functional groups. This advantage allows the implementation of group contribution methods, which are predictive in nature, when the data available is scarce. Although these techniques have their limitations they can be easily improved whenever more experimental information is available.
- As discussed in Chapter 3, the selected and validated thermophysical models were divided into two sets, the single value and the temperature dependent properties. Single value properties have shown a higher deviation in their accuracy as the carbon chain increases. This can be attributed to the fact that for long-chain compounds, the method is extrapolating the predictions.
- The selected temperature dependent properties are classified into two different groups depending on their behavior with respect to the temperature. In the first group, those with exponential behavior, properties such as vapor pressure, enthalpy of vaporization, and liquid density are found. In the second group, those with linear behavior, properties such as liquid heat capacity and surface tension are found. To highlight that liquid density is a property that, within the range of temperature in which most of the lipid-related processes take place, also shows a linear behavior.
- Vapor pressure and enthalpy of vaporization of lipids have shown to be inversely proportional to the carbon chain and directly proportional to the level of unsaturation of the carbon chain. In the case of the liquid viscosity, the behavior is the opposite; this property is directly proportional to the carbon chain length and inversely proportional to the level of unsaturation of the carbon chain.
- The behavior shown by the liquid heat capacity is similar to that shown for the liquid viscosity, the property increases as the carbon chain length increases and

decreases as the level of unsaturation increases. Surface tension is a property that decreases both as the carbon chain length and the degree of unsaturation increases. Finally, for the liquid density, it is not possible to establish a correlation between the carbon chain length, the degree of unsaturation, and the property behavior; this is because changes are not significant and they are not always constant.

With respect to the second significant contribution of this PhD work, the following issues in each case study could be mentioned:

- Case Study 1 - The analysis of solvent recovery section has shown the following:
  1. That the developed methods (property models) and tools (database) were sufficient to represent the typical composition of the crude soybean oil and to predict/estimate the thermophysical properties needed to analyze the selected process.
  2. That the major loss of hexane is in the crude oil and that the crude oil loss in the process is can be neglected.
  3. That the Plackett-Burman designs are a helpful tool for the reduction in the number of the design variables needed to faithfully represent the system (process) under analysis.
  4. That the full factorial design helped to further reduce the number of design variables that have significant impact in the overall solvent recovery section performance.
  5. That even the process is operating within the optimal zone, improvements can be achieved by manipulating the optimized design variables.

- Case Study 2 - The analysis of the simulation model of the crude palm oil deodorization process concluded that:
  1. The property models and the lipid compounds needed to model a typical crude palm oil and its thermophysical behavior were successfully retrieved from the CAPEC_Lipids_Database.

2. It is necessary to highlight that, even though, hydrolysis is considered to contribute to the neutral oil loss, the extent of this phenomenon is very uncertain. The only information available is the FFA content in the final product that is higher than the one that can be predicted in the absence of such phenomenon.
3. Consequently, based on information available in the open literature and a fine-tuned based on heuristic rules and the typical behavior observed in the industry it is possible to analyze the process in terms of their design variables and process parameters.
4. By means of the central composite design it is possible to generate second–order models that order to find the optimized values of the design variables that can reduce the neutral oil loss.

- Case Study 3 - In the analysis of the crude soybean oil deacidification process it to be concluded that:
  1. From the developed CAPEC_Lipids_Database is possible to retrieve the information (lipid compounds and property models) needed to represent a crude soybean oil and its thermophysical behavior under the given process conditions.
  2. Greater accuracy of the simulation model can be achieved as more information on the chemical reactions taking place at the process conditions. In the particular case of the tocopherol degradation, this phenomenon is not only temperature dependent. As presented by Verhé (2004), residence time, peroxide content, among variables have direct influence in this phenomenon.
  3. The central composite design helped to correlate the response variables (product specifications) to the design variables of the stripping column. Furthermore, it was possible to correlate all the identified design variables to the main response variable (tocopherol flowrate).
  4. Results showed that the optimized process parameters are in good agreement with the current process conditions. However, small changes on them can lead to an improvement in the amount of tocopherols produced

and a reduction in the amount of stripping steam needed to deacidify the crude soybean oil.

In general the achieved advances in the state of the art of lipid technology are as follows:

a) Collection of experimental data, for the most representative lipid compounds, available in the open literature for different single value and temperature dependent pure component properties and their inclusion in a comprehensive database.
b) Identification, selection, and extension of the predictive models that most accurately describe the thermophysical behavior of the most representative lipid compounds.
c) Linkage of the developed methods (property models) and tools (CAPEC_Lipids_Database) to commercial computer-aided tools such as the process simulator PRO/II.
d) Simulation of key lipid properties through the developed computer-aided methods and tools. For example, the solvent recovery section of the crude soybean oil extraction process and the physical refining (deodorization and deacidification) process of crude vegetable oils.
e) Application of the design of experiments theory to processes involving lipid technology (the solvent recovery and the deacidification processes) to observe individual and combined effects that the design variables have on the overall performance of the selected process.

5.2. Future Work

In this PhD thesis the development of computer aided tools suitable for the design/analysis of involving lipid technology addressed. From the creation of a database, that contains the identified main sources of vegetable oils and fats, the most significant lipid compounds, their molecular structure, and the model parameters needed to predict/estimate the selected thermophysical properties, to the design/analysis and optimization of three key lipid processes with respect to their design variables.

Even though important advances were achieved, refer to Section 6.1, suggestions on the work that can be done to continue developing more accurate and efficient methods and tools are presented below.

1. Improvements in the accuracy of the selected thermophysical property models can be achieved if additional experimental data is obtained. For example, vapor pressure data of tri-, di-, and mono-glycerides, liquid viscosity of partial glycerides, and single value pure compound properties of long-chain lipid compounds.
2. Uncertainty analysis on the predictions of the single value and temperature dependent properties.
3. Development of mixture property models and fine-tuning of the UNIFAC-CI model for the description of phase equilibria of lipid systems.
4. A more accurate description and analysis of processes such as the deodorization and deacidifications processes can be achieved if experimental data describing the most significant chemical reactions (hydrolysis of glycerides, thermal breakdown of carotenes, tocopherols, and/or the hydrolysis of glycerides) is obtained.
5. As the accuracy of thermophysical models is improved and the physicochemical phenomena is better described, the analysis/design of alternative unit operations or process configurations can be implemented, *i.e.* distillation column to replace the double scrubber system for the distillate treatment or the addition of a post-stripping column to eliminate the FFAs generated during the deodorization process.

A.

Surface Tension Model Development: Experimental Data & Predictions

The experimental data found for the development of this surface tension model for lipid compounds are given in Table A.1.

Table A.1 Experimental data used to regress the model parameters of Eq. A.1

No.	Name	Surf. Ten. (mN/m)	Temp (K)	No.	Name	Surf. Ten. (mN/m)	Temp (K)
1	Hexanoic Acid	31.20	253.15	189	Ethyl Palmitate	25.99	353.15
2	Hexanoic Acid	30.70	263.05	190	Ethyl Palmitate	25.13	363.15
3	Hexanoic Acid	29.60	274.75	191	Ethyl Palmitate	24.27	373.15
4	Hexanoic Acid	28.90	279.15	192	Ethyl Oleate	25.13	298.15
5	Hexanoic Acid	27.00	298.85	193	Propyl tridecanoate	28.84	298.15
6	Hexanoic Acid	26.20	308.75	194	Propyl tridecanoate	27.92	308.15
7	Hexanoic Acid	25.10	322.75	195	Propyl tridecanoate	27.00	318.15
8	Hexanoic Acid	23.40	343.00	196	Propyl tridecanoate	26.08	328.15
9	Hexanoic Acid	23.00	348.15	197	Propyl tridecanoate	25.16	338.15
10	Hexanoic Acid	21.60	363.85	198	Butyl Laurate	28.33	298.15
11	Hexanoic Acid	20.70	373.95	199	Butyl Laurate	27.54	308.15
12	Heptanoic Acid	29.84	273.00	200	Butyl Laurate	26.76	318.15
13	Heptanoic Acid	29.05	283.00	201	Butyl Laurate	25.98	328.15
14	Heptanoic Acid	28.14	293.00	202	Butyl Laurate	25.19	338.15
15	Heptanoic Acid	27.39	303.00	203	Pentyl Undecanoate	28.20	298.15
16	Heptanoic Acid	26.49	313.00	204	Pentyl Undecanoate	27.37	308.15
17	Heptanoic Acid	25.59	323.00	205	Pentyl Undecanoate	26.54	318.15
18	Heptanoic Acid	24.82	332.00	206	Pentyl Undecanoate	25.72	328.15
19	Octanoic Acid	29.20	293.00	207	Pentyl Undecanoate	24.89	338.15
20	Octanoic Acid	24.20	343.00	208	Hexyl Caprate	28.29	298.15
21	Decanoic Acid	25.10	343.00	209	Hexyl Caprate	27.36	308.15
22	Lauric Acid	27.40	333.15	210	Hexyl Caprate	26.43	318.15
23	Lauric Acid	26.51	343.15	211	Hexyl Caprate	25.50	328.15
24	Lauric Acid	25.97	348.15	212	Hexyl Caprate	24.57	338.15
25	Lauric Acid	25.64	353.15	213	Heptyl Nonanoate	28.14	298.15
26	Lauric Acid	24.85	363.15	214	Heptyl Nonanoate	27.29	308.15
27	Myristic Acid	28.40	313.00	215	Heptyl Nonanoate	26.44	318.15
28	Myristic Acid	27.86	343.15	216	Heptyl Nonanoate	25.59	328.15
29	Myristic Acid	27.41	348.15	217	Heptyl Nonanoate	24.74	338.15
30	Myristic Acid	27.15	353.15	218	Octyl Octanoate	29.99	298.15
31	Myristic Acid	26.83	358.15	219	Octyl Octanoate	27.12	308.15

32	Myristic Acid	26.53	363.15	220	Octyl Octanoate	26.29	318.15
33	Palmitic Acid	28.20	343.15	221	Octyl Octanoate	25.47	328.15
34	Palmitic Acid	27.85	348.15	222	Octyl Octanoate	24.65	338.15
35	Palmitic Acid	27.57	353.15	223	Nonyl Heptanoate	28.24	298.15
36	Palmitic Acid	27.36	358.15	224	Nonyl Heptanoate	27.46	308.15
37	Palmitic Acid	27.04	363.15	225	Nonyl Heptanoate	26.68	318.15
38	Stearic Acid	27.70	348.00	226	Nonyl Heptanoate	25.90	328.15
39	Oleic Acid	32.79	293.15	227	Nonyl Heptanoate	25.12	338.15
40	Oleic Acid	32.12	303.15	228	Decyl Hexanoate	28.59	298.15
41	Oleic Acid	31.90	313.15	229	Decyl Hexanoate	27.66	308.15
42	Oleic Acid	31.04	323.15	230	Decyl Hexanoate	26.72	318.15
43	Oleic Acid	30.21	333.15	231	Decyl Hexanoate	25.79	328.15
44	Oleic Acid	29.60	343.15	232	Decyl Hexanoate	24.85	338.15
45	Oleic Acid	29.29	353.15	233	Glycerol tricaproate	29.93	293.15
46	Oleic Acid	28.56	363.15	234	Glycerol tricaproate	28.79	313.15
47	Methyl Caproate	27.42	283.15	235	Glycerol tricaproate	28.21	323.15
48	Methyl Caproate	26.38	293.15	236	Glycerol tricaproate	27.64	333.15
49	Methyl Caproate	25.33	303.15	237	Glycerol tricaproate	27.40	337.73
50	Methyl Caproate	24.10	313.15	238	Glycerol tricaproate	26.50	353.15
51	Methyl Caproate	23.24	323.15	239	Glycerol tricaproate	25.90	363.03
52	Methyl Caproate	22.50	333.15	240	Glycerol tricaproate	25.36	373.15
53	Methyl Caproate	21.15	343.15	241	Glycerol tricaproate	24.79	383.15
54	Methyl Caproate	20.70	353.15	242	Glycerol tricaproate	24.50	388.33
55	Methyl Caproate	19.06	363.15	243	Glycerol tricaproate	24.22	393.15
56	Methyl Caproate	18.02	373.15	244	Glycerol tricaproate	23.90	398.85
57	Methyl Heptanoate	27.96	283.15	245	Glycerol tricaproate	23.65	403.15
58	Methyl Heptanoate	26.98	293.15	246	Glycerol tricaproate	23.08	413.15
59	Methyl Heptanoate	25.99	303.15	247	Glycerol tricaproate	22.50	423.15
60	Methyl Heptanoate	25.00	313.15	248	Glycerol tricaproate	22.20	428.51
61	Methyl Heptanoate	24.01	323.15	249	Glycerol tricaproate	21.30	441.9
62	Methyl Heptanoate	23.03	333.15	250	Glycerol tricaproate	20.50	457.94
63	Methyl Heptanoate	22.04	343.15	251	Glycerol tricaproate	19.60	473.45
64	Methyl Heptanoate	21.05	353.15	252	Glycerol tricaprylate	29.21	293.15
65	Methyl Heptanoate	20.07	363.15	253	Glycerol tricaprylate	28.39	307.97
66	Methyl Heptanoate	19.08	373.15	254	Glycerol tricaprylate	28.17	313.15
67	Methyl Caprylate	28.93	283.15	255	Glycerol tricaprylate	27.57	323.15
68	Methyl Caprylate	27.93	293.15	256	Glycerol tricaprylate	27.13	333.15
69	Methyl Caprylate	26.92	303.15	257	Glycerol tricaprylate	26.86	338.03
70	Methyl Caprylate	25.30	313.15	258	Glycerol tricaprylate	26.36	348.03
71	Methyl Caprylate	24.92	323.15	259	Glycerol tricaprylate	26.08	353.15
72	Methyl Caprylate	23.60	333.15	260	Glycerol tricaprylate	25.53	363.03
73	Methyl Caprylate	22.92	343.15	261	Glycerol tricaprylate	25.04	373.15
74	Methyl Caprylate	21.80	353.15	262	Glycerol tricaprylate	24.52	383.15
75	Methyl Caprylate	20.91	363.15	263	Glycerol tricaprylate	24.00	393.15
76	Methyl Caprylate	19.91	373.15	264	Glycerol tricaprylate	23.48	403.15
77	Methyl Caprate	29.42	283.15	265	Glycerol tricaprylate	22.96	413.15
78	Methyl Caprate	28.51	293.15	266	Glycerol tricaprylate	22.44	423.15
79	Methyl Caprate	27.59	303.15	267	Glycerol tricaprylate	22.01	427.61
80	Methyl Caprate	26.20	313.15	268	Glycerol tricaprylate	21.51	443.69
81	Methyl Caprate	25.77	323.15	269	Glycerol tricaprylate	20.48	457.97
82	Methyl Caprate	24.60	333.15	270	Glycerol tricaprylate	19.63	473.75
83	Methyl Caprate	23.95	343.15	271	Glycerol tridecanoate	27.64	313.15
84	Methyl Caprate	22.80	353.15	272	Glycerol tridecanoate	27.11	323.85
85	Methyl Caprate	22.12	363.15	273	Glycerol tridecanoate	26.54	333.15
86	Methyl Caprate	21.21	373.15	274	Glycerol tridecanoate	25.45	353.15
87	Methyl Laurate	30.40	283.15	275	Glycerol tridecanoate	24.94	362.44

88	Methyl Laurate	29.58	293.15	276	Glycerol tridecanoate	24.36	373.15
89	Methyl Laurate	27.69	303.15	277	Glycerol tridecanoate	23.81	383.15
90	Methyl Laurate	27.10	313.15	278	Glycerol tridecanoate	23.27	393.15
91	Methyl Laurate	26.99	323.15	279	Glycerol tridecanoate	22.72	403.15
92	Methyl Laurate	25.40	333.15	280	Glycerol tridecanoate	22.18	413.15
93	Methyl Laurate	25.12	343.15	281	Glycerol tridecanoate	21.63	423.15
94	Methyl Laurate	23.80	353.15	282	Glycerol tridecanoate	20.11	444.281
95	Methyl Laurate	23.34	363.15	283	Glycerol tridecanoate	19.43	457.971
96	Methyl Laurate	22.44	373.15	284	Glycerol tridecanoate	18.77	474.638
97	Methyl Myristate	29.40	293.15	285	Glycerol trilaurate	29.36	333.15
98	Methyl Myristate	28.60	303.15	286	Glycerol trilaurate	28.26	353.15
99	Methyl Myristate	27.80	313.15	287	Glycerol trilaurate	27.17	373.15
100	Methyl Myristate	27.00	323.15	288	Glycerol trilaurate	26.62	383.15
101	Methyl Myristate	26.00	333.15	289	Glycerol trilaurate	26.08	393.15
102	Methyl Myristate	25.40	343.15	290	Glycerol trilaurate	25.53	403.15
103	Methyl Myristate	24.60	353.15	291	Glycerol trilaurate	24.98	413.15
104	Methyl Myristate	23.80	363.15	292	Glycerol trilaurate	24.44	423.15
105	Methyl Myristate	23.00	373.15	293	Glycerol tripalmitate	26.88	353.15
106	Methyl Pentadecanoate	29.38	298.15	294	Glycerol tripalmitate	25.54	373.15
107	Methyl Pentadecanoate	28.56	308.15	295	Glycerol tripalmitate	24.87	383.15
108	Methyl Pentadecanoate	27.75	318.15	296	Glycerol tripalmitate	24.20	393.15
109	Methyl Pentadecanoate	26.93	328.15	297	Glycerol tripalmitate	23.52	403.15
110	Methyl Pentadecanoate	26.11	338.15	298	Glycerol tristearate	28.62	333.15
111	Methyl Palmitate	29.95	293.15	299	Glycerol tristearate	27.25	353.15
112	Methyl Palmitate	29.17	303.15	300	Glycerol tristearate	25.88	373.15
113	Methyl Palmitate	28.40	313.15	301	Glycerol tristearate	25.19	383.15
114	Methyl Palmitate	27.62	323.15	302	Glycerol tristearate	24.51	393.15
115	Methyl Palmitate	26.80	333.15	303	Glycerol tristearate	23.82	403.15
116	Methyl Palmitate	26.07	343.15	304	Glycerol trioleate	28.71	293.15
117	Methyl Palmitate	25.30	353.15	305	Glycerol trioleate	27.34	313.15
118	Methyl Palmitate	24.52	363.15	306	Glycerol trioleate	25.95	333.15
119	Methyl Palmitate	23.75	373.15	307	Glycerol trioleate	24.56	353.15
120	Methyl Stearate	30.65	293.15	308	Glycerol trioleate	23.17	373.15
121	Methyl Stearate	29.87	303.15	309	Glycerol trioleate	28.34	383.15
122	Methyl Stearate	29.05	313.15	310	Glycerol trioleate	27.64	393.15
123	Methyl Stearate	28.32	323.15	311	Glycerol trioleate	26.94	403.15
124	Methyl Stearate	27.50	333.15	312	Glycerol trioleate	26.24	413.15
125	Methyl Stearate	26.77	343.15	313	Glycerol trioleate	25.54	423.15
126	Methyl Stearate	26.00	353.15	314	Glycerol trilinoleate	20.28	293.15
127	Methyl Stearate	25.22	363.15	315	Glycerol trilinoleate	19.70	313.15
128	Methyl Stearate	24.45	373.15	316	Glycerol trilinoleate	19.13	333.15
129	Ethyl Caproate	26.77	283.15	317	Glycerol trilinoleate	18.56	353.15
130	Ethyl Caproate	25.81	293.15	318	Glycerol trilinoleate	17.99	373.15
131	Ethyl Caproate	24.83	303.15	319	Glycerol trilinoleate	17.70	383.15
132	Ethyl Caproate	23.89	313.15	320	Glycerol trilinoleate	17.41	393.15
133	Ethyl Caproate	22.93	323.15	321	Glycerol trilinoleate	17.12	403.15
134	Ethyl Caproate	21.97	333.15	322	Glyc. 1,2-diacetin,3-oleate	21.88	293.15
135	Ethyl Caproate	21.01	343.15	323	Glyc. 1,2-diacetin,3-oleate	20.82	313.15
136	Ethyl Caproate	20.05	353.15	324	Glyc. 1,2-diacetin,3-oleate	19.75	333.15
137	Ethyl Caproate	19.09	363.15	325	Glyc. 1,2-diacetin,3-oleate	18.69	353.15
138	Ethyl Caproate	18.13	373.15	326	Glyc. 1,2-diacetin,3-oleate	17.62	373.15
139	Ethyl Heptanoate	27.38	283.15	327	Glyc. 1,2-diacetin,3-oleate	17.09	383.15
140	Ethyl Heptanoate	26.44	293.15	328	Glyc. 1,2-diacetin,3-oleate	16.55	393.15
141	Ethyl Heptanoate	25.50	303.15	329	Glyc. 1,2-diacetin,3-oleate	16.02	403.15
142	Ethyl Heptanoate	24.56	313.15	330	Glyc. 1,2-diacetin,3-stearate	26.40	333.15

143	Ethyl Heptanoate	23.62	323.15	331	Glyc. 1,2-diacetin,3-stearate	24.53	353.15
144	Ethyl Heptanoate	22.69	333.15	332	Glycerol 1,2-diacetin,3-stearate	22.66	373.15
145	Ethyl Heptanoate	21.75	343.15	333	Glycerol 1,2-diacetin,3-stearate	21.73	383.15
146	Ethyl Heptanoate	20.89	353.15	334	Glycerol 1,2-diacetin,3-stearate	20.79	393.15
147	Ethyl Heptanoate	19.87	363.15	335	Glycerol 1,2-diacetin,3-stearate	19.86	403.15
148	Ethyl Heptanoate	18.93	373.15	336	Glycerol 1,3-diolein,2-palmitin	26.90	293.15
149	Ethyl Caprylate	28.41	283.15	337	Glycerol 1,3-diolein,2-palmitin	25.60	313.15
150	Ethyl Caprylate	27.44	293.15	338	Glycerol 1,3-diolein,2-palmitin	24.72	333.15
151	Ethyl Caprylate	26.47	303.15	339	Glycerol 1,3-diolein,2-palmitin	23.83	353.15
152	Ethyl Caprylate	25.49	313.15	340	Glycerol 1,3-diolein,2-palmitin	22.94	373.15
153	Ethyl Caprylate	24.52	323.15	341	Glycerol 1,3-diolein,2-palmitin	22.49	383.15
154	Ethyl Caprylate	23.55	333.15	342	Glycerol 1,3-diolein,2-palmitin	22.05	393.15
155	Ethyl Caprylate	22.58	343.15	343	Glycerol 1,3-diolein,2-palmitin	21.61	403.15
156	Ethyl Caprylate	21.61	353.15	344	Glycerol 1,3-diolein,2-palmitin	21.16	413.15
157	Ethyl Caprylate	20.64	363.15	345	Glycerol dicaprin	34.50	310.15
158	Ethyl Caprylate	19.66	373.15	346	Glycerol 1,3-dipalmitin	24.90	293.15
159	Ethyl Caprate	29.07	283.15	347	Glycerol 1,3-dipalmitin	24.00	313.15
160	Ethyl Caprate	28.15	293.15	348	Glycerol 1,3-dipalmitin	23.10	333.15
161	Ethyl Caprate	27.23	303.15	349	Glycerol 1,3-dipalmitin	22.15	353.15
162	Ethyl Caprate	26.31	313.15	350	Glycerol 1,3-dipalmitin	21.23	373.15
163	Ethyl Caprate	25.38	323.15	351	Glycerol 1,3-dipalmitin	20.76	383.15
164	Ethyl Caprate	24.46	333.15	352	Glycerol 1,3-dipalmitin	20.30	393.15
165	Ethyl Caprate	23.54	343.15	353	Glycerol 1,3-dipalmitin	19.84	403.15
166	Ethyl Caprate	22.62	353.15	354	Glycerol 1,3-dipalmitin	19.37	413.15
167	Ethyl Caprate	21.70	363.15	355	Glycerol 1-caproin	28.90	310.15
168	Ethyl Caprate	20.78	373.15	356	Glycerol 1-caprylin	25.40	310.15
169	Ethyl Laurate	29.19	283.15	357	Glycerol 1-caprin	24.00	310.15
170	Ethyl Laurate	28.32	293.15	358	Glycerol 1-palmitin	26.16	293.15
171	Ethyl Laurate	27.46	303.15	359	Glycerol 1-palmitin	24.79	313.15
172	Ethyl Laurate	26.60	313.15	360	Glycerol 1-palmitin	23.45	333.15
173	Ethyl Laurate	25.74	323.15	361	Glycerol 1-palmitin	22.12	353.15
174	Ethyl Laurate	24.87	333.15	362	Glycerol 1-palmitin	20.78	373.15
175	Ethyl Laurate	24.01	343.15	363	Glycerol 1-palmitin	20.11	383.15
176	Ethyl Laurate	23.15	353.15	364	Glycerol 1-palmitin	19.45	393.15
177	Ethyl Laurate	22.28	363.15	365	Glycerol 1-palmitin	18.78	403.15
178	Ethyl Laurate	21.42	373.15	366	Glycerol 1-palmitin	18.11	413.15
179	Ethyl Myristate	29.27	298.15	367	Glycerol 1-stearin	23.35	293.15
180	Ethyl Myristate	28.26	308.15	368	Glycerol 1-stearin	22.17	313.15
181	Ethyl Myristate	27.24	318.15	369	Glycerol 1-stearin	21.00	333.15
182	Ethyl Myristate	26.23	328.15	370	Glycerol 1-stearin	19.82	353.15
183	Ethyl Myristate	25.21	338.15	371	Glycerol 1-stearin	18.62	373.15
184	Ethyl Palmitate	30.28	303.15	372	Glycerol 1-stearin	18.06	383.15
185	Ethyl Palmitate	29.42	313.15	373	Glycerol 1-stearin	17.47	393.15
186	Ethyl Palmitate	28.56	323.15	374	Glycerol 1-stearin	16.88	403.15
187	Ethyl Palmitate	27.71	333.15	375	Glycerol 1-stearin	16.29	413.15
188	Ethyl Palmitate	26.85	343.15				

Table A.2 gives an overview of the collected experimental data for the development of the model to predict/estimate the surface tension of lipid compounds.

Table A.2 Overview of the collected experimental data

Compound Class	Fatty Acids	Fatty Esters	TAG	DAG	MAG	Total
Data points	46	186	107	9	21	**591**
Unsaturated	8	1	30	0	0	**39**
Carbon Length	6 - 18	7 - 19	21 - 57	21 - 57	21 - 57	**6 - 57**
T. Range(K)	293 – 363	283-373	293 - 413	293 - 413	293 - 413	**283-413**

The linear dependency of the surface tension of lipids to the temperature in the range given in Table A.1 is shown in

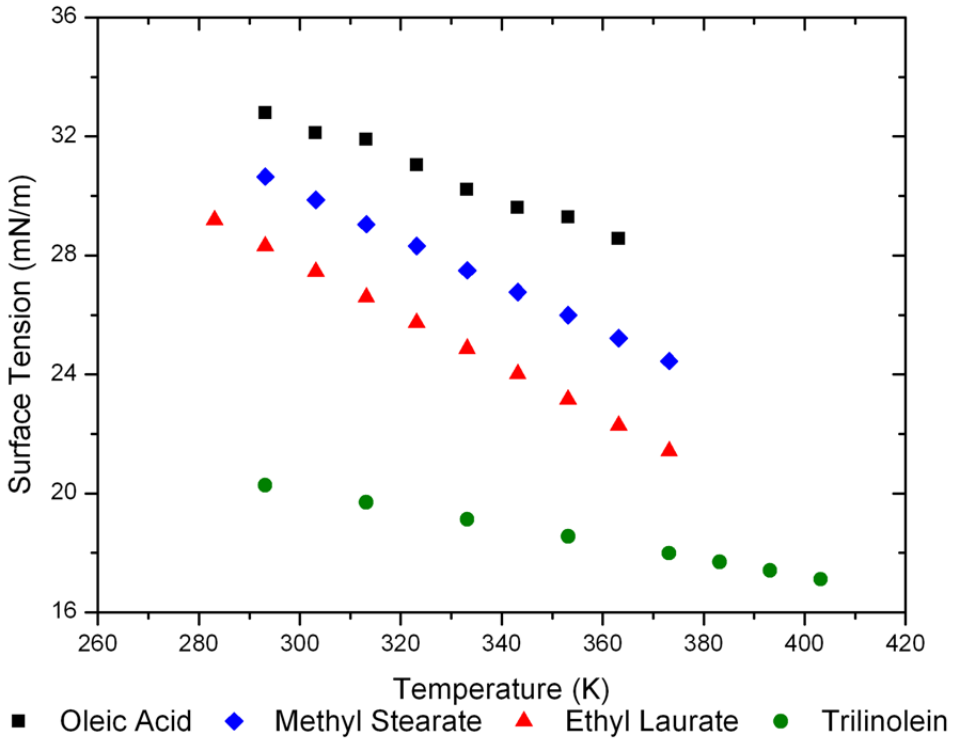


Figure A.1 Surface tension behavior of lipid compound with respect to temperature

The proposed model is given in Eq. (A.1).

$$\sigma_i\left(\frac{dyn}{cm}\right)=\sum_{k=1}N_k\left(A_{1k}+B_{1k}*T\right)+\left[M_i\sum_{k=1}N_k\left(A_{2k}+B_{2k}*T\right)\right]+Q \qquad \text{(A.1)}$$

where N_k is the number of groups k in the molecule; MW_i the component molecular weight that multiplies the "perturbation term"; A_{1k}, B_{1k}, A_{2k}, and B_{2k}, are

parameters obtained from the regression of the experimental data; *k* represents the groups of component *i*; and *Q* is a correction term expressed as

$$Q = \xi_1 \cdot q + \xi_2 \tag{A.2}$$

where ξ_1 and ξ_2 are related to each class of lipid compounds.

In Eq. (A.2), *q* is function of the temperature, expressed as

$$q = \alpha + \beta * T \tag{A.3}$$

where, α, β, γ, and δ are parameters obtained by regression.

In Eq. (A.2), ξ_1 is a function of the total number of carbon-atoms (N_c) in the molecule and is calculated as follows:

$$\xi_1 = f_0 + N_C \cdot f \tag{A.4}$$

Where, f_0 and f_1 are optimized constants.

The term ξ_2 (see Eq. (A.2)) describes the differences between the values in the properties of the isomers of esters at the same temperature, and is related to the number of carbons of the substitute fraction (N_{cs}) as follows:

$$\xi_2 = s_0 + N_{CS} \cdot s_1 \tag{A.5}$$

Where, s_0 and s_1 are regressed constants. Eq. (A.5) is mainly used to account for the effect of the alcoholic portion of the fatty esters. Since they are obtained from the reaction of fatty acids and short-chain alcohols (C1–C4), the molecule can be split in two parts; N_{cs} represents the number of carbons of the alcoholic part.

The parameter regression was performed with the commercial software STATISTICA 9.0 trial. The selected numerical method was xxx and the objective function selected is given in Eq. (A.6).

$$OF = \left(\sigma\{\exp\} - \sigma\{pred\}\right)^2 \tag{A.6}$$

The accuracy of the proposed model is determined by computing the deviations between the predicted and the experimental values (see Eq. (A.7))

$$ARD(\%) = \frac{1}{N}\left[\frac{abs\left(\sigma_i\{\exp\} - \sigma_i\{pred\}\right)}{\sigma\{\exp\}}\right] * 100 \qquad (A.7)$$

Where N is the number of experimental data points; $\sigma_i\{\exp\}$ and $\sigma_i\{pred\}$ are the experimental and predicted values of the compound *i* respectively.

The regressed parameters are given in Table A.3 and the overall performance of the model for each one of the different chemical species included in data bank.

Table A.3 Regressed parameters of Eq. (A.1)

Group	A_{1k}	B_{1k}	A_{2k}	B_{2k}
CH3	20978.9597	-4.7904	-2.2445	1.8415E-01
CH2	-18.4297	-4.3541E-03	-1.9717E-04	3.9985E-07
CH=	-22.6378	-1.0788E-03	5.4319E-03	3.4910E-06
COO-	-39955.0269	13.5233	5.7343	-3.6777E-01
COOH	-47851.5601	-48.1566	13.5181	-1.6383E-01
OH	-18883.2650	8.7282	3.4323	-1.8348E-01
CH2-CH-CH2	62161.8264	-15.5010	-7.8669	5.5356E-01

Compound Class	f_0	f_1	s_0	s_1
Fatty Alcohol	20.700	-2.4347E-03	0	0
Fatty Acids	-262.959	1.3936E+00	0	0
Fatty Esters	20.534	-1.1554E-03	54.5150	-0.1586
Acylglycerides	55.534	1.7450E-01	0	0

Table A.4 GTD-Model performance expressed as the average relative deviation (ARD)

Family	Number of Data Points	Carbon Length	Unsaturated Compounds	ARD(%)
TAGs	104	21-51	30	2.55
DAGs	9	16	0	2.76
MAGs	21	6-18	0	4.65
Fatty Acids	46	6-18	8	0.81
Fatty Esters	186	7-19	0	1.45
Total	**366**	**6-51**	**38**	**1.92**

B.
General Temperature Dependent (GTD) Model Parameters

B.1. Vapor Pressure

The model proposed by Ceriani and Meirelles (2004) was addressed in Chapter 3. By substituting the model coefficients given in Table 3.6 in Eq. 3.2 the GTD model has the following form:

$$P_i^{vp} = \exp\left[A_i^{'} + \frac{B_i^{'}}{T^{1.5}} - C_i^{'} \cdot \ln T - D_i^{'} \cdot T \right] \tag{B.1}$$

where P^{vp} is the vapor pressure in Pa, T is the temperature in K, and A_i', B_i', C_i' and D_i' are the group contribution parameters given as:

$$A_i^{'} = \sum_k N_k \cdot \left(A_{1k} + M_i \cdot A_{2k} \right) + \alpha \cdot \left(f_0 + N_c \cdot f_1 \right) + \left(s_0 + N_{cs} \cdot s_1 \right) \tag{B.2}$$

$$B_i^{'} = \sum_k N_k \cdot \left(B_{1k} + M_i \cdot B_{2k} \right) + \beta \cdot \left(f_0 + N_c \cdot f_1 \right) \tag{B.3}$$

$$C_i^{'} = \sum_k N_k \cdot \left(C_{1k} + M_i \cdot C_{2k} \right) + \gamma \cdot \left(f_0 + N_c \cdot f_1 \right) \tag{B.4}$$

$$D_i^{'} = \sum_k N_k \cdot \left(D_{1k} + M_i \cdot D_{2k} \right) + \delta \cdot \left(f_0 + N_c \cdot f_1 \right) \tag{B.5}$$

where N_k is the number of group k in the molecule, M_i is the molecular weight of component i, A_{1k}, B_{1k}, C_{1k}, D_{1k}, A_{2k}, B_{2k}, C_{2k}, D_{2k}, f_0, f_1, s_0, s_1, α, β, γ, and δ are parameters obtained from the regression of experimental data, k represents the

groups in component i, N_c is the total number of carbon atoms in the molecule, and N_{cs} is the number of carbons of the substitute fraction in fatty esters.

Table B.1 GTD model parameters for vapor pressure

Group	A_{1k}	B_{1k}	C_{1k}	D_{1k}	A_{2k}	B_{2k}	C_{2k}	D_{2k}
$-CH_3$	−117.5	7232.3	−22.7939	0.0361	0.00338	−63.3963	−0.00106	0.000015
$-CH_2-$	8.4816	−10987.8	1.4067	−0.00167	−0.00091	6.7157	0.000041	−0.00000126
−COOH	8.0734	−20478.3	0.0359	−0.00207	0.00399	−63.9929	−0.00132	0.00001
$-CH=CH-_{cis}$	2.4317	1410.3	0.7868	−0.004	0	0	0	0
−COO−	1.843	526.5	0.6584	−0.00368	0	0	0	0
−OH	28.4723	−16694	3.257	0	0.00485	0	0	0
$-CH_2-CH-CH_2-$	688.3	−349293	122.5	−0.1814	−0.00145	0	0	0

Compound	f_0	f_1	s_0	s_1
Esters	0.2773	−0.00444	−0.4476	0.0751
Glycerides	0	0	0	0
Fatty acids	0.001	0	0	0
Alcohols	0.7522	−0.0203	0	0

q			
α	β	γ	δ
3.4443	−499.3	0.6136	−0.00517

B.2. Enthalpy of Vaporization

Ceriani *et al.* (2010) extended the group contribution model proposed to estimate the vapor pressure (Ceriani & Meirelles, 2004) by combining it with the Clausius-Claperyon equation that correlates the heat of vaporization with vapor pressure and temperature:

$$\frac{dP_i^{vap}}{dT} = \frac{P_i^{vap} \cdot \Delta H_i^{vap}}{R \cdot T^2} \tag{B.6}$$

After a few manipulations, we can present ΔH_i^{vap} as:

$$\Delta H_i^{vap} = -R \cdot \left(\frac{1.5 B_i^{'}}{\sqrt{T}} + C_i^{'} \cdot T + D_i^{'} \cdot T^2 \right) \tag{B.7}$$

where R is the gas constant, B_i', C_i' and D_i' are the same group contribution parameters used in vapor pressure estimation (see Table B.1).

Under high temperature and high vapor pressure condition, the ΔH_i^{vap} becomes:

$$\Delta H_i^{vap} = -R \cdot \left(\frac{1.5 B_i^{'}}{\sqrt{T}} + C_i^{'} \cdot T + D_i^{'} \cdot T^2 \right) \cdot \left(1 - \frac{T_c^3 \cdot P_i^{vap}}{T^3 \cdot P_c} \right)^{0.5} \tag{B.8}$$

where P_i^{vap} is the vapor pressure of component *i*, T_c and P_c are the critical temperature and critical vapor pressure, respectively.

B.3. Heat Capacity

The concept of group contribution has also been applied to the prediction of heat capacity for fatty compounds and oils by Ceriani et al. The equation is given as:

$$Cp_i^l = \sum_k N_k \cdot \left(A_k + B_k \cdot T \right) \tag{B.9}$$

where N_k is the number of group *k* in the molecule, A_k and B_k are parameters obtained from the regression.

In Table B.2 the contribution of each one of the identified functional groups is given.

Table B.2 GTD model parameters for liquid heat capacity

Group	A_k	B_k
$–CH_3$	14.5504	0.05406
$–CH_2–$	19.539	0.038211
–COOH	–49.7595	0.42115
–CH=CH–	–130.42	0.54731
–OH	–205.8	0.89618
–COO–	26.261	0.12317
$–CH_2–CH–CH_2–$	181.89	–0.37671

B.4. Liquid Viscosity

In addition to estimating the vapor pressure and heat capacity, Ceriani *et al* (2007). apply the group contribution approach to predict the viscosity of lipid compounds:

$$\ln(\eta_i) = \sum_k N_k \left(A_{1k} + \frac{B_{1k}}{T} - C_{1k} \ln T - D_{1k} T \right) + \left[M_i \sum_k N_k \left(A_{2k} + \frac{B_{2k}}{T} - C_{2k} \ln T - D_{2k} T \right) \right] + Q \quad \text{(B.10)}$$

where N_k is the number of groups k in the molecule i; M is the component molecular weight that multiplies the "perturbation term"; A_{1k}, B_{1k}, C_{1k}, D_{1k}, A_{2k}, B_{2k}, C_{2k}, and D_{2k} are parameters obtained from the regression of the experimental data; k represents the groups of component i; Q is a correction term expressed as:

$$Q = \xi_1 q + \xi_2 \quad \text{(B.11)}$$

where q is a function of the absolute temperature shown as:

$$q = \alpha + \frac{\beta}{T} - \gamma \ln(T) - \delta T \quad \text{(B.12)}$$

where α, β, γ, and δ are optimized parameters obtained by regression of the data bank as a whole. The effect of functional groups on the dynamic viscosity is corrected by the term Q according to the total number of carbon atoms N_c in the molecules. ξ_1 is a function of applicable to all compounds and ξ_2 describes the differences between the vapor pressures of N_c isomer esters at the same temperature and is related to the number of carbons of the alcoholic part (N_{cs}) in fatty esters, they are given as:

$$\xi_1 = f_0 + N_c f_1 \tag{B.13}$$

$$\xi_2 = s_0 + N_{cs} s_1 \tag{B.14}$$

where f_0, f_1, s_0 and s_1 are optimized constants.

Table B.3 GTD model parameters for liquid viscosity

Group	A_{1k}	B_{1k}	C_{1k}	D_{1k}	A_{2k}	B_{2k}	C_{2k}	D_{2k}
CH_3	−0.2579	210.6	0.2275	−0.00389	0.000423	−0.0466	−0.00037	0.00000624
CH_3	−0.13	70.688	−0.0271	0.000449	0.000018	−0.0175	0.000038	−0.000000636
COOH	14.017	−2477.4	−0.8944	0.0375	−0.0435	17.2293	0.0108	−0.00018
CH=	49.8378	−1759.1	8.1803	−0.00867	0.000307	0.1681	0.000247	−0.00000206
OH	−8.6357	2483.6	0.0092	−0.00012	0.00856	0.0317	−0.00023	0.000004028
COO	−828.4	25192.6	−140.8	0.2041	1.0924	−32.5558	0.1852	−0.00026324
CH_2—CH—CH_2	1997.2	−56987.6	343.1	−0.5253	−2.8043	81.0608	−0.47675	0.000687

Compound	f_0	f_1	s_0	s_1
Fatty acids	−11.1293	−21.1798	0	0
Alcohols	−4196.4	516.7	0	0
Esters	−5291.2	354	0.1984	−0.0512
Glycerides	−236.9	2.4799	0	0

Q	α	β	γ	Δ
	−0.3157	9.324	−0.054	0.00007812

C.
Application of the Thermophysical Property Models

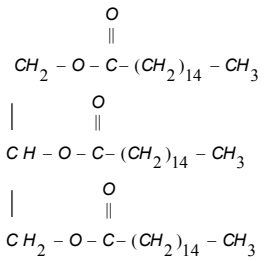
In this Appendix, the applicability of the adopted models for the prediction of the temperature dependent models is illustrated. For this purpose different lipid compounds were selected as examples. Table C.1 selected lipid compound as well as the correspondent temperature dependent property to be estimated.

Table C.1

Property	Lipid Compound	Model
Vapor Pressure	Tripalmitin	GTD
Enthalpy of Vaporization	Ethyl laurate	Eq. 3.11
Liquid Heat Capacity	Stearic acid	GTD
Liquid Viscosity	Methyl myristate	GTD
Surface Tension	Monopalmitin	GTD
Liquid Density	Brazil nut	Modified Rackett Eq.
	Monostearin	CFFA

C.1. Calculation of Vapor Pressure of Tripalmitin at 512.15K through the GTD-Model.

Tripalmitin has the following structure:



According to the group contribution method proposed by Ceriani & Meirelles (2004), the molecule is described by the following groups:

CH_3 = 3; CH_2=42; COO = 3; CH_2-CH-CH_2 = 1;

N_c =51; MW_i = 807.34 g/grmol.

Therefore, from Equations (3.2) – (3.6) and the GTD-model coefficients (Table 3.6) for the vapor pressure physical property.

$$\begin{aligned}\ln\left(P_i^{vp}\right) = &\left\{\left[3(-117.5)+42(8.4816)+3(7.116)+1(688.3)\right]\right.\\ &\left.+807.34\left[3(0.00338)+42(-0.00091)+3(0.00279)+1(-0.00145)\right]\right\}\\ &+\left\{\left[3(7232.3)+42(-10987.8)+3(49152.6)+1(-349293)\right]\right.\\ &\left.+807.34\left[3(-63.3963)+42(6.7157)+3(10.0396)+1(0)\right]\right\}/T^{1.5}\\ &-\left\{\left[3(-22.7939)+42(1.4067)+3(2.337)+1(122.5)\right]\right.\\ &\left.+807.34\left[3(-0.00106)+42(0.000041)+3(-0.00034)+1(0)\right]\right\}\ln T\\ &-\left\{\left[3(0.0361)+42(-0.00167)+3(-0.00848)+1(-0.1814)\right]\right.\\ &\left.+807.34\left[3(0.000015)+42(-0.00000126)+3(0.00000295)+1(0)\right]\right\}T\\ &+0\end{aligned}$$

$P_i^{vp}(512.15K) = 0.1310\text{Pa}$. The experimental value is 0.1333Pa; corresponding to an error of 1.70%.

C.2. Calculation of Enthalpy of Vaporization of Ethyl Laurate at 293K through Eq. 3.11

Ethyl laurate has the following structure:

CH_3-$(CH_2)_{10}$-COO- CH_2- CH_3

And it is defined by the following function groups (Ceriani & Meirelles, 2004):

CH_3 = 2; CH_2 = 11; COO = 1; Mw = 228.0000g/gmol

$$\Delta H_i^{vap} = -R \cdot \left\{ \left[2\left(7232.3 + 228.0 * -63.3963\right) + 11\left(-10987.8 + 228.0 * 6.7157\right) \right.\right.$$
$$\left. + 1\left(49152.6 + 228.0 * 10.0396\right) \right] \frac{1.5}{\sqrt{T}} + \left[2\left(-22.7939 + 228.0 * -0.00106\right) \right.$$
$$\left. + 11\left(1.4067 + 228.0 * 0.000041\right) + 1\left(2.337 + 228.0 * -0.00034\right) \right] \cdot T$$
$$+ \left[2\left(0.0361 + 228.0 * 0.000015\right) + 11\left(-0.00167 + 228.0 * -0.00000126\right) \right.$$
$$\left. \left. + + 1\left(-0.00848 + 228.0 * 0.00000295\right) \right] \cdot T^2 \right\}$$

$\Delta H_i^{vap} = 72634.70 J/gmol$ The experimental value is 71421J/gmol; corresponding to an error of 1.70%.

C.3. Calculation of Liquid Heat Capacity of Stearic Acid at 350K through the GTD-Model

Stearic acid has the following structure

CH_3-$(CH_2)_{16}$-COOH

And it is defined by the next set of functional groups (Ceriani & Meirelles, 2004):

$CH_3 = 1$; $CH_2 = 16$; COOH = 1.

Therefore, from Equations (3.2) – (3.6) and the GTD model coefficients (Table 3.6) for the liquid heat capacity model

$$Cp_i^l = \left[1\left(14.5504\right) + 16\left(19.539\right) + 1\left(-49.7595\right) \right] + \left[1\left(0.05406\right) + 16\left(0.038211\right) + 1\left(0.42115\right) \right] T$$

$Cp_i^l \left(T = 350K\right) = 657.72 \text{J/mol} \cdot \text{K}$ The experimental value is 656.08 J/mol*K; corresponding to an error of 0.25%.

C.4. Calculation of Liquid Viscosity of Methyl Myristate at 333.15K through the GTD-Model

Methyl myristate has the following structure

CH_3-$(CH_2)_{12}$-COO-CH_3

According to the group contribution method proposed by Ceriani and Meirelles (2004), the molecule can be described by the following functional groups:

$CH_3 = 2$; $CH_2 = 12$; COO = 1;

$N_c = 15$; $N_{cs} = 1$; $MW_i = 242.40$ g/grmol.

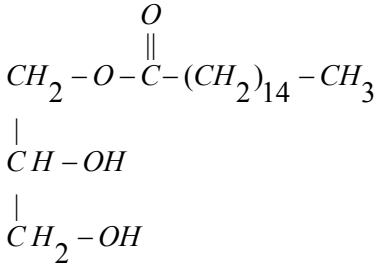
From Equations (3.2) – (3.6) and the GTD model coefficients (Table 3.6)) for the liquid viscosity.

$$\begin{aligned}\ln(\eta_i) = &\{[2(-0.2579)+12(-0.13)+1(-828.4)]\\ &+242.40[2(0.000423)+12(0.000018)+1(1.0924)]\}\\ &+\{[2(210.6)+12(70.6888)+1(25192.6)]\\ &+242.40[2(-0.0466)+12(-0.0175)+1(-32.5558)]\}/T\\ &-\{[2(0.2275)+12(-0.0271)+1(-140.8)]\\ &+242.40[2(-0.00037)+12(0.000038)+1(0.1852)]\}\ln T\\ &-\{[2(-0.00389)+12(0.000449)+1(0.2041)]\\ &+242.40[2(0.00000624)+12(-0.000000636)+1(-0.00026324)]\}T\\ &+[-5291.2+15(354)][-0.3157+9.324/T+5.40\cdot10^{-2}\ln T\\ &-7.812\cdot10^{-5}T]+[0.1984+1(-0.0512)]\end{aligned}$$

$\eta_i(T = 333.15) = 1.9119\,\text{mPa}\cdot\text{s}$. The experimental value is 1.943mPa*s; corresponding to an error of 1.60%.

C.5. Appendix D. Calculation of Surface Tension of Monopalmitin at 413.15K through the GTD-Model

Monopalmitin has the following structure



And it is defined by the next set of functional groups

$CH_3 = 1$; $CH_2 = 14$; COO = 1; CH_2-CH-CH_2 = 1; OH = 2

N_c = 19; MW_i = 330.50 g/grmol.

From Equations (3.2) – (3.6) and the GTD model coefficients (Table 3.6) for the surface tension

$$\begin{aligned}\sigma_i =& \left[1(4443.60)+14(-8.29208)+1(-753.105)+1(-11146.5)\right.\\ &\left.+2(3720.79)\right]+330.5\left[1(1.40269)+14(0.000858228)+1(-2.25435)\right.\\ &\left.+1(3.12202)+2(-0.875560)\right]+\left\{\left[1(-1.72984)+14(0.281576)+1(10.7682)\right.\right.\\ &\left.\left.+1(-24.3862)+2(8.25908)\right]+330.5\left[1(0.113988)+14(-0.00000212011)\right.\right.\\ &\left.\left.+1(-0.247943)+1(0.387547)+2(-0.133909)\right]\right\}T\\ &+\left[2.42268+19(-0.184330)\right]\left[1.78095+(0.428859)T\right]\end{aligned}$$

$\sigma_i\left(413.15K\right)=17.43\text{dyn/cm}$. Experimental value is 18.11dyn/cm; corresponding to an error of 3.79%.

C.6. Calculation of Liquid Density of Brazil Nut at 413.15K through the Modified Rackett Equation

Brazil Nut fatty acids composition, critical properties, and are given in Table C.2. As established in the methodology proposed by Halvorsen *et al*. (1993):

$T_{c,mix}$ = 782.26K; $P_{c,mix}$ = 14.07052bar; MW_{oil} = 870.50 g/grmol;

$Z_{RA,mix} = \Sigma(Z_{RAi})x_i$ = 0.23711; F_c = 0.02397.

Table C.2 Brazil nut oil fatty acid composition and their Modified Rackett's equation parameters

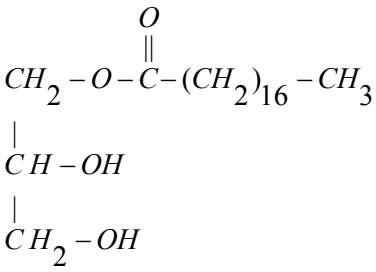
Fatty Acid	Composition (%)	Tc (K)	Pc(bar)	MW (gr/grmol)	Zr
Myristic	0.11	765.00	16.44	228.38	0.23517
Palmitic	17.23	785.22	14.68	256.43	0.23379
Palmitoleic	0.38	800.34	14.71	254.41	0.23120
Stearic	10.11	804.00	13.60	284.48	0.23518
Oleic	37.08	781.00	13.90	282.47	0.23849
Linoleic	34.56	775.00	14.10	280.45	0.23800
Linoleninc	0.05	780.00	14.40	278.44	0.23718
Arachidic	0.36	821.00	12.40	312.54	0.23288
Gadoleic	0.05	837.03	11.18	310.51	0.21788
Behenic	0.07	855.00	11.00	340.59	0.22588

$$\rho_{oil}^{l}\left(333.15K\right)=\frac{\left(277.4824\right)}{83.144\left(55.64\right)\left(0.23711\right)^{\left[1+\left(1-\frac{333.15}{782.258}\right)^{2/7}\right]}}+0.023969$$

$\rho_{oil}^{l}\left(333.15K\right)=0.8880\,\mathrm{gr/cm^3}$. The experimental value is 0.88642gr/cm^3; corresponding to an error of 0.172%.

C.7. Calculation of Liquid Density of Monostearin at 450.15K through the Chemical Constituent Fragment Approach

Monostearin has the following structure



And it is defined by the 2 fragments: Monoglycerol and stearin.

From Eqs. (3.1) - (3.2) and a Mw = 330.501g/gmol:

$$V^{lm}=1\left(\frac{1+6.9785\mathrm{E}^{-4}T}{17.412}\right)+1\left(\frac{1+1.3008\mathrm{E}^{-3}T}{5.052}\right)=0.3744\frac{kmol}{m^3}$$

$$\rho_i^l=0.8828\frac{gr}{cm^3}$$

D.
CAPEC_Lipids_Database Specifics

In this Appendix, more detailed specifics of the CAPEC_Lipids_Database are presented. This includes:

1. The typical qualitative lipid content of 14 commodity oils/fats (see Chapter 3)
2. Molecular description of the FFA and Minor Compounds through the Marrero and Gani (2001) functional groups.
3. Molecular description of glycerides through the Ceriani and Meirelles (2004) functional groups.
4. Partial sets of experimental thermophysical property data.
5. Lipids compounds specifics (name, code name, carbon chain length and number of double bounds, and CAS Nr.)
6. Single value pure component.

Note: Due to the confidentiality agreement, the model parameters of the selected thermophysical temperature dependent pure component properties are not to be disclosed.

D.1 *Typical Qualitative Lipid Composition of 14 Vegetable Oils and Fats*

GLOBAL PICTURE OILS AND FATS

X	COMPOUND	ABVT	NC:ND	C	H	O	SOURCE: OIL SEEDS: SOYBEAN	COTTON SEED	PEANUT	CORN	SUNFLOWER	RICEBRAN	SAFFLOWER	CASTOR	CANOLA	TREE FRUITS AND KERNELS: OLIVE	PALM	COCONUT	PALM K.	ANIMALS: LARD	TALLOW
FATTY ACIDS	heptanoic acid	HPTANOIC	C7:0	7	14	2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	caprylic acid	OCTANOIC	C8:0	8	16	2	-	-	-	-	-	-	-	-	-	-	-	X	X	-	-
	nonanoic acid	NONANOIC	C9:0	9	18	2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	capric acid	DECANOIC	C10:0	10	20	2	-	-	-	-	-	-	-	-	-	-	-	X	X	X	-
	undecanoic acid	UNDCNOIC	C11:0	11	22	2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	lauric acid	LAURIC	C12:0	12	24	2	-	-	-	-	-	-	-	-	-	-	X	X	X	-	X
	tridecanoic acid	TRDCNOIC	C13:0	13	26	2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	myristic acid	MYRISTIC	C14:0	14	28	2	X	X	X	X	X	X	X	-	X	X	X	X	X	X	X
	myristoleic acid	MYRISTOL	C14:1	14	26	2	-	-	-	-	-	-	-	-	-	-	-	-	-	X	X
	pentadecanoic acid	PNDCNIOC	C15:0	15	30	2	-	-	-	-	-	-	-	-	-	-	-	-	-	X	X
	palmitic acid	PALMITIC	C16:0	16	32	2	X	X	X	X	X	X	X	-	X	X	X	X	X	X	X
	palmitoleic acid	PALMTOL	C16:1	16	30	2	X	X	X	X	X	-	X	-	X	X	X	-	-	X	X
	Hexadecadienoic	MARGARIC	C16:2	16	28	2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	X
	margaric acid	MARGROL	C17:0	17	34	2	X	-	X	X	-	-	-	-	-	X	-	-	-	X	X
	margaroleic acid	STEARIC	C17:1	17	32	2	-	-	X	-	-	-	-	-	-	X	-	-	-	X	X
	stearic acid	OLEIC	C18:0	18	36	2	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
	oleic acid	LINOLEIC	C18:1	18	34	2	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
	linoleic acid	LINOLENI	C18:2	18	32	2	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
	linolenic acid	C20ACID	C18:3	18	30	2	X	X	X	X	X	X	X	-	X	X	X	-	-	X	X
	arachidic acid	GADOLEIC	C20:0	20	40	2	X	X	X	X	X	X	X	-	X	X	X	X	X	X	X
	gadoleic acid	GADOLENC	C20:1	20	38	2	X	X	X	X	X	-	X	-	X	X	-	X	X	X	X
	gadolenic acid	EPAACID	C20:2	20	36	2	-	-	-	-	-	-	-	-	-	-	-	-	-	X	-
	eicosatetraenoic acid	DPAACID	C20:4	20	32	2	-	-	-	-	-	-	-	-	-	-	-	-	-	X	X
	behenic acid	BEHENIC	C22:0	22	44	2	X	X	X	X	X	-	X	-	X	X	-	-	-	X	-
	erucic acid	ERUCIC	C22:1	22	42	2	X	X	X	-	X	-	-	-	X	-	-	-	-	-	-
	lignoceric acid	LIGNOCRC	C24:0	24	48	2	X	X	X	X	X	-	-	-	X	X	-	-	-	-	-
	nervonic acid	NERVNIC	C24:1	24	46	2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Figure D.1 Fatty acid qualitative composition of the selected 14 vegetable oils and fats

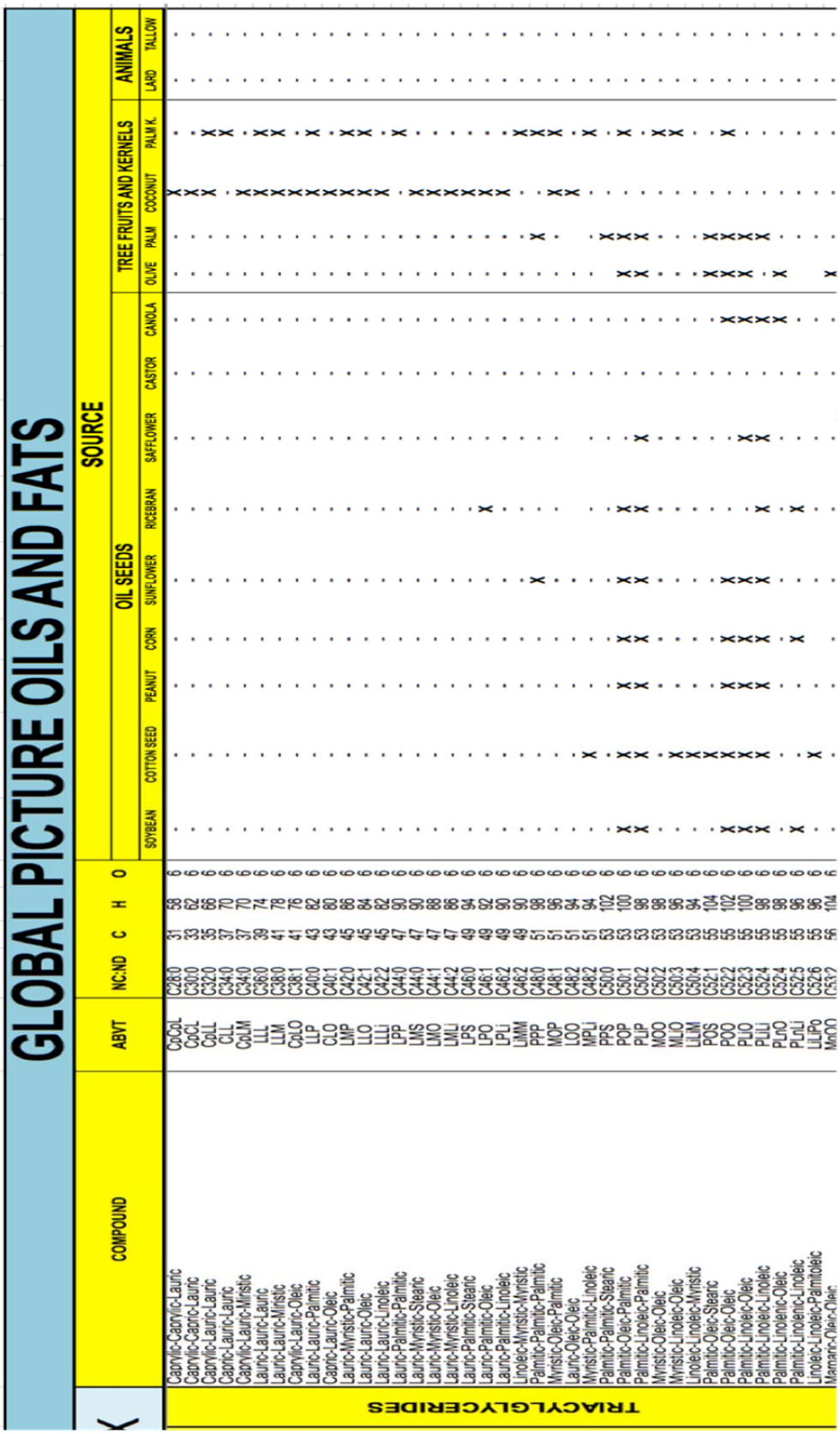


Figure D.2 Triglyceride qualitative composition of the selected 14 vegetable oils and fats

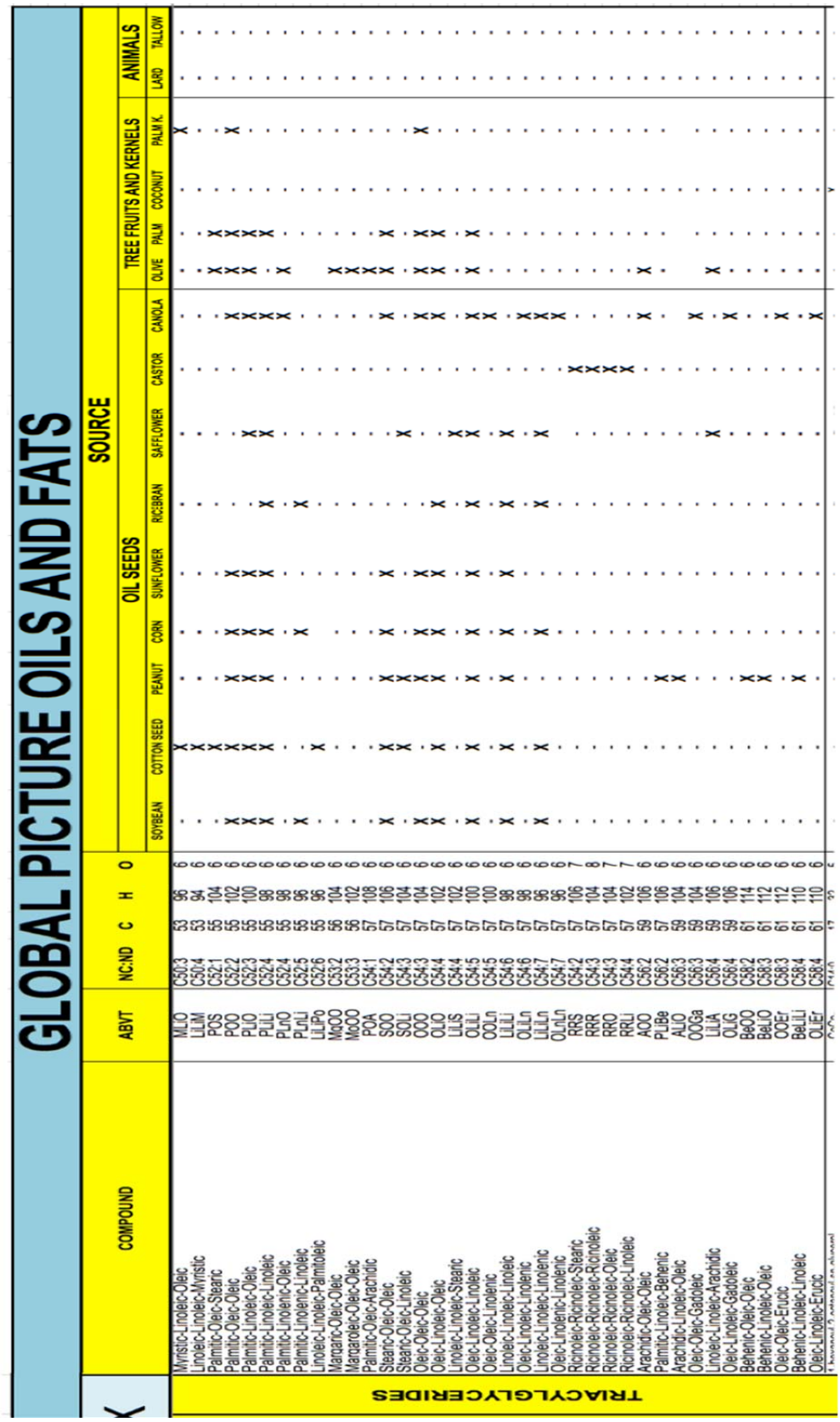
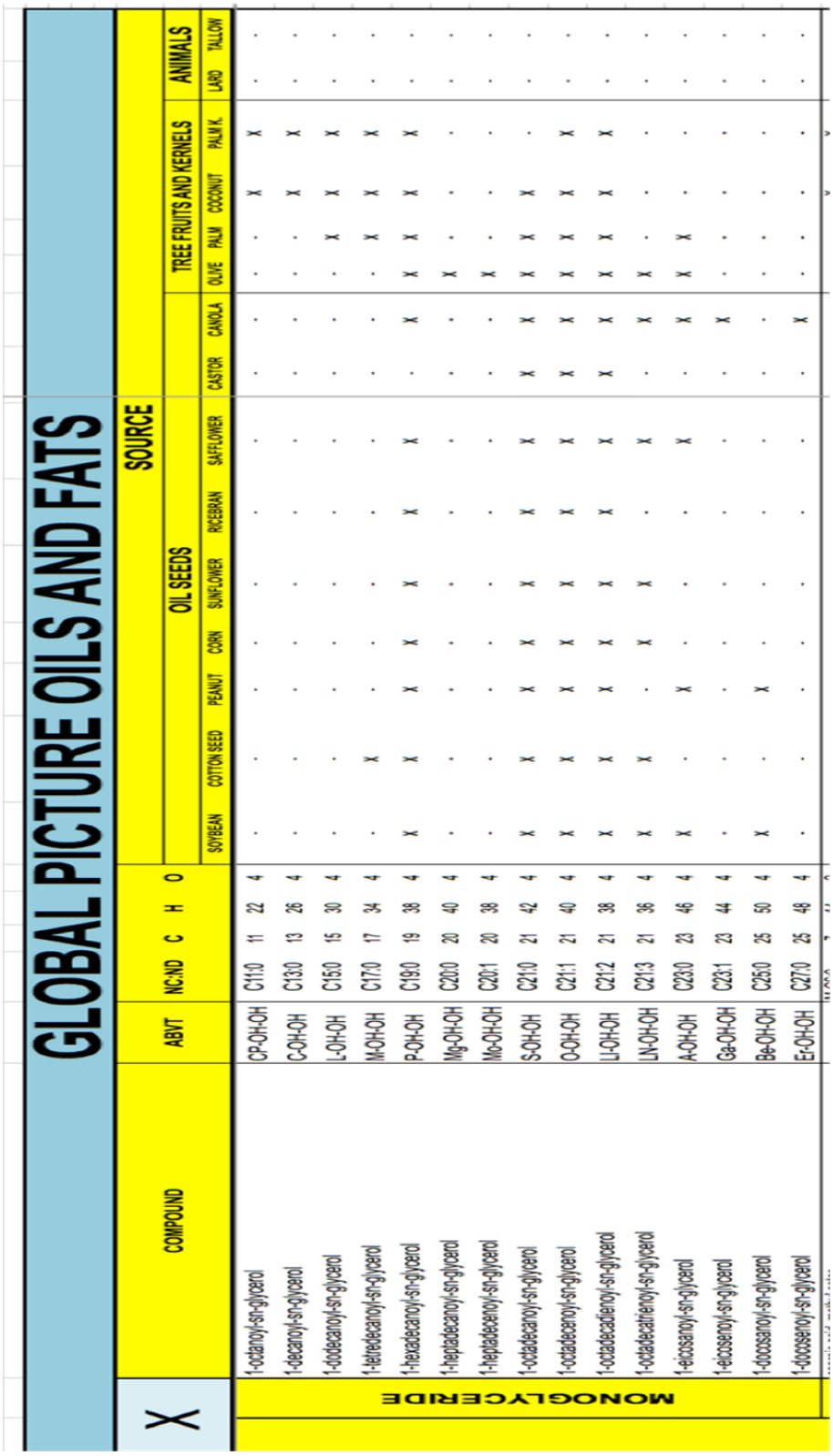


Figure D.3 Triglyceride qualitative composition of the selected 14 vegetable oils and fats



X	COMPOUND	ABVT	NC:ND	C	H	O	SOURCE																
							OIL SEEDS								TREE FRUITS AND KERNELS				ANIMALS				
							SOYBEAN	COTTON SEED	PEANUT	CORN	SUNFLOWER	RICEBRAN	SAFFLOWER	CASTOR	CANOLA	OLIVE	PALM	COCONUT	PALM K.	LARD	TALLOW
MONOGLYCERIDE	1-octanoyl-sn-glycerol	C8-OH-OH	C11:0	11	22	4	-	-	-	-	-	-	-	-	-	-	-	X	X	-	-
	1-decanoyl-sn-glycerol	C-OH-OH	C13:0	13	26	4	-	-	-	-	-	-	-	-	-	-	-	X	X	-	-
	1-dodecanoyl-sn-glycerol	L-OH-OH	C15:0	15	30	4	-	-	-	-	-	-	-	-	-	-	X	X	X	-	-
	1-tetradecanoyl-sn-glycerol	M-OH-OH	C17:0	17	34	4	-	X	-	-	-	-	-	-	-	-	X	X	X	-	-
	1-hexadecanoyl-sn-glycerol	P-OH-OH	C19:0	19	38	4	X	X	X	X	X	X	X	-	X	X	X	X	X	-	-
	1-heptadecanoyl-sn-glycerol	Mg-OH-OH	C20:0	20	40	4	-	-	-	-	-	-	-	-	-	X	-	-	-	-	-
	1-heptadecenoyl-sn-glycerol	Mo-OH-OH	C20:1	20	38	4	-	-	-	-	-	-	-	-	-	X	-	-	-	-	-
	1-octadecanoyl-sn-glycerol	S-OH-OH	C21:0	21	42	4	X	X	X	X	X	X	X	X	X	X	X	X	-	-	-
	1-octadecenoyl-sn-glycerol	O-OH-OH	C21:1	21	40	4	X	X	X	X	X	X	X	X	X	X	X	X	X	-	-
	1-octadecadienoyl-sn-glycerol	Li-OH-OH	C21:2	21	38	4	X	X	X	X	X	X	X	X	X	X	X	X	X	-	-
	1-octadecatrienoyl-sn-glycerol	Ln-OH-OH	C21:3	21	36	4	X	X	-	X	X	-	X	-	X	X	-	-	-	-	-
	1-eicosanoyl-sn-glycerol	A-OH-OH	C23:0	23	46	4	X	-	X	-	-	-	X	-	X	X	X	X	-	-	-
	1-eicosenoyl-sn-glycerol	Ga-OH-OH	C23:1	23	44	4	-	-	-	-	-	-	-	-	X	-	-	-	-	-	-
	1-docosanoyl-sn-glycerol	Be-OH-OH	C25:0	25	50	4	X	-	X	-	-	-	-	-	-	-	-	-	-	-	-
	1-docosenoyl-sn-glycerol	Er-OH-OH	C27:0	25	48	4	-	-	-	-	-	-	-	-	X	-	-	-	-	-	-

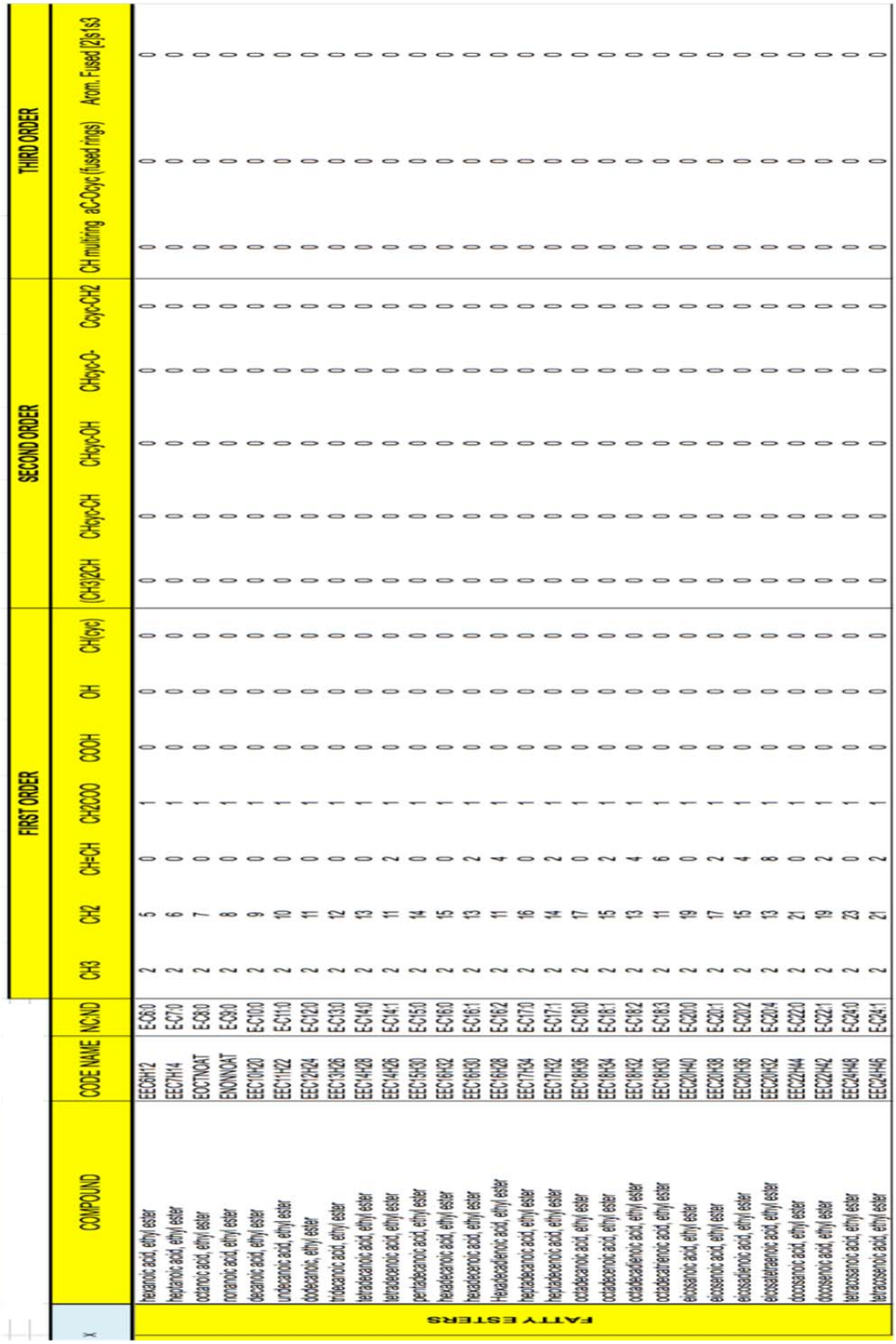
Figure D.4 monoglyceride qualitative composition of the selected 14 vegetable oils and fats

GLOBAL PICTURE OILS AND FATS

	COMPOUND	ABVT	NC:ND	C	H	O	SOURCE														
							OIL SEEDS									TREE FRUITS AND KERNELS				ANIMALS	
							SOYBEAN	COTTON SEED	PEANUT	CORN	SUNFLOWER	RICEBRAN	SAFFLOWER	CASTOR	CANOLA	OLIVE	PALM	COCONUT	PALM K.	LARD	TALLOW
MINOR COMPOUNDS	Brassicasterol	STEROLS	-	28	46	1	-	-	-	-	-	-	-		-	-	-	-	-		
	Campesterol		-	28	48	1	X	X	-	X	X	-	X		-	-	X	X	X		
	Delta-7-stigmastenol		-	29	50	1	-	-	-	-	-	-	X		-	-	-	-	-		
	Cycloartenol		-	30	50	1	-	-	-	-	X	-	-		-	X	-	X	-		
	24-methylencycloartanol		-	31	52	1	-	-	-	-	-	-	-		-	X	-	-	-		
	Gamma-Oryzanol		-	40	58	4	-	-	-	-	-	X	-		-	-	-	-	-		
	Citrostadienol		-	30	50	1	-	-	-	-	X	-	-		-	X	-	-	-		
	CHOLESTEROL		-	27	46	1	X	X	X	X	-	X	X	X	X	-	X	-	X	X	X
	SQUALENE			30	50	0	X	-	-	-	-	X	-	-	-	X	X	-	-	-	-
	BETA-CAROTENE	-	-	40	56	0	-	-	-	-	-	X	-	-	-	-	-	-	-	-	-
	Alfa-Tocopherol	TOCOPI	C29:0	29	50	2	X	X	X	X	X	X	X	-	X	X	X	-	X	-	-
	Beta-Tocopherol		C28:0	28	48	2	X	-	X	X	X	X	X	-	X	-	-	-	-	-	-
	Gama-Tocopherol		C28:0	28	48	2	X	X	X	X	X	X	X	-	X	X	X	X	-	-	-
	Delta-Tocopherol		C27:0	27	46	2	X	X	X	X	-	-	-	-	-	-	X	-	-	-	-
	Alfa-Tocotrienol	TOCOTI	C29:3	29	44	2	-	-	-	X	X	X	-	-	-	-	X	X	X	-	-
	Beta-Tocotrienol		C28:3	28	42	2	-	-	-	-	-	-	-	-	-	-	X	-	-	-	-
	Gama-Tocotrienol		C28:3	28	42	2	-	-	-	X	-	X	X	-	-	-	X	X	-	-	-
	Delta-Tocotrienol		C27:3	27	40	2	-	-	-	X	-	-	-	-	-	-	X	-	-	-	-

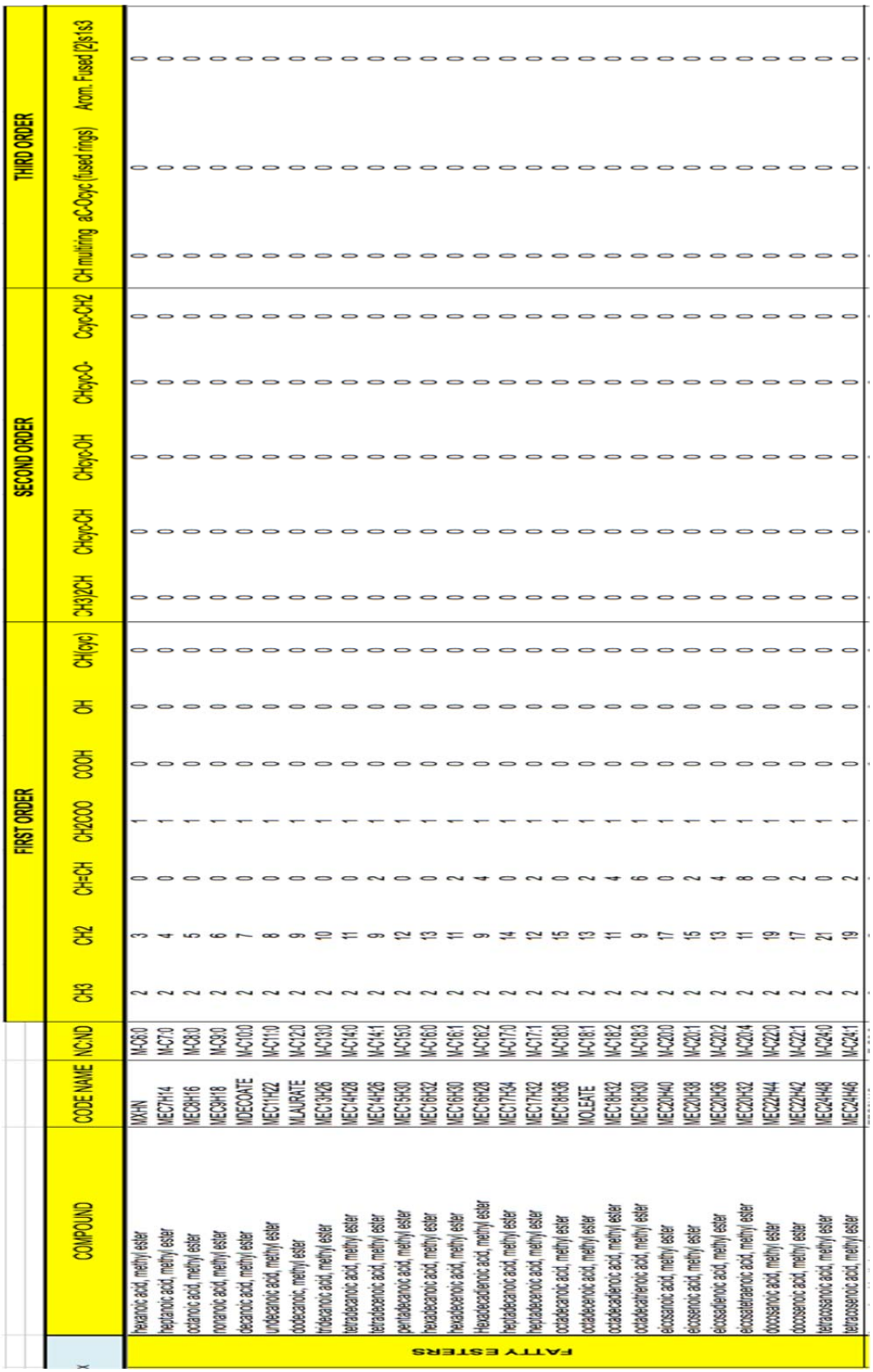
Figure D.5 Minor compounds qualitative composition of the selected 14 vegetable oils and fats

D.2 *Molecular Description through the MG Functional Groups*



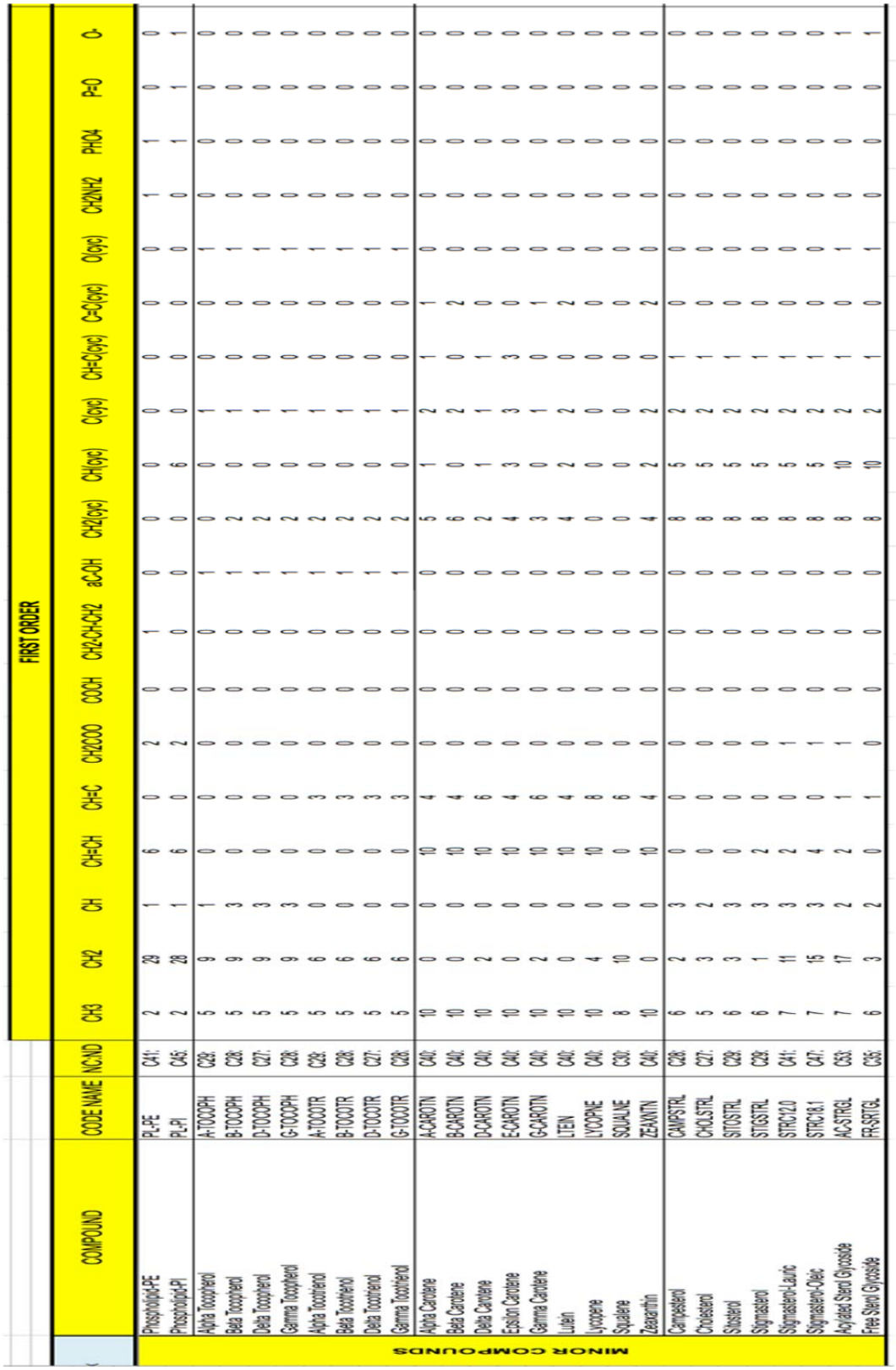
	COMPOUND	CODE NAME	NC/ND	FIRST ORDER							SECOND ORDER						THIRD ORDER		
				CH3	CH2	CH=CH	CH2COO	COOH	OH	CH(cyc)	(CH3)2CH	CHcyc-CH	CHcyc-OH	CHcyc-O-	Ccyc-CH2	CH multiring	acr-Ccyc (fused rings)	Arom. Fused (2)s ts3
FATTY ≡ STERS	hexanoic acid, ethyl ester	EEC6H12	E-C6:0	2	5	0	1	0	0	0	0	0	0	0	0	0	0	0
	heptanoic acid, ethyl ester	EEC7H14	E-C7:0	2	6	0	1	0	0	0	0	0	0	0	0	0	0	0
	octanoic acid, ethyl ester	EOCTNOAT	E-C8:0	2	7	0	1	0	0	0	0	0	0	0	0	0	0	0
	nonanoic acid, ethyl ester	ENONNOAT	E-C9:0	2	8	0	1	0	0	0	0	0	0	0	0	0	0	0
	decanoic acid, ethyl ester	EEC10H20	E-C10:0	2	9	0	1	0	0	0	0	0	0	0	0	0	0	0
	undecanoic acid, ethyl ester	EEC11H22	E-C11:0	2	10	0	1	0	0	0	0	0	0	0	0	0	0	0
	dodecanoic, ethyl ester	EEC12H24	E-C12:0	2	11	0	1	0	0	0	0	0	0	0	0	0	0	0
	tridecanoic acid, ethyl ester	EEC13H26	E-C13:0	2	12	0	1	0	0	0	0	0	0	0	0	0	0	0
	tetradecanoic acid, ethyl ester	EEC14H28	E-C14:0	2	13	0	1	0	0	0	0	0	0	0	0	0	0	0
	tetradecenoic acid, ethyl ester	EEC14H26	E-C14:1	2	11	2	1	0	0	0	0	0	0	0	0	0	0	0
	pentadecanoic acid, ethyl ester	EEC15H30	E-C15:0	2	14	0	1	0	0	0	0	0	0	0	0	0	0	0
	hexadecanoic acid, ethyl ester	EEC16H32	E-C16:0	2	15	0	1	0	0	0	0	0	0	0	0	0	0	0
	hexadecenoic acid, ethyl ester	EEC16H30	E-C16:1	2	13	2	1	0	0	0	0	0	0	0	0	0	0	0
	Hexadecadienoic acid, ethyl ester	EEC16H28	E-C16:2	2	11	4	1	0	0	0	0	0	0	0	0	0	0	0
	heptadecanoic acid, ethyl ester	EEC17H34	E-C17:0	2	16	0	1	0	0	0	0	0	0	0	0	0	0	0
	heptadecenoic acid, ethyl ester	EEC17H32	E-C17:1	2	14	2	1	0	0	0	0	0	0	0	0	0	0	0
	octadecanoic acid, ethyl ester	EEC18H36	E-C18:0	2	17	0	1	0	0	0	0	0	0	0	0	0	0	0
	octadecenoic acid, ethyl ester	EEC18H34	E-C18:1	2	15	2	1	0	0	0	0	0	0	0	0	0	0	0
	octadecadienoic acid, ethyl ester	EEC18H32	E-C18:2	2	13	4	1	0	0	0	0	0	0	0	0	0	0	0
	octadecatrienoic acid, ethyl ester	EEC18H30	E-C18:3	2	11	6	1	0	0	0	0	0	0	0	0	0	0	0
	eicosenoic acid, ethyl ester	EEC20H40	E-C20:0	2	19	0	1	0	0	0	0	0	0	0	0	0	0	0
	eicosenoic acid, ethyl ester	EEC20H38	E-C20:1	2	17	2	1	0	0	0	0	0	0	0	0	0	0	0
	eicosadienoic acid, ethyl ester	EEC20H36	E-C20:2	2	15	4	1	0	0	0	0	0	0	0	0	0	0	0
	eicosatetraenoic acid, ethyl ester	EEC20H32	E-C20:4	2	13	8	1	0	0	0	0	0	0	0	0	0	0	0
	docosanoic acid, ethyl ester	EEC22H44	E-C22:0	2	21	0	1	0	0	0	0	0	0	0	0	0	0	0
	docosenoic acid, ethyl ester	EEC22H42	E-C22:1	2	19	2	1	0	0	0	0	0	0	0	0	0	0	0
	tetracosenoic acid, ethyl ester	EEC24H48	E-C24:0	2	23	0	1	0	0	0	0	0	0	0	0	0	0	0
	tetracosenoic acid, ethyl ester	EEC24H46	E-C24:1	2	21	2	1	0	0	0	0	0	0	0	0	0	0	0

Figure D.6 Molecular description of fatty esters through the MG functional group.



	COMPOUND	CODE NAME	NC/ND	FIRST ORDER CH3	CH2	CH=CH	CH2COO	COOH	OH	CH(cyc)	SECOND ORDER CH3/2OH	CHcyc-CH	CHcyc-OH	CHcyc-O-	Ccyc-CH2	THIRD ORDER CH multiring	aC-Ocyc (fused rings)	Arom. Fused (2)s1s3
FATTY ESTERS	hexanoic acid, methyl ester	MXHN	M-C6:0	2	3	0	1	0	0	0	0	0	0	0	0	0	0	0
	heptanoic acid, methyl ester	MEC7H14	M-C7:0	2	4	0	1	0	0	0	0	0	0	0	0	0	0	0
	octanoic acid, methyl ester	MEC8H16	M-C8:0	2	5	0	1	0	0	0	0	0	0	0	0	0	0	0
	nonanoic acid, methyl ester	MEC9H18	M-C9:0	2	6	0	1	0	0	0	0	0	0	0	0	0	0	0
	decanoic acid, methyl ester	MDECOATE	M-C10:0	2	7	0	1	0	0	0	0	0	0	0	0	0	0	0
	undecanoic acid, methyl ester	MEC11H22	M-C11:0	2	8	0	1	0	0	0	0	0	0	0	0	0	0	0
	dodecanoic, methyl ester	MLAURATE	M-C12:0	2	9	0	1	0	0	0	0	0	0	0	0	0	0	0
	tridecanoic acid, methyl ester	MEC13H26	M-C13:0	2	10	0	1	0	0	0	0	0	0	0	0	0	0	0
	tetradecanoic acid, methyl ester	MEC14H28	M-C14:0	2	11	0	1	0	0	0	0	0	0	0	0	0	0	0
	tetradecenoic acid, methyl ester	MEC14H26	M-C14:1	2	9	2	1	0	0	0	0	0	0	0	0	0	0	0
	pentadecanoic acid, methyl ester	MEC15H30	M-C15:0	2	12	0	1	0	0	0	0	0	0	0	0	0	0	0
	hexadecanoic acid, methyl ester	MEC16H32	M-C16:0	2	13	0	1	0	0	0	0	0	0	0	0	0	0	0
	hexadecenoic acid, methyl ester	MEC16H30	M-C16:1	2	11	2	1	0	0	0	0	0	0	0	0	0	0	0
	Hexadecadienoic acid, methyl ester	MEC16H28	M-C16:2	2	9	4	1	0	0	0	0	0	0	0	0	0	0	0
	heptadecanoic acid, methyl ester	MEC17H34	M-C17:0	2	14	0	1	0	0	0	0	0	0	0	0	0	0	0
	heptadecenoic acid, methyl ester	MEC17H32	M-C17:1	2	12	2	1	0	0	0	0	0	0	0	0	0	0	0
	octadecanoic acid, methyl ester	MEC18H36	M-C18:0	2	15	0	1	0	0	0	0	0	0	0	0	0	0	0
	octadecenoic acid, methyl ester	MOLEATE	M-C18:1	2	13	2	1	0	0	0	0	0	0	0	0	0	0	0
	octadecadienoic acid, methyl ester	MEC18H32	M-C18:2	2	11	4	1	0	0	0	0	0	0	0	0	0	0	0
	octadecatrienoic acid, methyl ester	MEC18H30	M-C18:3	2	9	6	1	0	0	0	0	0	0	0	0	0	0	0
	eicosanoic acid, methyl ester	MEC20H40	M-C20:0	2	17	0	1	0	0	0	0	0	0	0	0	0	0	0
	eicosenoic acid, methyl ester	MEC20H38	M-C20:1	2	15	2	1	0	0	0	0	0	0	0	0	0	0	0
	eicosadienoic acid, methyl ester	MEC20H36	M-C20:2	2	13	4	1	0	0	0	0	0	0	0	0	0	0	0
	eicosatetraenoic acid, methyl ester	MEC20H32	M-C20:4	2	11	8	1	0	0	0	0	0	0	0	0	0	0	0
	docosanoic acid, methyl ester	MEC22H44	M-C22:0	2	19	0	1	0	0	0	0	0	0	0	0	0	0	0
	docosenoic acid, methyl ester	MEC22H42	M-C22:1	2	17	2	1	0	0	0	0	0	0	0	0	0	0	0
	tetracosanoic acid, methyl ester	MEC24H48	M-C24:0	2	21	0	1	0	0	0	0	0	0	0	0	0	0	0
	tetracosenoic acid, methyl ester	MEC24H46	M-C24:1	2	19	2	1	0	0	0	0	0	0	0	0	0	0	0

Figure D.7 Molecular description of fatty esters through the MG functional groups.

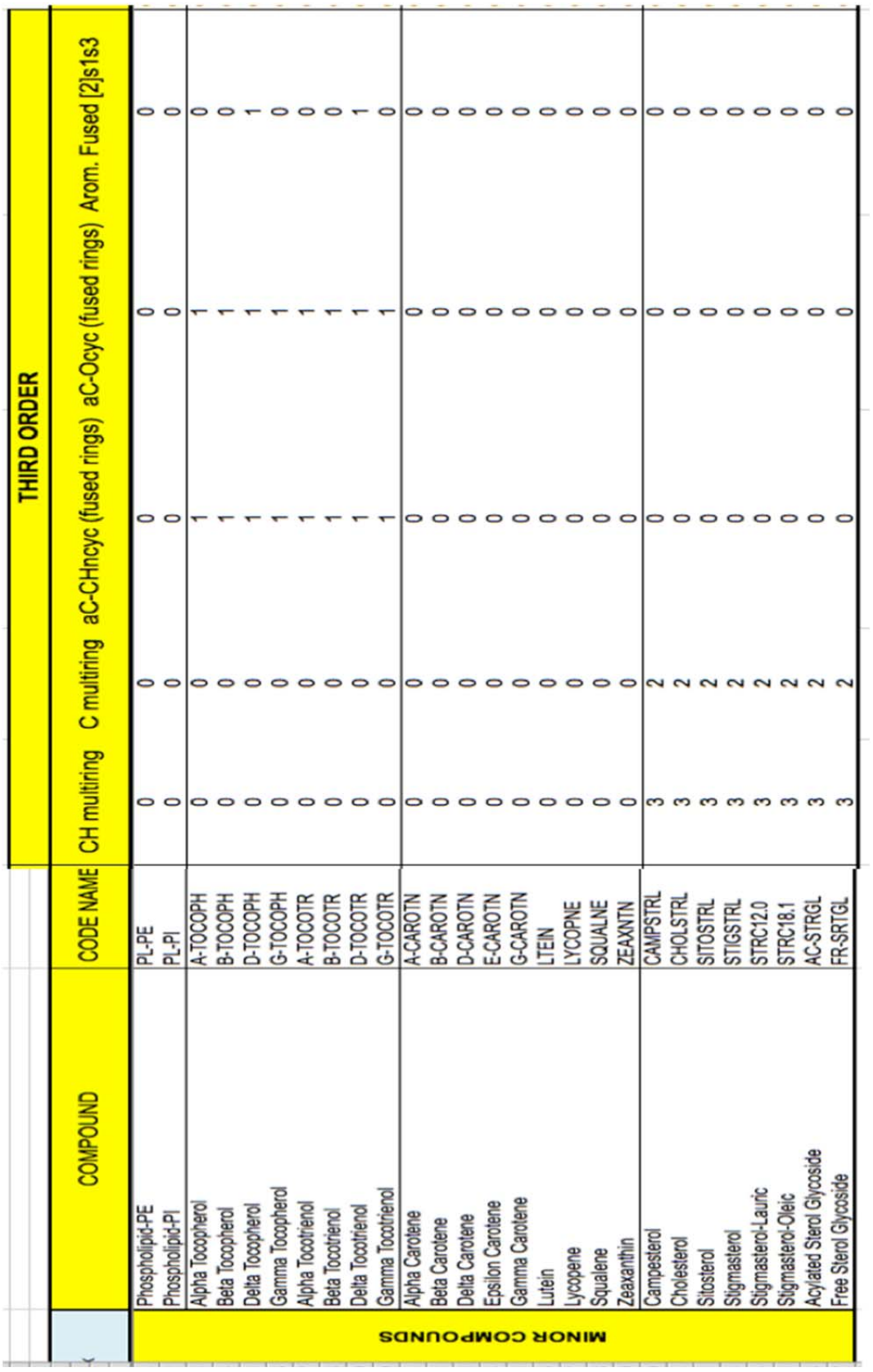


	COMPOUND	CODE NAME	NC/ND	FIRST ORDER CH3	CH2	CH	CH=CH	CH=C	CH2OOO	COOCH	CH2CH-CH2	aC-OH	CH2(cyc)	CH(cyc)	C(cyc)	CH=C(cyc)	C=O(cyc)	O(cyc)	CH2NH2	PHO4	P=O	C-
MINOR COMPOUNDS	Phosphotipid-PE	PL-PE	C41:	2	29	1	6	0	2	0	1	0	0	0	0	0	0	0	1	1	0	0
	Phosphotipid-PI	PL-PI	C45:	2	28	1	6	0	2	0	0	0	0	6	0	0	0	0	0	1	1	1
	Alpha Tocopherol	A-TOCOPH	C28:	5	9	1	0	0	0	0	0	1	0	0	1	0	0	1	0	0	0	0
	Beta Tocopherol	B-TOCOPH	C26:	5	9	3	0	0	0	0	0	1	2	0	1	0	0	1	0	0	0	0
	Delta Tocopherol	D-TOCOPH	C27:	5	9	3	0	0	0	0	0	1	2	0	1	0	0	1	0	0	0	0
	Gamma Tocopherol	G-TOCOPH	C28:	5	9	3	0	0	0	0	0	1	2	0	1	0	0	1	0	0	0	0
	Alpha Tocotrienol	A-TOCOTR	C29:	5	6	0	0	3	0	0	0	1	2	0	1	0	0	1	0	0	0	0
	Beta Tocotrienol	B-TOCOTR	C28:	5	6	0	0	3	0	0	0	1	2	0	1	0	0	1	0	0	0	0
	Delta Tocotrienol	D-TOCOTR	C27:	5	6	0	0	3	0	0	0	1	2	0	1	0	0	1	0	0	0	0
	Gamma Tocotrienol	G-TOCOTR	C28:	5	6	0	0	3	0	0	0	1	2	0	1	0	0	1	0	0	0	0
	Alpha Carotene	A-CAROTN	C40:	10	0	0	10	4	0	0	0	0	5	1	2	1	1	0	0	0	0	0
	Beta Carotene	B-CAROTN	C40:	10	0	0	10	4	0	0	0	0	6	0	2	0	2	0	0	0	0	0
	Delta Carotene	D-CAROTN	C40:	10	2	0	10	6	0	0	0	0	2	1	1	1	0	0	0	0	0	0
	Epsilon Carotene	E-CAROTN	C40:	10	0	0	10	4	0	0	0	0	4	3	3	3	0	0	0	0	0	0
	Gamma Carotene	G-CAROTN	C40:	10	2	0	10	6	0	0	0	0	3	0	1	0	1	0	0	0	0	0
	Lutein	LTEIN	C40:	10	0	0	10	4	0	0	0	0	4	2	2	0	2	0	0	0	0	0
	Lycopene	LYCOPNE	C40:	10	4	0	10	8	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	Squalene	SQUALNE	C30:	8	10	0	0	6	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	Zeaxanthin	ZEAXNTN	C40:	10	0	0	10	4	0	0	0	0	4	2	2	0	2	0	0	0	0	0
	Campesterol	CAMPSTRL	C28:	6	2	3	0	0	0	0	0	0	8	5	2	1	0	0	0	0	0	0
	Cholesterol	CHOLSTRL	C27:	5	3	2	0	0	0	0	0	0	8	5	2	1	0	0	0	0	0	0
	Sitosterol	SITOSTRL	C29:	6	3	3	0	0	0	0	0	0	8	5	2	1	0	0	0	0	0	0
	Stigmasterol	STIGSTRL	C29:	6	1	3	2	0	0	0	0	0	8	5	2	1	0	0	0	0	0	0
	Stigmastenol-Lauric	STRC12:0	C41:	7	11	3	2	0	1	0	0	0	8	5	2	1	0	0	0	0	0	0
	Stigmastenol-Oleic	STRC18:1	C47:	7	15	3	4	0	1	0	0	0	8	5	2	1	0	0	0	0	0	0
	Acylated Sterol Glycoside	AC-STRGL	C53:	7	17	2	2	1	1	0	0	0	8	10	2	1	0	1	0	0	0	1
	Free Sterol Glycoside	FR-SRTGL	C35:	6	3	2	0	1	0	0	0	0	8	10	2	1	0	1	0	0	0	1

Figure D.8 Molecular description of minor compounds through the 1st-order MG functional groups.

			SECOND ORDER															
	COMPOUND	CODE NAME	(CH3)2CH	CHn=CHm=CHp=CHk	CH3-CHm=CHn	CH2-CHm=CHn	CHp-CHm=CHn	CH(CH3)CH(CH3)	(CHn=C)cyc-CH3	CHcyc-CH=CHn	CHcyc-CH2	CHcyc-CH	CHcyc-OH	CHcyc-O-	CHcyc-OOC	)OO-CHn-CHm-OO(	Ccyc-CH3	Ccyc-CH2
MINOR COMPOUNDS	Phospholipid-PE	PL-PE	0	0	0	1	0	0	0	0	0	0	0	0	0	1	0	0
	Phospholipid-PI	PL-PI	0	0	0	6	0	0	0	0	0	0	4	2	0	1	0	0
	Alpha Tocopherol	A-TOCOPH	1	0	0	0	0	0	0	0	0	0	0	0	0	0	1	1
	Beta Tocopherol	B-TOCOPH	1	0	0	0	0	0	0	0	0	0	0	0	0	0	1	1
	Delta Tocopherol	D-TOCOPH	1	0	0	0	0	0	0	0	0	0	0	0	0	0	1	1
	Gamma Tocopherol	G-TOCOPH	1	0	0	0	0	0	0	0	0	0	0	0	0	0	1	1
	Alpha Tocotrienol	A-TOCOTR	0	0	4	5	0	0	0	0	0	0	0	0	0	0	1	1
	Beta Tocotrienol	B-TOCOTR	0	0	4	5	0	0	0	0	0	0	0	0	0	0	1	1
	Delta Tocotrienol	D-TOCOTR	0	0	4	5	0	0	0	0	0	0	0	0	0	0	1	1
	Gamma Tocotrienol	G-TOCOTR	0	0	4	5	0	0	0	0	0	0	0	0	0	0	1	1
	Alpha Carotene	A-CAROTN	0	8	4	0	0	0	1	4	0	0	0	0	0	0	4	0
	Beta Carotene	B-CAROTN	0	8	4	0	0	0	2	0	0	0	0	0	0	0	4	0
	Delta Carotene	D-CAROTN	0	9	7	2	0	0	1	1	0	0	0	0	0	0	2	0
	Epsilon Carotene	E-CAROTN	0	8	4	0	0	0	2	2	0	0	0	0	0	0	4	0
	Gamma Carotene	G-CAROTN	0	9	7	2	0	0	1	0	0	0	0	0	0	0	2	0
	Lutein	LTEIN	0	8	4	0	0	0	2	0	0	0	2	0	0	0	4	0
	Lycopene	LYCOPNE	0	10	10	4	0	0	0	0	0	0	0	0	0	0	0	0
	Squalene	SQUALNE	0	0	8	10	0	0	0	0	0	0	0	0	0	0	0	0
	Zeaxanthin	ZEAXNTN	0	8	4	0	0	0	2	0	0	0	2	0	0	0	4	0
	Campesterol	CAMPSTRL	1	0	0	0	0	1	0	0	0	1	1	0	0	0	0	0
	Cholesterol	CHOLSTRL	1	0	0	0	0	0	0	0	0	1	1	0	0	0	0	0
	Sitosterol	SITOSTRL	1	0	0	0	0	0	0	0	0	1	1	0	0	0	0	0
	Stigmasterol	STIGSTRL	1	0	0	0	2	0	0	0	0	1	1	0	0	0	0	0
	Stigmasterol-Lauric	STRC12.0	1	0	0	0	2	0	0	0	0	1	0	0	1	0	0	0
	Stigmasterol-Oleic	STRC18.1	1	0	0	2	2	0	0	0	0	1	0	0	1	0	0	0
	Acylated Sterol Glycoside	AC-STRGL	1	0	1	2	1	0	0	0	1	1	3	2	0	0	0	0
	Free Sterol Glycoside	FR-SRTGL	1	0	1	1	1	0	0	0	1	1	1	1	0	0	0	0

Figure D.9 Molecular description of minor compounds through the 2nd-order MG functional groups.



	COMPOUND	CODE NAME	THIRD ORDER				
			CH multiring	C multiring	aC-CHncyc (fused rings)	aC-Ocyc (fused rings)	Arom. Fused [2]s1s3
MINOR COMPOUNDS	Phospholipid-PE	PL-PE	0	0	0	0	0
	Phospholipid-PI	PL-PI	0	0	0	0	0
	Alpha Tocopherol	A-TOCOPH	0	0	1	1	0
	Beta Tocopherol	B-TOCOPH	0	0	1	1	0
	Delta Tocopherol	D-TOCOPH	0	0	1	1	1
	Gamma Tocopherol	G-TOCOPH	0	0	1	1	0
	Alpha Tocotrienol	A-TOCOTR	0	0	1	1	0
	Beta Tocotrienol	B-TOCOTR	0	0	1	1	0
	Delta Tocotrienol	D-TOCOTR	0	0	1	1	1
	Gamma Tocotrienol	G-TOCOTR	0	0	1	1	0
	Alpha Carotene	A-CAROTN	0	0	0	0	0
	Beta Carotene	B-CAROTN	0	0	0	0	0
	Delta Carotene	D-CAROTN	0	0	0	0	0
	Epsilon Carotene	E-CAROTN	0	0	0	0	0
	Gamma Carotene	G-CAROTN	0	0	0	0	0
	Lutein	LTEIN	0	0	0	0	0
	Lycopene	LYCOPNE	0	0	0	0	0
	Squalene	SQUALNE	0	0	0	0	0
	Zeaxanthin	ZEAXNTN	0	0	0	0	0
	Campesterol	CAMPSTRL	3	2	0	0	0
	Cholesterol	CHOLSTRL	3	2	0	0	0
	Sitosterol	SITOSTRL	3	2	0	0	0
	Stigmasterol	STIGSTRL	3	2	0	0	0
	Stigmasterol-Lauric	STRC12.0	3	2	0	0	0
	Stigmasterol-Oleic	STRC18.1	3	2	0	0	0
	Acylated Sterol Glycoside	AC-STRGL	3	2	0	0	0
	Free Sterol Glycoside	FR-SRTGL	3	2	0	0	0

Figure D.10 Molecular description of minor compounds through the 3rd-order MG functional groups.

D.3 Molecular Description through the Ceriani and Meirelles (2004) Functional Groups.

				FIRST ORDER					
x	COMPOUND	CODE NAME	NC:ND	CH3	CH2	CH=	COO	CH2-CH-CH2	OH
TRIACYLGLYCERIDES	1,2,3-trioctanoyl-sn-glycerol	CP-CP-CP	C27:0	3	18	0	3	1	0
	1,2-dioctanoyl-3-dodecanoyl-sn-glycerol	CP-CP-L	C31:0	3	22	0	3	1	0
	1-octanoyl-2-decanoyl-3-dodecanoyl-sn-glycerol	CP-C-L	C33:0	3	24	0	3	1	0
	1-octanoyl-2,3-didodecanoyl-sn-glycerol	CP-L-L	C35:0	3	26	0	3	1	0
	1-decanoyl-2,3-didodecanoyl-sn-glycerol	C-L-L	C37:0	3	28	0	3	1	0
	1-octanoyl-2-dodecanoyl-3-tetradecanoyl-sn-glycerol	CP-L-M	C37:0	3	28	0	3	1	0
	1,2,3-tridodecanoyl-sn-glycerol	L-L-L	C39:0	3	30	0	3	1	0
	1,2-didodecanoyl-3-tetradecanoyl-sn-glycerol	L-L-M	C41:0	3	32	0	3	1	0
	1-octanoyl-2-dodecanoyl-3-octadecenoyl-sn-glycerol	CP-L-O	C41:1	3	30	2	3	1	0
	1,2-didodecanoyl-3-hexadecanoyl-sn-glycerol	L-L-P	C43:0	3	34	0	3	1	0
	1-decanoyl-2-dodecanoyl-3-octadecenoyl-sn-glycerol	C-L-O	C43:1	3	32	2	3	1	0
	1-dodecanoyl-2-tetradecanoyl-3-hexadecanoyl-sn-glycerol	L-M-P	C45:0	3	36	0	3	1	0
	1,2,3-tritetradecanoyl-sn-glycerol	M-M-M	C45:0	3	36	0	3	1	0
	1,2-didodecanoyl-3-octadecenoyl-sn-glycerol	L-L-O	C45:1	3	34	2	3	1	0
	1,2-didodecanoyl-3-octadedecadienoyl-sn-glycerol	L-L-LI	C45:2	3	32	4	3	1	0
	1-dodecanoyl-2,3-dihexadecanoyl-sn-glycerol	L-P-P	C47:0	3	38	0	3	1	0
	1-dodecanoyl-2-tetradecanoyl-3-octadecanoyl-sn-glycerol	L-M-S	C47:0	3	38	0	3	1	0
	1-dodecanoyl-2-tetradecanoyl-3-octadecenoyl-sn-glycerol	L-M-O	C47:1	3	36	2	3	1	0
	1-dodecanoyl-2-tetradecanoyl-3-octadecadienoyl-sn-glycerol	L-M-LI	C47:2	3	34	4	3	1	0
	1-dodecanoyl-2-hexadecanoyl-3-octadecanoyl-sn-glycerol	L-P-S	C49:0	3	40	0	3	1	0
	1-dodecanoyl-2-hexadecanoyl-3-octadecenoyl-sn-glycerol	L-P-O	C49:1	3	38	2	3	1	0
	1-dodecanoyl-2-hexadecanoyl-3-octadecadienoyl-sn-glycerol	L-P-LI	C49:2	3	36	4	3	1	0
	1,2-ditetradecanoyl-3-octadecadienoyl-sn-glycerol	M-M-LI	C49:2	3	36	4	3	1	0
	1,2,3-trihexadecanoyl-sn-glycerol	P-P-P	C51:0	3	42	0	3	1	0
	1-tetradecanoyl-2-hexadecanoyl-3-octadecenoyl-sn-glycerol	M-P-O	C51:1	3	40	2	3	1	0
	1-dodecanoyl-2,3-dioctadecenoyl-sn-glycerol	L-O-O	C51:2	3	38	4	3	1	0
	1-tetradecanoyl-2-hexadecanoyl-3-octadecadienoyl-sn-glycerol	M-P-LI	C51:2	3	38	4	3	1	0
	1,2,3-trihexadecenoyl-sn-glycerol	PO-PO-PO	C51:3	3	36	6	3	1	0
	1,2-dihexadecanoyl-3-octadecanoyl-sn-glycerol	P-P-S	C53:0	3	44	0	3	1	0
	1,2-dihexadecanoyl-3-octadecenoyl-sn-glycerol	P-P-O	C53:1	3	42	2	3	1	0
	1,2-dihexadecanoyl-3-octadecadienoyl-sn-glycerol	P-P-LI	C53:2	3	40	4	3	1	0
	1-tetradecanoyl-2,3-dioctadecenoyl-sn-glycerol	M-O-O	C53:2	3	40	4	3	1	0
	1-tetradecanoyl-2-octadecenoyl-3-octadecadienoyl-sn-glycerol	M-O-LI	C53:3	3	38	6	3	1	0
	1,2-dihexadecenoyl-3-octadecenoyl-sn-glycerol	PO-PO-O	C53:3	3	38	6	3	1	0
	1-tetradecanoyl-2,3-octadecadienoyl-sn-glycerol	M-LI-LI	C53:4	3	36	8	3	1	0
	1-hexadecanoyl-2-octadecanoyl-3-octadecenoyl-sn-glycerol	P-S-O	C55:1	3	44	2	3	1	0
	1-hexadecanoyl-2,3-dioctadecenoyl-sn-glycerol	P-O-O	C55:2	3	42	4	3	1	0
	1-hexadecanoyl-2-octadecenoyl-3-octadecadienoyl-sn-glycerol	P-O-LI	C55:3	3	40	6	3	1	0
	1-hexadecenoyl-2,3-dioctadecenoyl-sn-glycerol	PO-O-O	C55:3	3	40	6	3	1	0
	1-hexadecenoyl-2-octadecenoyl-3-octadecadienoyl-sn-glycerol	PO-O-LI	C55:4	3	38	8	3	1	0
	1-hexadecanoyl-2,3-dioctadecadienoyl-sn-glycerol	P-LI-LI	C55:4	3	38	8	3	1	0
	1-hexadecanoyl-2-octadecenoyl-3-octadecatrienoyl-sn-glycerol	P-O-LN	C55:4	3	38	8	3	1	0
	1-hexadecanoyl-2-octadecadienoyl-3-octadecatrienoyl-sn-glycerol	P-LI-LN	C55:5	3	36	10	3	1	0
	1-hexadecenoyl-2,3-dioctadecadienoyl-sn-glycerol	PO-LI-LI	C55:5	3	36	10	3	1	0
	1-heptadecanoyl-2,3-dioctadecenoyl-sn-glycerol	MG-O-O	C56:2	3	43	4	3	1	0
	1-heptadecenoyl-2,3-dioctadecenoyl-sn-glycerol	MO-O-O	C56:3	3	41	6	3	1	0
	1,2,3-trioctadecanoyl-sn-glycerol	S-S-S	C57:0	3	48	0	3	1	0
	1-hexadecanoyl-2-octadecenoyl-3-eicosanoyl-sn-glycerol	P-O-A	C57:1	3	46	2	3	1	0
	1,2-dioctadecanoyl-3-octadecenoyl-sn-glycerol	S-S-O	C57:1	3	46	2	3	1	0
	1-octadecanoyl-2,3-dioctadecedienoyl-sn-glycerol	S-O-O	C57:2	3	44	4	3	1	0
	1-octadecanoyl-2-octadecenoyl-3-octadecadienoyl-sn-glycerol	S-O-LI	C57:3	3	42	6	3	1	0
	1,2,3-trioctadecedienoyl-sn-glycerol	O-O-O	C57:3	3	42	6	3	1	0
	1,2-dioctadecenoyl-3-octadecadienoyl-sn-glycerol	O-O-LI	C57:4	3	40	8	3	1	0
	1-octadecanoyl-2,3-dioctadecadienoyl-sn-glycerol	S-LI-LI	C57:4	3	40	8	3	1	0
	1-octadecenoyl-2,3-dioctadecadienoyl-sn-glycerol	O-LI-LI	C57:5	3	38	10	3	1	0
	1,2-dioctadecenoyl-3-octadecatrienoyl-sn-glycerol	O-O-LN	C57:5	3	38	10	3	1	0
	1,2,3-trioctadecadienoyl-sn-glycerol	LI-LI-LI	C57:6	3	36	12	3	1	0
	1-octadecenoyl-2-octadecadienoyl-3-octadecatrienoyl-sn-glycerol	O-LI-LN	C57:6	3	36	12	3	1	0
	1,2-dioctadecadienoyl-3-octadecatrienoyl-sn-glycerol	LI-LI-LN	C57:7	3	34	14	3	1	0
	1-dioctadecenoyl-2,3-dioctadecatrienoyl-sn-glycerol	O-LN-LN	C57:7	3	34	14	3	1	0
	1,2,3-trioctadecatrienoyl-sn-glycerol	LN-LN-LN	C57:9	3	30	18	3	1	0
	1,2-dioctadecenoyl-3-eicosanoyl-sn-glycerol	O-O-A	C59:2	3	46	4	3	1	0

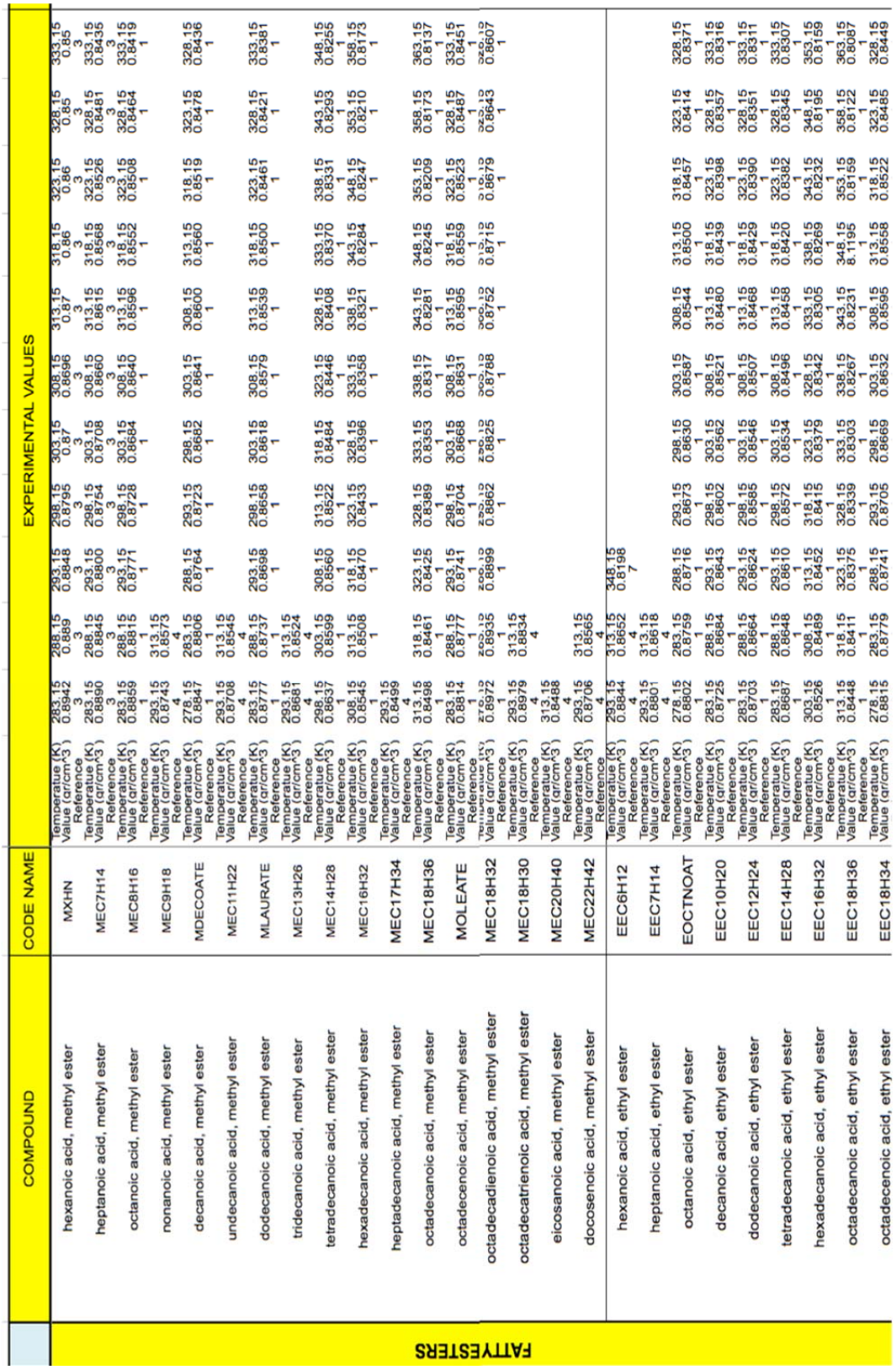
Figure D.11 Molecular description of triglycerides through the Ceriani & Meirelles (2004) MG functional groups.

Appendix D

	COMPOUND	CODE NAME	NC:ND	FIRST ORDER					
				CH3	CH2	CH=	COO	CH2-CH-CH2	OH
DIACYLGLYCERIDES	1-hexanoyl-2-octanoyl-sn-glycerol	CO-CP-OH	C17:0	2	10	0	2	1	1
	1,2-dioctanoyl-sn-glycerol	CP-CP-OH	C19:0	2	12	0	2	1	1
	1-octanoyl-2-dodecanoyl-sn-glycerol	CP-L-OH	C23:0	2	16	0	2	1	1
	1-decanoyl-2-dodecanoyl-sn-glycerol	C-L-OH	C25:0	2	18	0	2	1	1
	1,2-didodecanoyl-sn-glycerol	L-L-OH	C27:0	2	20	0	2	1	1
	1-dodecanoyl-2-tetradecanoyl-sn-glycerol	L-M-OH	C29:0	2	22	0	2	1	1
	1-octanoyl-2-octadecenoyl-sn-glycerol	CP-O-OH	C29:0	2	22	0	2	1	1
	1-dodecanoyl-2-hexadecanoyl-sn-glycerol	L-P-OH	C31:0	2	24	0	2	1	1
	1,2-ditetradecanoyl-sn-glycerol	M-M-OH	C31:0	2	24	0	2	1	1
	1-decanoyl-2-dodecanoyl-3-octadecenoyl-sn-glycerol	C-O-OH	C31:0	2	24	0	2	1	1
	1-dodecanoyl-2-octadecanoyl-sn-glycerol	L-S-OH	C33:0	2	26	0	2	1	1
	1-tetradecanoyl-2-hexadecanoyl-sn-glycerol	M-P-OH	C33:0	2	26	0	2	1	1
	1-dodecanoyl-2-octadecenoyl-sn-glycerol	L-O-OH	C33:1	2	24	2	2	1	1
	1,2-dihexadecanoyl-sn-glycerol	P-P-OH	C35:0	2	28	0	2	1	1
	1-tetradecanoyl-2-octadecenoyl-sn-glycerol	M-O-OH	C35:1	2	26	2	2	1	1
	1-tetradecanoyl-2-octadecadienoyl-sn-glycerol	M-LI-OH	C35:2	2	24	4	2	1	1
	1-hexadecanoyl-2-octadecanoyl-sn-glycerol	P-S-OH	C37:0	2	30	0	2	1	1
	1-hexadecanoyl-2-octadecenoyl-sn-glycerol	P-O-OH	C37:1	2	28	2	2	1	1
	1-hexadecanoyl-2-octadecadiienoyl-sn-glycerol	P-LI-OH	C37:2	2	26	4	2	1	1
	1-hexadecanoyl-2-octadecatrienoyl-sn-glycerol	P-LN-OH	C37:3	2	24	6	2	1	1
	1-heptadecanoyl-2-octadecenoyl-sn-glycerol	MG-O-OH	C38:1	2	29	2	2	1	1
	1-heptadecenoyl-2-octadecenoyl-sn-glycerol	MO-O-OH	C38:2	2	27	4	2	1	1
	1-hexadecanoyl-2-eicosanoyl-sn-glycerol	P-A-OH	C39:0	2	32	0	2	1	1
	1,2-dioctadecanoyl-sn-glycerol	S-S-OH	C39:0	2	32	0	2	1	1
	1-octadecanoyl-2-octadecedienoyl-sn-glycerol	S-O-OH	C39:1	2	30	2	2	1	1
	1,2-dioctadecenoyl-sn-glycerol	O-O-OH	C39:2	2	28	4	2	1	1
	1-octadecanoyl-2-octadecadienoyl-sn-glycerol	S-LI-OH	C39:2	2	28	4	2	1	1
	1-octadecenoyl-2-octadecadienoyl-sn-glycerol	O-LI-OH	C39:3	2	26	6	2	1	1
	1,2-dioctadecadienoyl-sn-glycerol	LI-LI-OH	C39:4	2	24	8	2	1	1
	1-octadecenoyl-2-octadecadienoyl-sn-glycerol	O-LN-OH	C39:4	2	24	8	2	1	1
	1-octadecadienoyl-2-octadecatrienoyl-sn-glycerol	LI-LN-OH	C39:5	2	22	10	2	1	1
	1,2-dioctadecatrienoyl-sn-glycerol	LN-LN-OH	C39:6	2	20	12	2	1	1
	1-hexadecanoyl-2-docosanoyl-sn-glycerol	P-BE-OH	C41:0	2	34	0	2	1	1
	1-octadecenoyl-2-eicosenoyl-sn-glycerol	O-A-OH	C41:1	2	32	2	2	1	1
	1-octadecadienoyl-2-eicosenoyl-sn-glycerol	LI-A-OH	C41:2	2	30	4	2	1	1
	1-octadecenoyl-2-eicosenoyl-sn-glycerol	O-GA-OH	C41:2	2	30	4	2	1	1
	1-octadecadienoyl-2-eicosenoyl-sn-glycerol	LI-GA-OH	C41:3	2	28	6	2	1	1
	1-octadecenoyl-2-docosanoyl-sn-glycerol	O-BE-OH	C43:1	2	34	2	2	1	1
	1-octadecadienoyl-2-docosanoyl-sn-glycerol	LI-BE-OH	C43:1	2	34	2	2	1	1
	1-octadecenoyl-2-docosenoyl-sn-glycerol	O-ER-OH	C43:2	2	32	4	2	1	1
	1-octadecadienoyl-2-docosenoyl-sn-glycerol	LI-ER-OH	C43:3	2	30	6	2	1	1
MONOGLYCERIDES	1-octanoyl-sn-glycerol	CP-OH-OH	C11:0	1	6	0	1	1	2
	1-decanoyl-sn-glycerol	C-OH-OH	C13:0	1	8	0	1	1	2
	1-dodecanoyl-sn-glycerol	L-OH-OH	C15:0	1	10	0	1	1	2
	1-tetredecanoyl-sn-glycerol	M-OH-OH	C17:0	1	12	0	1	1	2
	1-hexadecanoyl-sn-glycerol	P-OH-OH	C19:0	1	14	0	1	1	2
	1-heptadecanoyl-sn-glycerol	Mg-OH-OH	C20:0	1	15	0	1	1	2
	1-heptadecenoyl-sn-glycerol	Mo-OH-OH	C20:1	1	13	2	1	1	2
	1-octadecanoyl-sn-glycerol	S-OH-OH	C21:0	1	16	0	1	1	2
	1-octadecenoyl-sn-glycerol	O-OH-OH	C21:1	1	14	2	1	1	2
	1-octadecadienoyl-sn-glycerol	LI-OH-OH	C21:2	1	12	4	1	1	2
	1-octadecatrienoyl-sn-glycerol	LN-OH-OH	C21:3	1	10	6	1	1	2
	1-eicosanoyl-sn-glycerol	A-OH-OH	C23:0	1	18	0	1	1	2
	1-eicosenoyl-sn-glycerol	Ga-OH-OH	C23:1	1	16	2	1	1	2
	1-docosanoyl-sn-glycerol	Be-OH-OH	C25:0	1	20	0	1	1	2
	1-docosenoyl-sn-glycerol	Er-OH-OH	C27:0	1	22	0	1	1	2

Figure D.12 Molecular description of di- and mono- through the Ceriani & Meirelles (2004) MG functional groups.

D.4 Partial Experimental Data Sets

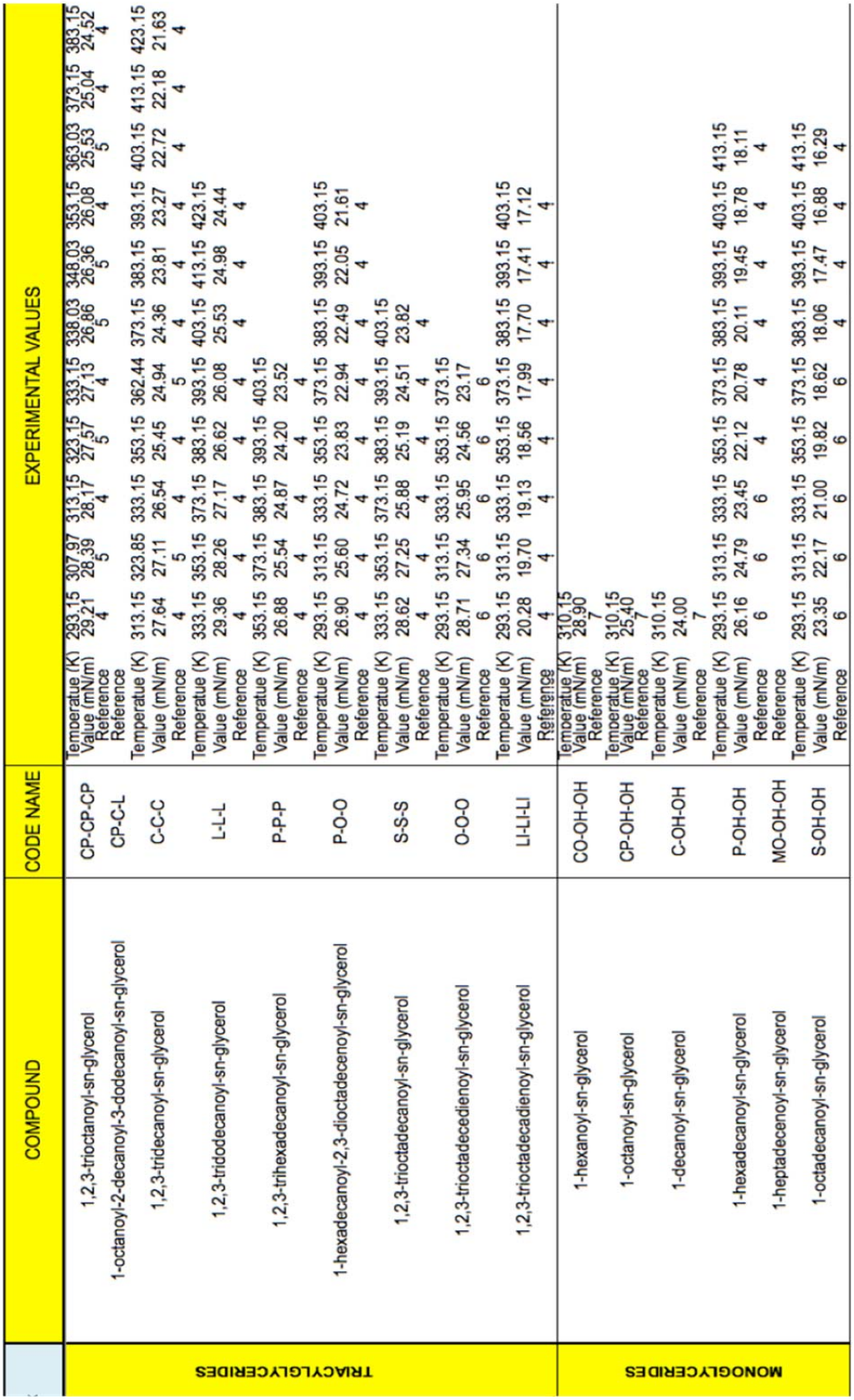


FATTYESTERS	COMPOUND	CODE NAME	EXPERIMENTAL VALUES													
	hexanoic acid, methyl ester	MXHN	Temperature (K)	283.15	288.15	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15
			Value (ar/cm^3)	0.8942	0.889	0.8848	0.8795	0.87	0.8696	0.87	0.86	0.86	0.85	0.85
			Reference	3	3	3	3	3	3	3	3	3	3	3
	heptanoic acid, methyl ester	MEC7H14	Temperature (K)	283.15	288.15	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15
			Value (ar/cm^3)	0.8890	0.8845	0.8800	0.8754	0.8708	0.8660	0.8615	0.8568	0.8526	0.8481	0.8435
			Reference	3	3	3	3	3	3	3	3	3	3	3
	octanoic acid, methyl ester	MEC8H16	Temperature (K)	283.15	288.15	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15
			Value (ar/cm^3)	0.8859	0.8815	0.8771	0.8728	0.8684	0.8640	0.8596	0.8552	0.8508	0.8464	0.8419
			Reference	1	1	1	1	1	1	1	1	1	1	1
	nonanoic acid, methyl ester	MEC9H18	Temperature (K)	293.15	313.15									
			Value (ar/cm^3)	0.8743	0.8573									
			Reference	4	4									
	decanoic acid, methyl ester	MDECOATE	Temperature (K)	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15
			Value (ar/cm^3)	0.8847	0.8806	0.8764	0.8723	0.8682	0.8641	0.8600	0.8560	0.8519	0.8478	0.8436
			Reference	1	1	1	1	1	1	1	1	1	1	1
	undecanoic acid, methyl ester	MEC11H22	Temperature (K)	293.15	313.15									
			Value (ar/cm^3)	0.8708	0.8545									
			Reference	4	4									
	dodecanoic acid, methyl ester	MLAURATE	Temperature (K)	283.15	288.15	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15
			Value (ar/cm^3)	0.8777	0.8737	0.8698	0.8658	0.8618	0.8579	0.8539	0.8500	0.8461	0.8421	0.8381
			Reference	1	1	1	1	1	1	1	1	1	1	1
	tridecanoic acid, methyl ester	MEC13H26	Temperature (K)	293.15	313.15									
			Value (ar/cm^3)	0.8681	0.8524									
			Reference	4	4									
	tetradecanoic acid, methyl ester	MEC14H28	Temperature (K)	298.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15	338.15	343.15	348.15
			Value (ar/cm^3)	0.8637	0.8599	0.8560	0.8522	0.8484	0.8446	0.8408	0.8370	0.8331	0.8293	0.8255
			Reference	1	1	1	1	1	1	1	1	1	1	1
	hexadecanoic acid, methyl ester	MEC16H32	Temperature (K)	308.15	313.15	318.15	323.15	328.15	333.15	338.15	343.15	348.15	353.15	358.15
			Value (ar/cm^3)	0.8545	0.8508	0.8470	0.8433	0.8396	0.8358	0.8321	0.8284	0.8247	0.8210	0.8173
			Reference	1	1	1	1	1	1	1	1	1	1	1
	heptadecanoic acid, methyl ester	MEC17H34	Temperature (K)	293.15										
			Value (ar/cm^3)	0.8499										
			Reference	4										
	octadecanoic acid, methyl ester	MEC18H36	Temperature (K)	313.15	318.15	323.15	328.15	333.15	338.15	343.15	348.15	353.15	358.15	363.15
			Value (ar/cm^3)	0.8498	0.8461	0.8425	0.8389	0.8353	0.8317	0.8281	0.8245	0.8209	0.8173	0.8137
			Reference	1	1	1	1	1	1	1	1	1	1	1
	octadecenoic acid, methyl ester	MOLEATE	Temperature (K)	283.15	288.15	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15
			Value (ar/cm^3)	0.8814	0.8777	0.8741	0.8704	0.8668	0.8631	0.8595	0.8559	0.8523	0.8487	0.8451
			Reference	1	1	1	1	1	1	1	1	1	1	1
	octadecadienoic acid, methyl ester	MEC18H32	Temperature (K)	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15
			Value (ar/cm^3)	0.8972	0.8935	0.8899	0.8862	0.8825	0.8788	0.8752	0.8715	0.8679	0.8643	0.8607
			Reference	1	1	1	1	1	1	1	1	1	1	1
	octadecatrienoic acid, methyl ester	MEC18H30	Temperature (K)	293.15	313.15									
			Value (ar/cm^3)	0.8979	0.8834									
			Reference	4	4									
	eicosanoic acid, methyl ester	MEC20H40	Temperature (K)	313.15										
			Value (ar/cm^3)	0.8488										
			Reference	4										
	docosenoic acid, methyl ester	MEC22H42	Temperature (K)	293.15	313.15									
			Value (ar/cm^3)	0.8706	0.8565									
			Reference	4	4									
	hexanoic acid, ethyl ester	EEC6H12	Temperature (K)	293.15	313.15	348.15								
			Value (ar/cm^3)	0.8844	0.8652	0.8198								
			Reference	4	4	7								
	heptanoic acid, ethyl ester	EEC7H14	Temperature (K)	293.15	313.15									
			Value (ar/cm^3)	0.8801	0.8618									
			Reference	4	4									
	octanoic acid, ethyl ester	EOCTNOAT	Temperature (K)	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15
			Value (ar/cm^3)	0.8802	0.8759	0.8716	0.8673	0.8630	0.8587	0.8544	0.8500	0.8457	0.8414	0.8371
			Reference	1	1	1	1	1	1	1	1	1	1	1
	decanoic acid, ethyl ester	EEC10H20	Temperature (K)	283.15	288.15	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15
			Value (ar/cm^3)	0.8725	0.8684	0.8643	0.8602	0.8562	0.8521	0.8480	0.8439	0.8398	0.8357	0.8316
			Reference	1	1	1	1	1	1	1	1	1	1	1
	dodecanoic acid, ethyl ester	EEC12H24	Temperature (K)	283.15	288.15	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15
			Value (ar/cm^3)	0.8703	0.8664	0.8624	0.8585	0.8546	0.8507	0.8468	0.8429	0.8390	0.8351	0.8311
			Reference	1	1	1	1	1	1	1	1	1	1	1
	tetradecanoic acid, ethyl ester	EEC14H28	Temperature (K)	283.15	288.15	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15
			Value (ar/cm^3)	0.8687	0.8648	0.8610	0.8572	0.8534	0.8496	0.8458	0.8420	0.8382	0.8345	0.8307
			Reference	1	1	1	1	1	1	1	1	1	1	1
	hexadecanoic acid, ethyl ester	EEC16H32	Temperature (K)	303.15	308.15	313.15	318.15	323.15	328.15	333.15	338.15	343.15	348.15	353.15
			Value (ar/cm^3)	0.8526	0.8489	0.8452	0.8415	0.8379	0.8342	0.8305	0.8269	0.8232	0.8195	0.8159
			Reference	1	1	1	1	1	1	1	1	1	1	1
	octadecanoic acid, ethyl ester	EEC18H36	Temperature (K)	313.15	318.15	323.15	328.15	333.15	338.15	343.15	348.15	353.15	358.15	363.15
			Value (ar/cm^3)	0.8448	0.8411	0.8375	0.8339	0.8303	0.8267	0.8231	0.8195	0.8159	0.8122	0.8087
			Reference	1	1	1	1	1	1	1	1	1	1	1
	octadecenoic acid, ethyl ester	EEC18H34	Temperature (K)	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15
			Value (ar/cm^3)	0.8815	0.8779	0.8741	0.8705	0.8669	0.8632	0.8595	0.8558	0.8522	0.8485	0.8449

Figure D.13 Partial set of experimental density data contained in the CAPEC_Lipids_Database

x	COMPOUND	CODE NAME	EXPERIMENTAL VALUES											
FATTY ACIDS	hexanoic acid	HEXANOIC	Temperatue (K)	293.15	348.15									
			Value (cP)	3.19	1.28									
			Reference											
	heptanoic acid	HPTANOIC	Temperatue (K)	293.15	293.15	298.15	323.15	348.15	373.15					
			Value (cP)	4.33	4.35	3.84	2.28	1.49	1.04					
			Reference	1	2	3	3	3	3					
	octanoic acid	OCTANOIC	Temperatue (K)	293.15	293.15	298.15	298.15	303.15	313.15	323.15	323.15	323.15	323.15	333.15
			Value (cP)	5.74	5.74	5.02	5.25	4.59	3.67	2.66	2.66	2.62	2.99	2.42
			Reference	2	4	3	4	4	4	3	5	2	4	4
	nonanoic acid	NONANOIC	Temperatue (K)	293.15	293.15	297.05	298.15	303.15	310.95	313.15	322.05	323.15	323.15	323.15
			Value (cP)	8.17	8.08	7.25	7.01	6.03	4.97	5.32	3.92	3.71	3.66	3.79
			Reference	6	2	7	3	6	7	6	7	3	6	1
	decanoic acid	DECANOIC	Temperatue (K)	308.15	308.30	310.95	312.50	313.15	313.15	313.15	317.60	318.15	322.05	323.10
			Value (cP)	6.68	6.76	6.33	6.07	5.86	6.10	4.98	5.31	5.15	4.96	4.70
			Reference	4	8	7	8	4	6	9	8	4	7	8
	dodecanoic acid	LAURIC	Temperatue (K)	319.15	321.15	322.05	323.15	323.15	323.15	323.40	325.50	328.15	330.00	330.20
			Value (cP)	7.54	7.17	7.47	6.86	7.30	6.96	6.89	6.51	6.03	5.87	5.82
			Reference	4	4	7	4	2	6	8	8	4	8	8
	tetradecenoic acid	MYRISTOL	Temperatue (K)	329.15	331.15	333.15	333.15	333.15	334.00	338.15	339.10	343.15	343.15	343.15
			Value (cP)	8.16	7.76	7.48	7.45	7.33	7.40	6.53	6.53	5.83	6.76	5.98
			Reference	4	4	7	4	6	8	4	8	2	2	10
	hexadecanoic acid	PALMITIC	Temperatue (K)	338.00	338.15	338.30	340.80	343.00	343.15	343.15	343.15	343.15	343.50	344.25
			Value (cP)	8.48	8.48	8.89	8.31	7.52	7.52	7.69	7.80	7.68	7.76	7.64
			Reference	11	12	8	8	11	12	6	2	10	8	7
	octadecanoic acid	STEARIC	Temperatue (K)	340.70	341.90	343.15	343.15	343.15	344.20	345.60	348.00	348.00	348.15	348.15
			Value (cP)	10.54	10.17	9.87	9.40	9.58	9.59	9.22	8.70	8.55	8.22	8.18
			Reference	8.00	8.00	2.00	2.00	10.00	8.00	8.00	8.00	11	12	6
	octadecenoic acid	OLEIC	Temperatue (K)	293.15	297.05	298.00	298.15	303.00	303.15	303.15	303.15	308.00	308.15	310.95
			Value (cP)	34.90	29.00	29.22	29.22	24.16	24.16	23.77	24.08	20.24	20.24	17.70
			Reference	13	7	11	12	11	12	6	13	11	12	7
	octadecatrienoic acid	LINOLENI	Temperatue (K)	293.15	303.15	313.15	323.15	333.15	343.15					
			Value (cP)	14.10	11.25	8.01	6.48	5.28	4.51					
			Reference	14	14	14	14	14	14					
	docosenoic acid	ERUCIC	Temperatue (K)	310.95	322.05	333.15	344.25	355.35	372.05	383.15				
			Value (cP)	32.30	22.40	15.90	11.90	8.90	6.18	5.16				
			Reference	7	7	7	7	7	7	7				

Figure D.14 Partial set of experimental surface tension data contained in the CAPEC_Lipids_Database



	COMPOUND	CODE NAME	EXPERIMENTAL VALUES												
TRIACYLGLYCERIDES	1,2,3-trioctanoyl-sn-glycerol	CP-CP-CP	Temperature (K)	293.15	307.97	313.15	323.15	333.15	338.03	348.03	353.15	363.03	373.15	383.15
			Value (mN/m)	29.21	28.39	28.17	27.57	27.13	26.86	26.36	26.08	25.53	25.04	24.52
			Reference	4	5	4	5	4	5	5	4	5	4	4
	1-octanoyl-2-decanoyl-3-dodecanoyl-sn-glycerol	CP-C-L	Temperature (K)	313.15	323.85	333.15	353.15	362.44	373.15	383.15	393.15	403.15	413.15	423.15
			Value (mN/m)	27.64	27.11	26.54	25.45	24.94	24.36	23.81	23.27	22.72	22.18	21.63
			Reference	4	5	4	4	5	4	4	4	4	4	4
	1,2,3-tridecanoyl-sn-glycerol	C-C-C	Temperature (K)	333.15	353.15	373.15	383.15	393.15	403.15	413.15	423.15			
			Value (mN/m)	29.36	28.26	27.17	26.62	26.08	25.53	24.98	24.44			
			Reference	4	4	4	4	4	4	4	4			
	1,2,3-tridodecanoyl-sn-glycerol	L-L-L	Temperature (K)	353.15	373.15	383.15	393.15	403.15						
			Value (mN/m)	26.88	25.54	24.87	24.20	23.52						
			Reference	4	4	4	4	4						
	1,2,3-trihexadecanoyl-sn-glycerol	P-P-P	Temperature (K)	293.15	313.15	333.15	353.15	373.15	383.15	393.15	403.15			
			Value (mN/m)	26.90	25.60	24.72	23.83	22.94	22.49	22.05	21.61			
			Reference	4	4	4	4	4	4	4	4			
	1-hexadecanoyl-2,3-dioctadecenoyl-sn-glycerol	P-O-O	Temperature (K)	333.15	353.15	373.15	383.15	393.15	403.15					
			Value (mN/m)	28.62	27.25	25.88	25.19	24.51	23.82					
			Reference	4	4	4	4	4	4					
	1,2,3-trioctadecanoyl-sn-glycerol	S-S-S	Temperature (K)	293.15	313.15	333.15	353.15	373.15						
			Value (mN/m)	28.71	27.34	25.95	24.56	23.17						
			Reference	6	6	6	6	6						
	1,2,3-trioctadecedienoyl-sn-glycerol	O-O-O	Temperature (K)	293.15	313.15	333.15	353.15	373.15	383.15	393.15	403.15			
			Value (mN/m)	20.28	19.70	19.13	18.56	17.99	17.70	17.41	17.12			
			Reference	4	4	4	4	4	4	4	4			
	1,2,3-trioctadecadienoyl-sn-glycerol	LI-LI-LI	Temperature (K)	310.15										
			Value (mN/m)	28.90										
			Reference	7										
MONOGLYCERIDES	1-hexanoyl-sn-glycerol	CO-OH-OH	Temperature (K)	310.15										
			Value (mN/m)	25.40										
			Reference	7										
	1-octanoyl-sn-glycerol	CP-OH-OH	Temperature (K)	310.15										
			Value (mN/m)	24.00										
			Reference	7										
	1-decanoyl-sn-glycerol	C-OH-OH	Temperature (K)	293.15	313.15	333.15	353.15	373.15	383.15	393.15	403.15	413.15		
			Value (mN/m)	26.16	24.79	23.45	22.12	20.78	20.11	19.45	18.78	18.11		
			Reference	6	6	6	4	4	4	4	4	4		
	1-hexadecanoyl-sn-glycerol	P-OH-OH	Temperature (K)	293.15	313.15	333.15	353.15	373.15	383.15	393.15	403.15	413.15		
			Value (mN/m)	23.35	22.17	21.00	19.82	18.62	18.06	17.47	16.88	16.29		
			Reference	6	6	6	6	6	4	4	4	4		
	1-heptadecenoyl-sn-glycerol	MO-OH-OH	Temperature (K)	293.15	313.15	333.15	353.15	373.15	383.15	393.15	403.15	413.15		
			Value (mN/m)	23.35	22.17	21.00	19.82	18.62	18.06	17.47	16.88	16.29		
			Reference	6	6	6	6	6	4	4	4	4		
	1-octadecanoyl-sn-glycerol	S-OH-OH	Temperature (K)	293.15	313.15	333.15	353.15	373.15	383.15	393.15	403.15	413.15		
			Value (mN/m)	23.35	22.17	21.00	19.82	18.62	18.06	17.47	16.88	16.29		
			Reference	6	6	6	6	6	4	4	4	4		

Figure D.15 Partial set of experimental surface tension data contained in the CAPEC_Lipids_Databa

D.1 Single Value Pure Component Property Estimations

FATTY ACID	CODE NAME	NC:ND	CAS NR
hexanoic acid	HEXANOIC	C6:0	000142-62-1
heptanoic acid	HPTANOIC	C7:0	000111-14-8
octanoic acid	OCTANOIC	C8:0	000124-07-2
nonanoic acid	NONANOIC	C9:0	
decanoic acid	DECANOIC	C10:0	000334-48-5
undecanoic acid	UNDCNOIC	C11:0	000112-37-8
dodecanoic acid	LAURIC	C12:0	000143-07-7
tridecanoic acid	TRDCNOIC	C13:0	000638-53-9
tetradecanoic acid	MYRISTIC	C14:0	000544-63-8
tetradecenoic acid	MYRISTOL	C14:1	000544-64-9
pentadecanoic acid	PNDCNIOC	C15:0	001002-84-2
hexadecanoic acid	PALMITIC	C16:0	000057-10-3
hexadecenoic acid	PALMTOL	C16:1	002091-29-4
heptadecanoic acid	MARGARIC	C17:0	000506-12-7
heptadecenoic acid	MARGROL	C17:1	029743-97-3
octadecanoic acid	STEARIC	C18:0	000057-11-4
octadecenoic acid	OLEIC	C18:1	000112-80-1
octadecadienoic acid	LINOLEIC	C18:2	000060-33-3
octadecatrienoic acid	LINOLENI	C18:3	000463-40-1
eicosanoic acid	C20ACID	C20:0	000506-30-9
eicosenoic acid	GADOLEIC	C20:1	000506-31-0
eicosadienoic acid	GADOLENC	C20:2	002091-39-6
eicosatetraenoic acid	EPAACID	C20:4	000506-32-1
eicosapentaenoic acid	DPAACID	C20:5	010417-94-4
docosanoic acid	BEHENIC	C22:0	000112-85-6
docosenoic acid	ERUCIC	C22:1	000112-86-7
tetracosanoic acid	LIGNOCRC	C24:0	000557-59-5
tetracosenoic acid	NERVNIC	C24:1	000506-37-6

TRIGLYCERIDE	CODE NAME	NC:ND	CAS NR
1,2,3-trioctanoyl-sn-glycerol	CP-CP-CP	C27:0	-
1,2-dioctanoyl-3-dodecanoyl-sn-glycerol	CP-CP-L	C31:0	-
1-octanoyl-2-decanoyl-3-dodecanoyl-sn-glycerol	CP-C-L	C33:0	-
1-octanoyl-2,3-didodecanoyl-sn-glycerol	CP-L-L	C35:0	-
1-decanoyl-2,3-didodecanoyl-sn-glycerol	C-L-L	C37:0	-
1-octanoyl-2-dodecanoyl-3-tetradecanoyl-sn-glycerol	CP-L-M	C37:0	-
1,2,3-tridodecanoyl-sn-glycerol	L-L-L	C39:0	000538-24-9
1,2-didodecanoyl-3-tetradecanoyl-sn-glycerol	L-L-M	C41:0	-
1-octanoyl-2-dodecanoyl-3-octadecenoyl-sn-glycerol	CP-L-O	C41:1	-
1,2-didodecanoyl-3-hexadecanoyl-sn-glycerol	L-L-P	C43:0	-
1-decanoyl-2-dodecanoyl-3-octadecenoyl-sn-glycerol	C-L-O	C43:1	-
1-dodecanoyl-2-tetradecanoyl-3-hexadecanoyl-sn-glycerol	L-M-P	C45:0	-
1,2,3-tritetradecanoyl-sn-glycerol	M-M-M	C45:0	-
1,2-didodecanoyl-3-octadecenoyl-sn-glycerol	L-L-O	C45:1	-
1,2-didodecanoyl-3-octadedecadienoyl-sn-glycerol	L-L-LI	C45:2	-
1-dodecanoyl-2,3-dihexadecanoyl-sn-glycerol	L-P-P	C47:0	-

Appendix D

TRIGLYCERIDE	CODE NAME	NC:ND	CAS NR
1-dodecanoyl-2-tetradecanoyl-3-octadecanoyl-sn-glycerol	L-M-S	C47:0	-
1-dodecanoyl-2-tetradecanoyl-3-octadecenoyl-sn-glycerol	L-M-O	C47:1	-
1-dodecanoyl-2-tetradecanoyl-3-octadecadienoyl-sn-glycerol	L-M-LI	C47:2	-
1-dodecanoyl-2-hexadecanoyl-3-octadecanoyl-sn-glycerol	L-P-S	C49:0	-
1-dodecanoyl-2-hexadecanoyl-3-octadecenoyl-sn-glycerol	L-P-O	C49:1	-
1-dodecanoyl-2-hexadecanoyl-3-octadecadienoyl-sn-glycerol	L-P-LI	C49:2	-
1,2-ditetradecanoyl-3-octadecadienoyl-sn-glycerol	M-M-LI	C49:2	-
1,2,3-trihexadecanoyl-sn-glycerol	P-P-P	C51:0	000555-44-2
1-tetradecanoyl-2-hexadecanoyl-3-octadecenoyl-sn-glycerol	M-P-O	C51:1	-
1-dodecanoyl-2,3-dioctadecenoyl-sn-glycerol	L-O-O	C51:2	-
1-tetradecanoyl-2-hexadecanoyl-3-octadecadienoyl-sn-glycerol	M-P-LI	C51:2	-
1,2,3-trihexadecenoyl-sn-glycerol	PO-PO-PO	C51:3	-
1,2-dihexadecanoyl-3-octadecanoyl-sn-glycerol	P-P-S	C53:0	-
1,2-dihexadecanoyl-3-octadecenoyl-sn-glycerol	P-P-O	C53:1	002442-56-0
1,2-dihexadecanoyl-3-octadecadienoyl-sn-glycerol	P-P-LI	C53:2	-
1-tetradecanoyl-2,3-dioctadecenoyl-sn-glycerol	M-O-O	C53:2	-
1-tetradecanoyl-2-octadecenoyl-3-octadecadienoyl-sn-glycerol	M-O-LI	C53:3	-
1,2-dihexadecenoyl-3-octadecenoyl-sn-glycerol	PO-PO-O	C53:3	-
1-tetradecanoyl-2,3-octadecadienoyl-sn-glycerol	M-LI-LI	C53:4	-
1-hexadecanoyl-2-octadecanoyl-3-octadecenoyl-sn-glycerol	P-S-O	C55:1	002190-27-4
1-hexadecanoyl-2,3-dioctadecenoyl-sn-glycerol	P-O-O	C55:2	-
1-hexadecanoyl-2-octadecenoyl-3-octadecadienoyl-sn-glycerol	P-O-LI	C55:3	-
1-hexadecenoyl-2,3-dioctadecenoyl-sn-glycerol	PO-O-O	C55:3	-
1-hexadecenoyl-2-octadecenoyl-3-octadecadienoyl-sn-glycerol	PO-O-LI	C55:4	-
1-hexadecanoyl-2,3-dioctadecadienoyl-sn-glycerol	P-LI-LI	C55:4	-
1-hexadecanoyl-2-octadecenoyl-3-octadecatrienoyl-sn-glycerol	P-O-LN	C55:4	-
1-hexadecanoyl-2-octadecadienoyl-3-octadecatrienoyl-sn-glycerol	P-LI-LN	C55:5	-
1-hexadecenoyl-2,3-dioctadecadienoyl-sn-glycerol	PO-LI-LI	C55:5	-
1-heptadecanoyl-2,3-dioctadecenoyl-sn-glycerol	MG-O-O	C56:2	-
1-heptadecenoyl-2,3-dioctadecenoyl-sn-glycerol	MO-O-O	C56:3	-
1,2,3-trioctadecanoyl-sn-glycerol	S-S-S	C57:0	000555-43-1
1-hexadecanoyl-2-octadecenoyl-3-eicosanoyl-sn-glycerol	P-O-A	C57:1	-
1,2-dioctadecanoyl-3-octadecenoyl-sn-glycerol	S-S-O	C57:1	-
1-octadecanoyl-2,3-dioctadecedienoyl-sn-glycerol	S-O-O	C57:2	-
1-octadecanoyl-2-octadecenoyl-3-octadecadienoyl-sn-glycerol	S-O-LI	C57:3	-
1,2,3-trioctadecedienoyl-sn-glycerol	O-O-O	C57:3	000122-32-7
1,2-dioctadecenoyl-3-octadecadienoyl-sn-glycerol	O-O-LI	C57:4	-
1-octadecanoyl-2,3-dioctadecadienoyl-sn-glycerol	S-LI-LI	C57:4	-
1-octadecenoyl-2,3-dioctadecadienoyl-sn-glycerol	O-LI-LI	C57:5	-
1,2-dioctadecenoyl-3-octadecatrienoyl-sn-glycerol	O-O-LN	C57:5	-
1,2,3-trioctadecadienoyl-sn-glycerol	LI-LI-LI	C57:6	000537-40-6
1-octadecenoyl-2-octadecadienoyl-3-octadecatrienoyl-sn-glycerol	O-LI-LN	C57:6	-
1,2-dioctadecadienoyl-3-octadecatrienoyl-sn-glycerol	LI-LI-LN	C57:7	-
1-dioctadecenoyl-2,3-dioctadecatrienoyl-sn-glycerol	O-LN-LN	C57:7	-
1,2,3-trioctadecatrienoyl-sn-glycerol	LN-LN-LN	C57:9	-
1,2-dioctadecenoyl-3-eicosanoyl-sn-glycerol	O-O-A	C59:2	-

Appendix D

TRIGLYCERIDE	CODE NAME	NC:ND	CAS NR
1-hexadecanoyl-2-octadecadienoyl-3-docosanoyl-sn-glycerol	P-LI-BE	C59:2	-
1-octadecenoyl-2-octadecadienoyl-3-eicosanoyl-sn-glycerol	O-LI-A	C59:3	-
1,2-dioctadecenoyl-3-eicosenoyl-sn-glycerol	O-O-GA	C59:3	-
1,2-dioctadecadienoyl-3-eicosanoyl-sn-glycerol	LI-LI-A	C59:3	-
1-octadecenoyl-2-octadecadienoyl-3-eicosenoyl-sn-glycerol	O-LI-GA	C59:4	-
1,2-dioctadecenoyl-3-docosanoyl-sn-glycerol	O-O-BE	C61:2	-
1-octadecenoyl-2-octadecadienoyl-3-docosanoyl-sn-glycerol	O-LI-BE	C61:3	-
1,2-dioctadecenoyl-3-docosenoyl-sn-glycerol	O-O-ER	C61:3	-
1,2-dioctadecadienoyl-3-docosanoyl-sn-glycerol	LI-LI-BE	C61:4	-
1-octadecenoyl-2-octadecadienoyl-3-docosenoyl-sn-glycerol	O-LI-ER	C61:4	-
1,2,3-trieicosanoyl-sn-glycerol	A-A-A	C63:0	-

DIGLYCERIDE	CODE NAME	NC:ND	CAS NR
1-hexanoyl-2-octanoyl-sn-glycerol	CO-CP-OH	C17:0	
1,2-dioctanoyl-sn-glycerol	CP-CP-OH	C19:0	
1-octanoyl-2-dodecanoyl-sn-glycerol	CP-L-OH	C23:0	-
1-decanoyl-2-dodecanoyl-sn-glycerol	C-L-OH	C22:0	-
1,2-didodecanoyl-sn-glycerol	L-L-OH	C24:0	040431-02-5
1-dodecanoyl-2-tetradecanoyl-sn-glycerol	L-M-OH	C26:0	-
1-octanoyl-2-octadecenoyl-sn-glycerol	CP-O-OH	C29:0	-
1-dodecanoyl-2-hexadecanoyl-sn-glycerol	L-P-OH	C31:0	-
1,2-ditetradecanoyl-sn-glycerol	M-M-OH	C31:0	007770-09-4
1-decanoyl-2-dodecanoyl-3-octadecenoyl-sn-glycerol	C-O-OH	C31:0	-
1-dodecanoyl-2-octadecanoyl-sn-glycerol	L-S-OH	C33:0	-
1-tetradecanoyl-2-hexadecanoyl-sn-glycerol	M-P-OH	C33:0	-
1-dodecanoyl-2-octadecenoyl-sn-glycerol	L-O-OH	C33:1	-
1,2-dihexadecanoyl-sn-glycerol	P-P-OH	C35:0	026657-95-4
1-tetradecanoyl-2-octadecenoyl-sn-glycerol	M-O-OH	C35:1	-
1-tetradecanoyl-2-octadecadienoyl-sn-glycerol	M-LI-OH	C35:2	-
1-hexadecanoyl-2-octadecanoyl-sn-glycerol	P-S-OH	C37:0	-
1-hexadecanoyl-2-octadecenoyl-sn-glycerol	P-O-OH	C37:1	003123-73-7
1-hexadecanoyl-2-octadecadiienoyl-sn-glycerol	P-LI-OH	C37:2	-
1-hexadecanoyl-2-octadecatrienoyl-sn-glycerol	P-LN-OH	C37:3	-
1-heptadecanoyl-2-octadecenoyl-sn-glycerol	MG-O-OH	C38:1	-
1-heptadecenoyl-2-octadecenoyl-sn-glycerol	MO-O-OH	C38:2	-
1-hexadecanoyl-2-eicosanoyl-sn-glycerol	P-A-OH	C39:0	-
1,2-dioctadecanoyl-sn-glycerol	S-S-OH	C39:0	001323-83-7
1-octadecanoyl-2-octadecedienoyl-sn-glycerol	S-O-OH	C39:1	-
1,2-dioctadecenoyl-sn-glycerol	O-O-OH	C39:2	025637-84-7
1-octadecanoyl-2-octadecadienoyl-sn-glycerol	S-LI-OH	C39:2	-
1-octadecenoyl-2-octadecadienoyl-sn-glycerol	O-LI-OH	C39:3	-
1,2-dioctadecadienoyl-sn-glycerol	LI-LI-OH	C39:4	030606-27-0
1-octadecenoyl-2-octadecadienoyl-sn-glycerol	O-LN-OH	C39:4	-
1-octadecadienoyl-2-octadecatrienoyl-sn-glycerol	LI-LN-OH	C39:5	-
1,2-dioctadecatrienoyl-sn-glycerol	LN-LN-OH	C39:6	-
1-hexadecanoyl-2-docosanoyl-sn-glycerol	P-BE-OH	C39:0	-
1-octadecenoyl-2-eicosenoyl-sn-glycerol	O-A-OH	C41:1	-
1-octadecadienoyl-2-eicosenoyl-sn-glycerol	LI-A-OH	C41:2	-
1-octadecenoyl-2-eicosenoyl-sn-glycerol	O-GA-OH	C41:2	-
1-octadecadienoyl-2-eicosenoyl-sn-glycerol	LI-GA-OH	C41:3	-

Appendix D

DIGLYCERIDE	CODE NAME	NC:ND	CAS NR
1-octadecenoyl-2-docosanoyl-sn-glycerol	O-BE-OH	C43:1	-
1-octadecadienoyl-2-docosanoyl-sn-glycerol	LI-BE-OH	C43:1	-
1-octadecenoyl-2-docosenoyl-sn-glycerol	O-ER-OH	C43:2	-
1-octadecadienoyl-2-docosenoyl-sn-glycerol	LI-ER-OH	C43:3	-

MONOGLYCERIDE	CODE NAME	NC:ND	CAS NR
1-octanoyl-sn-glycerol	CP-OH-OH	C11:0	026402-26-6
1-decanoyl-sn-glycerol	C-OH-OH	C13:0	026402-22-2
1-dodecanoyl-sn-glycerol	L-OH-OH	C15:0	027215-38-9
1-tetredecanoyl-sn-glycerol	M-OH-OH	C17:0	027214-38-6
1-hexadecanoyl-sn-glycerol	P-OH-OH	C19:0	026657-96-5
1-heptadecanoyl-sn-glycerol	Mg-OH-OH	C20:0	-
1-heptadecenoyl-sn-glycerol	Mo-OH-OH	C20:1	-
1-octadecanoyl-sn-glycerol	S-OH-OH	C21:0	031566-31-1
1-octadecenoyl-sn-glycerol	O-OH-OH	C21:1	025496.72-4
1-octadecadienoyl-sn-glycerol	LI-OH-OH	C21:2	026545-74-4
1-octadecatrienoyl-sn-glycerol	LN-OH-OH	C21:3	026545-75-5
1-eicosanoyl-sn-glycerol	A-OH-OH	C23:0	035474-99-8
1-eicosenoyl-sn-glycerol	Ga-OH-OH	C23:1	-
1-docosanoyl-sn-glycerol	Be-OH-OH	C25:0	-
1-docosenoyl-sn-glycerol	Er-OH-OH	C27:0	-

FATTY ESTER	CODE NAME	NC:ND	CAS NR
hexanoic acid, methyl ester	MXHN	M-C6:0	000106-70-7
heptanoic acid, methyl ester	MEC7H14	M-C7:0	000106-73-0
octanoic acid, methyl ester	MEC8H16	M-C8:0	000111-11-5
nonanoic acid, methyl ester	MEC9H18	M-C9:0	001731-84-6
decanoic acid, methyl ester	MDECOATE	M-C10:0	000110-42-9
undecanoic acid, methyl ester	MEC11H22	M-C11:0	001731-86-8
dodecanoic, methyl ester	MLAURATE	M-C12:0	000111-82-0
tridecanoic acid, methyl ester	MEC13H26	M-C13:0	001731-88-0
tetradecanoic acid, methyl ester	MEC14H28	M-C14:0	000124-10-7
tetradecenoic acid, methyl ester	MEC14H26	M-C14:1	56219-06-8
pentadecanoic acid, methyl ester	MEC15H30	M-C15:0	007132-64-1
hexadecanoic acid, methyl ester	MEC16H32	M-C16:0	000112-39-0
hexadecenoic acid, methyl ester	MEC16H30	M-C16:1	001120-25-8
Hexadecadienoic acid, methyl ester	MEC16H28	M-C16:2	-
heptadecanoic acid, methyl ester	MEC17H34	M-C17:0	001731-92-6
heptadecenoic acid, methyl ester	MEC17H32	M-C17:1	075190-82-8
octadecanoic acid, methyl ester	MEC18H36	M-C18:0	000112-61-8
octadecenoic acid, methyl ester	MOLEATE	M-C18:1	000112-62-9
octadecadienoic acid, methyl ester	MEC18H32	M-C18:2	000112-63-0
octadecatrienoic acid, methyl ester	MEC18H30	M-C18:3	000301-00-8
eicosanoic acid, methyl ester	MEC20H40	M-C20:0	001120-28-1
eicosenoic acid, methyl ester	MEC20H38	M-C20:1	017735-94-3
eicosadienoic acid, methyl ester	MEC20H36	M-C20:2	-
eicosatetraenoic acid, methyl ester	MEC20H32	M-C20:4	-
docosanoic acid, methyl ester	MEC22H44	M-C22:0	000929-77-1
docosenoic acid, methyl ester	MEC22H42	M-C22:1	001120-34-9
tetracosanoic acid, methyl ester	MEC24H48	M-C24:0	002442-49-1
tetracosenoic acid, methyl ester	MEC24H46	M-C24:1	002733-88-2

FATTY ESTER	CODE NAME	NC:ND	CAS NR
hexanoic acid, ethyl ester	EEC6H12	E-C6:0	000123-66-0
heptanoic acid, ethyl ester	EEC7H14	E-C7:0	000106-30-9
octanoic acid, ethyl ester	EOCTNOAT	E-C8:0	000106-32-1
nonanoic acid, ethyl ester	ENONNOAT	E-C9:0	000123-29-5
decanoic acid, ethyl ester	EEC10H20	E-C10:0	000110-38-3
undecanoic acid, ethyl ester	EEC11H22	E-C11:0	000627-90-7
dodecanoic, ethyl ester	EEC12H24	E-C12:0	000106-33-2
tridecanoic acid, ethyl ester	EEC13H26	E-C13:0	028267-29-0
tetradecanoic acid, ethyl ester	EEC14H28	E-C14:0	000124-06-1
tetradecenoic acid, ethyl ester	EEC14H26	E-C14:1	-
pentadecanoic acid, ethyl ester	EEC15H30	E-C15:0	041114-00-5
hexadecanoic acid, ethyl ester	EEC16H32	E-C16:0	000628-97-7
hexadecenoic acid, ethyl ester	EEC16H30	E-C16:1	056219-10-4
Hexadecadienoic acid, ethyl ester	EEC16H28	E-C16:2	-
heptadecanoic acid, ethyl ester	EEC17H34	E-C17:0	014010-23-2
heptadecenoic acid, ethyl ester	EEC17H32	E-C17:1	-
octadecanoic acid, ethyl ester	EEC18H36	E-C18:0	000111-61-5
octadecenoic acid, ethyl ester	EEC18H34	E-C18:1	000111-62-6
octadecadienoic acid, ethyl ester	EEC18H32	E-C18:2	000544-35-4
octadecatrienoic acid, ethyl ester	EEC18H30	E-C18:3	001191-41-9
eicosanoic acid, ethyl ester	EEC20H40	E-C20:0	018281-05-5
eicosenoic acid, ethyl ester	EEC20H38	E-C20:1	
eicosadienoic acid, ethyl ester	EEC20H36	E-C20:2	103213-62-3
eicosatetraenoic acid, ethyl ester	EEC20H32	E-C20:4	001808-26-0
docosanoic acid, ethyl ester	EEC22H44	E-C22:0	-
docosenoic acid, ethyl ester	EEC22H42	E-C22:1	006045-37-0
tetracosanoic acid, ethyl ester	EEC24H48	E-C24:0	024634-95-5
tetracosenoic acid, ethyl ester	EEC24H46	E-C24:1	-

MINOR COMPOUNDS	CODE NAME	NC:ND	CAS NR
Phospholipid-PE	PL-PE	C41:	-
Phospholipid-PI	PL-PI	C45:	-
Alpha Tocopherol	A-TOCOPH	C29:	-
Beta Tocopherol	B-TOCOPH	C28:	-
Delta Tocopherol	D-TOCOPH	C27:	-
Gamma Tocopherol	G-TOCOPH	C28:	-
Alpha Tocotrienol	A-TOCOTR	C29:	-
Beta Tocotrienol	B-TOCOTR	C28:	-
Delta Tocotrienol	D-TOCOTR	C27:	-
Gamma Tocotrienol	G-TOCOTR	C28:	-
Alpha Carotene	A-CAROTN	C40:	-
Beta Carotene	B-CAROTN	C40:	-
Delta Carotene	D-CAROTN	C40:	-
Epsilon Carotene	E-CAROTN	C40:	-
Gamma Carotene	G-CAROTN	C40:	-
Lutein	LTEIN	C40:	-
Lycopene	LYCOPNE	C40:	-
Squalene	SQUALNE	C30:	-
Zeaxanthin	ZEAXNTN	C40:	-

MINOR COMPOUNDS	CODE NAME	NC:ND	CAS NR
Campesterol	CAMPSTRL	C28:	-
Cholesterol	CHOLSTRL	C27:	-
Sitosterol	SITOSTRL	C29:	-
Stigmasterol	STIGSTRL	C29:	-
Stigmasterol-Lauric	STRC12.0	C41:	-
Stigmasterol-Oleic	STRC18.1	C47:	-
Acylated Sterol Glycoside	AC-STRGL	C53:	-
Free Sterol Glycoside	FR-SRTGL	C35:	-

D.2 Single Value Pure Component Properties

FFA	MW	NMP (K)	NBP (K)	Tc (K)	Pc (kPa)	Vc (m^3/kgmol)	Zc
HEXANOIC	116.160	270.15	478.85	659.10	3308.00	0.37720	0.22800
HPTANOIC	130.187	265.83	496.15	676.84	3043.00	0.42970	0.23200
OCTANOIC	144.214	289.65	512.85	694.26	2779.00	0.49900	0.24000
DECANOIC	172.268	304.75	543.15	722.10	2250.00	0.60800	0.22800
UNDCNOIC	186.295	301.63	557.35	732.00	2080.00	0.65300	0.22300
LAURIC	200.321	316.98	571.85	743.00	1940.00	0.70500	0.22100
TRDCNOIC	214.348	315.01	585.25	754.00	1810.00	0.75800	0.21900
MYRISTIC	228.375	327.37	599.35	765.00	1700.00	0.81100	0.21700
MYRISTOL	226.354	358.12	595.93	807.18	1727.37	0.83581	0.21514
PNDCNIOC	242.402	325.68	612.05	775.00	1600.00	0.86400	0.21500
PALMITIC	256.429	335.66	624.15	785.00	1510.00	0.91700	0.21200
PALMTOL	254.407	364.52	608.00	825.24	1546.80	0.94921	0.21400
MARGARIC	270.456	334.25	635.75	793.00	1430.00	0.96900	0.21000
MARGROL	268.434	367.62	618.00	833.77	1472.34	1.00591	0.21365
STEARIC	284.483	342.75	648.35	804.00	1360.00	1.02000	0.20800
OLEIC	282.467	286.53	633.00	781.00	1390.00	1.00000	0.21400
LINOLEIC	280.451	268.15	628.00	775.00	1410.00	0.99000	0.21700
LINOLENI	278.435	262.05	632.00	780.00	1440.00	1.07000	0.23800
C20ACID	312.536	348.23	670.15	821.00	1240.00	1.13000	0.20500
GADOLEIC	310.513	376.54	644.10	857.62	1294.88	1.17601	0.21357
GADOLENC	308.497	379.13	630.00	860.21	1304.02	1.16441	0.21231
EPAACID	304.466	384.17	609.60	865.32	1322.84	1.14121	0.20984
DPAACID	302.450	386.63	601.70	867.84	1332.54	1.12961	0.20862
BEHENIC	340.590	352.15	690.00	855.00	1100.00	1.27562	0.19738
ERUCIC	338.566	382.20	659.50	872.25	1205.00	1.28941	0.21425
LIGNOCRC	368.635	356.15	694.00	883.69	1125.45	1.41441	0.21667
NERVNIC	366.619	387.65	672.50	886.01	1131.46	1.40281	0.21547

TAG	MW	NMP (K)	NBP (K)	Tc (K)	Pc (kPa)	Vc (m^3/kgmol)	Zc
CP-CP-CP	470.68	354.11	705.92	902.16	1038.55	1.60779	0.22262
CP-CP-L	526.79	349.55	737.31	925.83	953.24	1.83459	0.22720
CP-C-L	554.84	356.32	748.59	936.81	919.60	1.94799	0.23000
CP-L-L	582.89	362.79	694.00	947.29	890.52	2.06139	0.23308
C-L-L	610.95	368.99	699.20	957.32	865.22	2.17479	0.23642
CP-L-M	610.95	368.99	769.57	957.32	865.22	2.17479	0.23642
L-L-L	639.00	388.67	703.92	966.93	843.07	2.28819	0.23997
L-L-M	667.05	380.66	708.10	976.16	823.56	2.40159	0.24370
CP-L-O	665.04	383.18	697.82	977.72	825.23	2.38999	0.24263
L-L-P	695.10	386.17	711.78	985.03	806.30	2.51499	0.24761
C-L-O	693.09	388.60	701.78	986.53	807.78	2.50339	0.24655
L-M-P	723.16	391.48	715.20	993.58	790.94	2.62839	0.25167
M-M-M	723.16	403.32	715.20	993.58	790.94	2.62839	0.25167
L-L-O	721.14	393.82	705.32	995.03	792.27	2.61679	0.25061
L-L-LI	719.13	396.12	696.48	996.46	793.60	2.60519	0.24956
L-P-P	751.21	396.60	717.99	1001.82	777.23	2.74179	0.25585
L-M-S	751.21	396.60	717.99	1001.82	777.23	2.74179	0.25585
L-M-O	749.19	398.86	708.50	1003.22	778.41	2.73019	0.25480
L-M-LI	747.18	401.09	699.87	1004.61	779.61	2.71859	0.25376
L-P-S	779.26	401.55	720.55	1009.78	764.93	2.85519	0.26015
L-P-O	777.25	403.74	711.34	1011.13	765.99	2.84359	0.25911
L-P-LI	775.23	405.90	702.00	1012.47	767.07	2.83199	0.25807
M-M-LI	775.23	405.90	702.93	1012.47	767.07	2.83199	0.25807
P-P-P	807.32	339.00	721.80	1017.47	753.85	2.96859	0.26455
M-P-O	805.30	408.46	713.86	1018.78	754.81	2.95699	0.26351
L-O-O	803.28	410.55	705.69	1020.07	755.78	2.94539	0.26248
M-P-LI	803.28	410.55	705.69	1020.07	755.78	2.94539	0.26248
PO-PO-PO	801.27	424.66	826.24	1021.37	756.76	2.93379	0.26146
P-P-S	835.37	410.99	837.97	1024.92	743.85	3.08199	0.26904
P-P-O	833.35	413.04	716.10	1026.18	744.72	3.07039	0.26801
P-P-LI	831.34	415.06	708.16	1027.44	745.59	3.05879	0.26699
M-O-O	831.34	415.06	708.16	1027.44	745.59	3.05879	0.26699
M-O-LI	829.32	417.06	700.81	1028.69	746.48	3.04719	0.26596
PO-PO-O	829.32	417.06	700.81	1028.69	746.48	3.04719	0.26596
M-LI-LI	827.31	419.03	694.00	1029.93	747.37	3.03559	0.26495
P-S-O	861.41	417.48	718.07	1033.36	735.57	3.18379	0.27259
P-O-O	859.39	419.44	710.36	1034.57	736.36	3.17219	0.27157
P-O-LI	857.37	421.38	703.25	1035.79	737.16	3.16059	0.27055
PO-O-O	857.37	421.38	703.25	1035.79	737.16	3.16059	0.27055
PO-O-LI	855.36	423.29	696.57	1036.99	737.97	3.14899	0.26954
P-LI-LI	855.36	423.29	696.57	1036.99	737.97	3.14899	0.26954
P-O-LN	855.36	423.29	696.57	1036.99	737.97	3.14899	0.26954
P-LI-LN	853.34	425.18	690.37	1038.19	738.79	3.13739	0.26854
PO-LI-LI	853.34	425.18	690.37	1038.19	738.79	3.13739	0.26854
MG-O-O	873.42	421.58	711.37	1038.06	732.07	3.22889	0.27389
MO-O-O	871.40	423.49	704.33	1039.26	732.83	3.21729	0.27287
S-S-S	885.43	425.58	705.00	1042.67	728.70	3.27399	0.27521
P-O-A	889.46	421.78	719.80	1040.31	727.25	3.29719	0.27724
S-S-O	889.46	421.78	719.80	1040.31	727.25	3.29719	0.27724
S-O-O	887.44	423.69	712.33	1041.50	727.97	3.28559	0.27622
S-O-LI	891.48	428.87	727.70	1039.12	726.53	3.30879	0.27826
O-O-O	891.48	428.87	727.70	1039.12	726.53	3.30879	0.27826

TAG	MW	NMP (K)	NBP (K)	Tc (K)	Pc (kPa)	Vc (m^3/kgmol)	Zc
O-O-LI	883.41	427.44	698.90	1043.84	729.44	3.26239	0.27421
S-LI-LI	883.41	427.44	698.90	1043.84	729.44	3.26239	0.27421
O-LI-LI	881.40	429.27	692.84	1045.01	730.18	3.25079	0.27321
O-O-LN	881.40	429.27	692.84	1045.01	730.18	3.25079	0.27321
LI-LI-LI	879.38	431.09	687.20	1046.17	730.93	3.23919	0.27221
O-LI-LN	879.38	431.09	687.20	1046.17	730.93	3.23919	0.27221
LI-LI-LN	877.36	432.88	681.18	1047.32	731.68	3.22759	0.27121
O-LN-LN	877.36	432.88	681.18	1047.32	731.68	3.22759	0.27121
LN-LN-LN	873.33	450.03	672.10	1049.61	733.21	3.20439	0.26924
O-O-A	915.50	427.82	714.06	1048.22	720.32	3.39899	0.28094
P-LI-BE	913.48	429.66	714.07	1049.36	720.99	3.38739	0.27994
O-LI-A	913.48	429.66	707.32	1049.36	720.99	3.38739	0.27994
O-O-GA	913.48	429.66	707.32	1049.36	720.99	3.38739	0.27994
LI-LI-A	911.47	431.47	701.00	1050.50	721.66	3.37579	0.27894
O-LI-GA	911.47	431.47	701.00	1050.50	721.66	3.37579	0.27894
O-O-BE	943.55	431.84	715.60	1054.75	713.33	3.51239	0.28572
O-LI-BE	941.53	433.63	709.06	1055.86	713.94	3.50079	0.28472
O-O-ER	941.53	433.63	709.05	1055.86	713.94	3.50079	0.28472
LI-LI-BE	939.52	435.39	702.91	1056.97	714.56	3.48919	0.28372
O-LI-ER	939.52	435.39	702.91	1056.97	714.56	3.48919	0.28372
A-A-A	975.63	440.15	867.98	1058.92	705.82	3.64899	0.29254

DAG	MW	NMP (K)	NBP (K)	Tc (K)	Pc (kPa)	Vc (m^3/kgmol)	Zc
CO-CP-OH	316.43	324.64	621.00	731.86	1495.85	1.05366	0.22457
CP-CP-OH	344.48	332.63	629.20	752.84	1366.13	1.16706	0.21346
CP-L-OH	400.59	347.40	642.60	788.68	1178.73	1.39386	0.19521
C-L-OH	428.64	354.27	648.30	804.25	1109.77	1.50726	0.18770
L-L-OH	456.70	360.83	653.40	818.59	1052.41	1.62066	0.18105
L-M-OH	484.75	367.12	657.80	831.87	1004.18	1.73406	0.17517
CP-O-OH	482.73	369.87	649.60	830.65	1008.24	1.72246	0.17181
L-P-OH	512.80	373.14	661.80	844.25	963.25	1.84746	0.16995
M-M-OH	512.80	373.14	661.80	844.25	963.25	1.84746	0.16995
C-O-OH	510.79	375.79	653.80	843.11	966.70	1.83586	0.16690
L-S-OH	540.86	378.93	665.50	855.83	928.21	1.96086	0.16531
M-P-OH	540.86	378.93	665.50	855.83	928.21	1.96086	0.16531
L-O-OH	538.84	381.48	657.50	854.76	931.18	1.94926	0.16252
P-P-OH	568.91	384.50	668.70	866.72	897.98	2.07426	0.16118
M-O-OH	566.89	386.95	661.00	865.71	900.55	2.06266	0.15862
M-LI-OH	564.88	389.37	654.00	864.71	903.16	2.05106	0.15613
P-S-OH	596.96	389.87	671.50	876.99	871.73	2.18766	0.15750
P-O-OH	594.95	392.23	664.00	876.04	873.97	2.17606	0.15514
P-LI-OH	592.93	402.05	767.35	875.09	876.00	2.16446	0.15300
P-LN-OH	590.91	396.86	651.00	874.13	878.53	2.15286	0.15059
MG-O-OH	608.97	394.81	665.50	880.99	861.97	2.23276	0.15355
MO-O-OH	606.96	397.09	658.70	880.06	864.09	2.22116	0.15134
P-A-OH	625.01	395.05	674.00	886.71	848.78	2.30106	0.15421
S-S-OH	625.01	395.05	674.00	886.71	848.78	2.30106	0.15421
S-O-OH	623.00	397.33	666.80	885.81	850.74	2.28946	0.15204

DAG	MW	NMP (K)	NBP (K)	Tc (K)	Pc (kPa)	Vc (m^3/kgmol)	Zc
O-O-OH	620.98	399.58	660.50	884.91	852.73	2.27786	0.14992
S-LI-OH	620.98	399.58	660.20	884.91	852.73	2.27786	0.14992
O-LI-OH	618.97	401.80	654.00	884.00	854.74	2.26626	0.14783
LI-LI-OH	616.95	402.00	648.30	883.00	463.68	2.20450	0.06629
O-LN-OH	616.95	403.98	648.40	883.09	856.77	2.25466	0.14580
LI-LN-OH	614.94	406.13	643.30	882.17	858.83	2.24306	0.14380
LN-LN-OH	612.92	408.26	638.50	881.25	860.91	2.23146	0.14184
P-BE-OH	653.07	400.05	676.50	895.93	828.60	2.41446	0.15129
O-A-OH	651.05	402.26	669.30	895.08	830.33	2.40286	0.14928
LI-A-OH	649.04	404.44	662.70	894.22	832.08	2.39126	0.14730
O-GA-OH	649.04	404.44	662.80	894.22	832.08	2.39126	0.14730
LI-GA-OH	647.02	406.58	656.70	893.36	833.85	2.37966	0.14537
O-BE-OH	679.10	407.03	671.50	903.89	812.30	2.51626	0.14681
LI-BE-OH	677.09	409.14	665.00	903.08	813.85	2.50466	0.14498
O-ER-OH	677.09	409.14	665.20	903.08	813.85	2.50466	0.14498
LI-ER-OH	675.07	411.22	659.50	902.26	815.41	2.49306	0.14318

MAG	MW	NMP (K)	NBP (K)	Tc (K)	Pc (kPa)	Vc (m^3/kgmol)	Zc
CP-OH-OH	218.289	324.86	617.29	738.31	2375.85	0.72285	0.23008
C-OH-OH	246.342	332.84	622.88	758.60	2030.06	0.83625	0.22057
L-OH-OH	274.395	340.40	627.73	776.84	1776.16	0.94965	0.21137
M-OH-OH	302.448	347.59	631.94	793.42	1584.26	1.06305	0.20277
P-OH-OH	330.501	354.45	635.60	808.60	1435.71	1.17645	0.19486
Mg-OH-OH	344.528	357.77	637.30	815.74	1373.717	1.23315	0.19118
Mo-OH-OH	342.512	360.70	629.70	814.41	1384.456	1.22155	0.18604
S-OH-OH	358.554	361.01	638.80	822.61	1318.36	1.28985	0.18767
O-OH-OH	356.538	363.88	631.35	821.33	1327.97	1.27825	0.18282
LI-OH-OH	354.523	366.70	624.60	820.04	1337.77	1.26665	0.17814
LN-OH-OH	352.507	369.46	618.50	818.74	1347.77	1.25505	0.17362
A-OH-OH	386.607	367.28	641.70	835.61	1224.06	1.40325	0.18117
Ga-OH-OH	384.591	370.04	634.40	834.42	1231.835	1.39165	0.17684
Be-OH-OH	414.660	373.30	644.12	847.74	1147.135	1.51665	0.17530
Er-OH-OH	412.644	375.95	637.10	846.63	1153.519	1.50505	0.17141

Appendix D

FATTY ESTER	MW	NMP (K)	NBP (K)	Tc (K)	Pc (kPa)	Vc (m^3/kgmol)	Zc
MXHN	130.187	208.15	424.14	605.00	3000.00	0.45362	0.27054
MEC7H14	144.211	217.15	446.85	625.36	2532.12	0.50351	0.24419
MEC8H16	158.237	236.15	468.43	642.95	2320.78	0.56021	0.24322
MEC9H18	172.264	238.80	489.80	661.31	2142.27	0.61691	0.24037
MDECOATE	186.295	255.15	505.00	671.00	1990.00	0.65300	0.23300
MEC11H22	200.317	261.80	533.43	694.17	1859.44	0.73031	0.23530
MLAURATE	214.348	278.15	540.00	712.00	1740.00	0.75800	0.22300
MEC13H26	228.370	278.25	581.33	722.93	1647.77	0.84371	0.23130
MEC14H28	242.396	292.15	608.72	736.07	1561.38	0.90041	0.22973
MEC14H26	240.381	264.63	585.13	740.45	1576.26	0.88881	0.22758
MEC15H30	256.423	291.65	640.89	748.50	1485.23	0.95711	0.22843
MEC16H32	270.449	303.15	686.62	760.30	1417.77	1.01381	0.22739
MEC16H30	268.434	276.46	627.10	764.25	1429.44	1.00221	0.22546
MEC16H28	266.418	281.52	604.34	768.13	1441.36	0.99061	0.22358
MEC17H34	284.476	303.15	695.00	771.53	1357.72	1.07051	0.22659
MEC17H32	282.460	282.04	648.82	775.29	1368.13	1.05891	0.22476
MEC18H36	298.502	312.25	690.50	782.24	1304.04	1.12721	0.22602
MOLEATE	296.494	293.05	617.00	764.00	1280.00	1.06000	0.21400
MEC18H32	294.471	253.25	636.57	789.37	1322.87	1.10401	0.22254
MEC18H30	292.455	296.68	616.78	792.85	1332.56	1.09241	0.22084
MEC20H40	326.555	327.65	628.18	802.27	1212.44	1.24061	0.22551
MEC20H38	324.540	297.62	716.74	805.57	1220.01	1.22901	0.22388
MEC20H36	322.524	302.01	666.93	808.82	1227.71	1.21741	0.22227
MEC20H32	318.492	310.42	625.05	815.18	1243.54	1.19421	0.21912
MEC22H44	324.540	297.62	716.74	805.57	1220.01	1.22901	0.22388
MEC22H42	352.593	307.16	761.39	823.75	1143.81	1.34241	0.22420
MEC24H48	382.661	312.13	663.08	837.78	1075.63	1.46741	0.22661
MEC24H46	380.646	316.12	798.00	840.61	1080.80	1.45581	0.22514
EEC6H12	144.21	206.15	443.84	623.01	2532.12	0.50351	0.24614
EEC7H14	158.24	207.05	465.18	642.95	2320.78	0.56021	0.24322
EOCTNOAT	172.27	233.15	481.70	659.00	1980.00	0.61746	0.22313
ENONNOAT	186.29	237.15	500.20	674.00	1810.00	0.67254	0.21722
EEC10H20	200.32	253.50	529.03	694.17	1859.44	0.73031	0.23530
EEC11H22	214.34	258.15	551.51	708.99	1746.32	0.78701	0.23316
EEC12H24	228.37	263.15	575.33	722.93	1647.77	0.84371	0.23130
EEC13H26	242.40	258.94	601.29	736.07	1561.38	0.90041	0.22973
EEC14H28	256.42	285.45	630.82	748.50	1485.23	0.95711	0.22843
EEC14H26	254.41	270.66	600.45	752.66	1498.37	0.94551	0.22640
EEC15H30	270.45	271.23	668.19	760.30	1417.77	1.01381	0.22739
EEC16H32	284.48	297.15	701.00	771.53	1357.72	1.07051	0.22659
EEC16H30	282.46	282.04	642.15	775.29	1368.13	1.05891	0.22476
EEC16H28	280.44	286.92	616.21	778.99	1378.75	1.04731	0.22296
EEC17H34	298.50	301.15	712.00	782.24	1304.04	1.12721	0.22602
EEC17H32	296.49	287.42	663.58	785.83	1313.36	1.11561	0.22426
EEC18H36	312.53	306.15	744.00	792.47	1255.86	1.18391	0.22567
EEC18H34	310.51	278.95	685.00	795.91	1264.24	1.17231	0.22397
EEC18H32	308.50	297.15	647.24	799.30	1272.78	1.16071	0.22231
EEC18H30	306.48	301.56	626.01	802.64	1281.48	1.14911	0.22067
EEC20H40	340.58	323.15	637.43	811.67	1173.19	1.29731	0.22554
EEC20H38	338.57	302.47	728.85	814.84	1180.04	1.28571	0.22395
EEC20H36	336.55	306.72	676.19	817.96	1187.01	1.27411	0.22239
EEC20H32	332.52	314.87	632.42	824.08	1201.33	1.25091	0.21933
EEC22H44	338.57	302.47	728.85	814.84	1180.04	1.28571	0.22395

FATTY ESTER	MW	NMP (K)	NBP (K)	Tc (K)	Pc (kPa)	Vc (m^3/kgmol)	Zc
EEC22H42	366.62	311.71	768.98	832.33	1110.85	1.39911	0.22460
EEC24H48	396.69	316.53	862.52	845.87	1048.58	1.52411	0.22725
EEC24H46	394.67	320.40	800.00	848.60	1053.32	1.51251	0.22581

MINOR COMPOUNDS	MW	NMP (K)	NBP (K)	Tc (K)	Pc (kPa)	Vc (m^3/kgmol)	Zc
PL-PE	742.01	431.74	820.34	865.43	398.07	2.93300	0.16227
PL-PI	941.07	554.42	N/A	898.00	181.80	3.47020	0.15210
A-TOCOPH	430.70	402.64	706.49	857.40	1070.00	1.46750	0.12382
B-TOCOPH	416.68	398.54	699.60	920.42	1157.60	1.41150	0.13080
D-TOCOPH	402.65	357.26	689.14	830.00	1160.00	1.35550	0.13824
G-TOCOPH	416.68	398.54	699.60	859.50	1117.00	1.41150	0.13080
A-TOCOTR	424.66	416.11	718.72	934.86	1124.12	1.42850	0.12985
B-TOCOTR	410.63	413.63	712.39	928.99	1158.64	1.37250	0.13718
D-TOCOTR	396.60	416.62	703.53	922.97	1196.68	1.31650	0.14501
G-TOCOTR	410.63	413.63	712.39	928.99	1158.64	1.37250	0.13718
A-CAROTN	536.87	468.40	756.52	903.09	501.03	1.98052	0.12956
B-CAROTN	536.87	466.70	758.68	905.40	708.15	1.93350	0.22277
D-CAROTN	536.87	405.81	758.49	943.33	879.68	1.98027	0.22211
E-CAROTN	536.87	470.08	754.33	944.79	904.96	1.94292	0.22384
G-CAROTN	536.87	457.50	760.64	901.39	462.52	2.01787	0.12110
LTEIN	568.87	506.03	786.59	929.60	495.07	2.05344	0.12506
LYCOPNE	536.87	453.20	762.58	957.64	849.11	2.01763	0.21518
SQUALNE	410.72	314.84	682.51	868.96	970.40	1.63493	0.21960
ZEAXNTN	568.87	506.03	786.59	929.60	495.07	2.05344	0.12506
CAMPSTRL	400.68	402.88	677.45	881.91	1222.17	1.42498	0.23752
CHOLSTRL	386.65	399.87	658.21	873.74	1251.60	1.38026	0.23781
SITOSTRL	414.70	403.00	681.63	885.82	1173.06	1.48586	0.23667
STIGSTRL	412.69	402.48	682.80	886.34	1185.43	1.46886	0.23629
STRC12.0	594.99	402.16	749.87	944.63	895.25	2.14560	0.24458
STRC18.1	677.13	418.02	780.63	975.39	828.47	2.47420	0.25277
AC-STRGL	839.27	488.25	858.36	1060.14	797.51	2.75892	0.13300
FR-SRTGL	574.83	469.84	793.83	998.59	1074.29	1.77550	0.09211

FFA	FORMATION (KJ/MOL)		ENERGY (KJ/MOL)	
	Gibbs	Enthalpy	Combustion	Fusion
HEXANOIC	-3.38000E+05	-5.11900E+05	-3.23048E+06	1.54000E+04
HPTANOIC	-3.34000E+05	-5.36200E+05	-3.83900E+06	1.54370E+04
OCTANOIC	-3.25000E+05	-5.56000E+05	-4.44830E+06	2.14000E+04
DECANOIC	-3.05000E+05	-5.94300E+05	-5.72000E+06	2.77980E+04
UNDCNOIC	-2.96630E+05	-6.14600E+05	-6.25310E+06	2.59800E+04
LAURIC	-2.93100E+05	-6.40000E+05	-6.84990E+06	3.62950E+04
TRDCNOIC	-2.84500E+05	-6.60200E+05	-7.45260E+06	3.37290E+04
MYRISTIC	-2.78000E+05	-6.83000E+05	-8.06030E+06	4.51000E+04
MYRISTOL	-1.82490E+05	-5.61300E+05	-	3.91130E+04

Appendix D

FFA	FORMATION (KJ/MOL)		ENERGY (KJ/MOL)	
	Gibbs	Enthalpy	Combustion	Fusion
PNDCNIOC	-2.66000E+05	-6.99000E+05	-8.66890E+06	4.15260E+04
PALMITIC	-2.60000E+05	-7.23000E+05	-9.27470E+06	5.37110E+04
PALMTOL	-1.64170E+05	-6.02900E+05	-9.32047E+06	4.43910E+04
MARGARIC	-2.52000E+05	-7.43000E+05	-9.87613E+06	5.13420E+04
MARGROL	-1.55010E+05	-6.23700E+05	-9.93499E+06	4.70300E+04
STEARIC	-2.43800E+05	-7.64000E+05	-1.05140E+07	6.12090E+04
OLEIC	-1.55400E+05	-6.37800E+05	-1.04460E+07	-
LINOLEIC	-9.39600E+04	-5.39900E+05	-1.03000E+07	-
LINOLENI	-4.92600E+03	-4.13900E+05	-1.01800E+07	-
C20ACID	-2.28100E+05	-8.06000E+05	-1.16950E+07	6.92040E+04
GADOLEIC	-1.27530E+05	-6.86100E+05	-1.17790E+07	5.49470E+04
GADOLENC	-5.04100E+04	-5.70100E+05	-1.16530E+07	5.28460E+04
EPAACID	1.03830E+05	-3.38100E+05	-1.14010E+07	4.86440E+04
DPAACID	1.80950E+05	-2.22100E+05	-1.12750E+07	4.65430E+04
BEHENIC	-2.02130E+05	-8.47388E+05	-	-
ERUCIC	-1.09210E+05	-7.27700E+05	-1.30080E+07	6.02250E+04
LIGNOCRC	-1.68010E+05	-8.85300E+05	-1.43620E+07	6.76040E+04
NERVNIC	-9.08900E+04	-7.69300E+05	-1.42370E+07	6.55030E+04

TAG	FORMATION (KJ/MOL)		ENERGY (KJ/MOL)	
	Gibbs	Enthalpy	Combustion	Fusion
CP-CP-L	-7.20282E+05	-1.65116E+06	-	8.61640E+04
CP-C-L	-7.01962E+05	-1.69276E+06	-	9.14420E+04
CP-L-L	-6.83642E+05	-1.73436E+06	-2.00180E+07	9.67200E+04
C-L-L	-6.65322E+05	-1.77596E+06	-2.12470E+07	1.01998E+05
CP-L-M	-6.65322E+05	-1.77596E+06	-	1.01998E+05
L-L-L	-6.47002E+05	-1.81756E+06	-2.24760E+07	1.07276E+05
L-L-M	-6.28682E+05	-1.85916E+06	-2.37060E+07	1.12554E+05
CP-L-O	-5.51562E+05	-1.74316E+06	-2.35800E+07	1.11717E+05
L-L-P	-6.10362E+05	-1.90076E+06	-2.49350E+07	1.17832E+05
C-L-O	-5.33242E+05	-1.78476E+06	-2.48090E+07	1.16995E+05
L-M-P	-5.92042E+05	-1.94236E+06	-2.61640E+07	1.23110E+05
M-M-M	-5.92042E+05	-1.94236E+06	-2.61640E+07	1.23110E+05
L-L-O	-5.14922E+05	-1.82636E+06	-2.60380E+07	1.22273E+05
L-L-LI	-4.37802E+05	-1.71036E+06	-2.59120E+07	1.21436E+05
L-P-P	-5.73722E+05	-1.98396E+06	-2.73930E+07	1.28388E+05
L-M-S	-5.73722E+05	-1.98396E+06	-2.73930E+07	1.28388E+05
L-M-O	-4.96602E+05	-1.86796E+06	-2.72670E+07	1.27551E+05
L-M-LI	-4.19482E+05	-1.75196E+06	-2.71410E+07	1.26714E+05
L-P-S	-5.55402E+05	-2.02556E+06	-2.86220E+07	1.33666E+05
L-P-O	-4.78282E+05	-1.90956E+06	-2.84960E+07	1.32829E+05
L-P-LI	-4.01162E+05	-1.79356E+06	-2.83700E+07	1.31992E+05
M-M-LI	-4.01162E+05	-1.79356E+06	-2.83700E+07	1.31992E+05
P-P-P	-5.37082E+05	-2.06716E+06	-2.98510E+07	1.38944E+05
M-P-O	-4.59962E+05	-1.95116E+06	-2.97250E+07	1.38107E+05
L-O-O	-3.82842E+05	-1.83516E+06	-2.95990E+07	1.37270E+05
M-P-LI	-3.82842E+05	-1.83516E+06	-2.95990E+07	1.37270E+05
PO-PO-PO	-3.05722E+05	-1.71916E+06	-	1.36433E+05
P-P-S	-5.18762E+05	-2.10876E+06	-	1.44222E+05
P-P-O	-4.41642E+05	-1.99276E+06	-3.09540E+07	1.43385E+05

Appendix D

TAG	FORMATION (KJ/MOL)		ENERGY (KJ/MOL)	
	Gibbs	Enthalpy	Combustion	Fusion
P-P-LI	-3.64522E+05	-1.87676E+06	-3.08280E+07	1.42548E+05
M-O-O	-3.64522E+05	-1.87676E+06	-3.08280E+07	1.42548E+05
M-O-LI	-2.87402E+05	-1.76076E+06	-3.07020E+07	1.41711E+05
PO-PO-O	-2.87402E+05	-1.76076E+06	-3.07020E+07	1.41711E+05
M-LI-LI	-2.10282E+05	-1.64476E+06	-3.05770E+07	1.40874E+05
P-S-O	-4.23322E+05	-2.03436E+06	-3.21830E+07	1.48663E+05
P-O-O	-3.46202E+05	-1.91836E+06	-3.20570E+07	1.47826E+05
P-O-LI	-2.69082E+05	-1.80236E+06	-3.19310E+07	1.46989E+05
PO-O-O	-2.69082E+05	-1.80236E+06	-3.19310E+07	1.46989E+05
PO-O-LI	-1.91962E+05	-1.68636E+06	-3.18060E+07	1.46152E+05
P-LI-LI	-1.91962E+05	-1.68636E+06	-3.18060E+07	1.46152E+05
P-O-LN	-1.91962E+05	-1.68636E+06	-3.18060E+07	1.46152E+05
P-LI-LN	-1.14842E+05	-1.57036E+06	-3.16800E+07	1.45315E+05
PO-LI-LI	-1.14842E+05	-1.57036E+06	-3.16800E+07	1.45315E+05
MG-O-O	-3.37042E+05	-1.93916E+06	-3.26720E+07	1.50465E+05
MO-O-O	-2.59922E+05	-1.82316E+06	-3.25460E+07	1.49628E+05
S-S-S	-2.50762E+05	-1.84396E+06	-3.31600E+07	1.52267E+05
P-O-A	-4.05002E+05	-2.07596E+06	-3.34120E+07	1.53941E+05
S-S-O	-4.05002E+05	-2.07596E+06	-3.34120E+07	1.53941E+05
S-O-O	-3.27882E+05	-1.95996E+06	-3.32860E+07	1.53104E+05
S-O-LI	-4.82122E+05	-2.19196E+06	-3.35380E+07	1.54778E+05
O-O-O	-4.82122E+05	-2.19196E+06	-3.35380E+07	1.54778E+05
O-O-LI	-1.73642E+05	-1.72796E+06	-3.30350E+07	1.51430E+05
S-LI-LI	-1.73642E+05	-1.72796E+06	-3.30350E+07	1.51430E+05
O-LI-LI	-9.65220E+04	-1.61196E+06	-3.29090E+07	1.50593E+05
O-O-LN	-9.65220E+04	-1.61196E+06	-3.29090E+07	1.50593E+05
LI-LI-LI	-1.94020E+04	-1.49596E+06	-3.27830E+07	1.49756E+05
O-LI-LN	-1.94020E+04	-1.49596E+06	-3.27830E+07	1.49756E+05
LI-LI-LN	5.77180E+04	-1.37996E+06	-3.26570E+07	1.48919E+05
O-LN-LN	5.77180E+04	-1.37996E+06	-3.26570E+07	1.48919E+05
LN-LN-LN	2.11958E+05	-1.14796E+06	-3.24060E+07	1.47245E+05
O-O-A	-3.09562E+05	-2.00156E+06	-3.45150E+07	1.58382E+05
P-LI-BE	-2.32442E+05	-1.88556E+06	-3.43890E+07	1.57545E+05
O-LI-A	-2.32442E+05	-1.88556E+06	-3.43890E+07	1.57545E+05
O-O-GA	-2.32442E+05	-1.88556E+06	-3.43890E+07	1.57545E+05
LI-LI-A	-1.55322E+05	-1.76956E+06	-3.42640E+07	1.56708E+05
O-LI-GA	-1.55322E+05	-1.76956E+06	-3.42640E+07	1.56708E+05
O-O-BE	-2.91242E+05	-2.04316E+06	-3.57440E+07	1.63660E+05
O-LI-BE	-2.14122E+05	-1.92716E+06	-3.56190E+07	1.62823E+05
O-O-ER	-2.14122E+05	-1.92716E+06	-3.56190E+07	1.62823E+05
LI-LI-BE	-1.37002E+05	-1.81116E+06	-3.54930E+07	1.61986E+05
O-LI-ER	-1.37002E+05	-1.81116E+06	-3.54930E+07	1.61986E+05
A-A-A	-4.27162E+05	-2.31676E+06	-	1.70612E+05

DAG	FORMATION (KJ/MOL)		ENERGY (KJ/MOL)	
	Gibbs	Enthalpy	Combustion	Fusion
CO-CP-OH	-6.10860E+05	-1.12968E+06	-9.42901E+06	5.45650E+04
CP-CP-OH	-5.92540E+05	-1.17128E+06	-1.06580E+07	5.98430E+04
CP-L-OH	-5.55900E+05	-1.25448E+06	-1.31160E+07	7.03990E+04
C-L-OH	-5.37580E+05	-1.29608E+06	-1.43450E+07	7.56770E+04
L-L-OH	-5.19260E+05	-1.33768E+06	-1.55740E+07	8.09550E+04
L-M-OH	-5.00940E+05	-1.37928E+06	-1.68030E+07	8.62330E+04
CP-O-OH	-4.23820E+05	-1.26328E+06	-1.66770E+07	8.41320E+04
L-P-OH	-4.82620E+05	-1.42088E+06	-1.80320E+07	9.15110E+04
M-M-OH	-4.82620E+05	-1.42088E+06	-1.80320E+07	9.15110E+04
C-O-OH	-4.05500E+05	-1.30488E+06	-1.79070E+07	8.94100E+04
L-S-OH	-4.64300E+05	-1.46248E+06	-1.92610E+07	9.67890E+04
M-P-OH	-4.64300E+05	-1.46248E+06	-1.92610E+07	9.67890E+04
L-O-OH	-3.87180E+05	-1.34648E+06	-1.91360E+07	9.46880E+04
P-P-OH	-4.45980E+05	-1.50408E+06	-2.04900E+07	1.02067E+05
M-O-OH	-3.68860E+05	-1.38808E+06	-2.03650E+07	9.99660E+04
M-LI-OH	-2.91740E+05	-1.27208E+06	-2.02390E+07	9.78650E+04
P-S-OH	-4.27660E+05	-1.54568E+06	-2.17190E+07	1.07345E+05
P-O-OH	-3.50540E+05	-1.42968E+06	-2.15940E+07	1.05244E+05
P-LI-OH	-3.50540E+05	-1.42968E+06	-2.15940E+07	1.05244E+05
P-LN-OH	-1.96300E+05	-1.19768E+06	-2.13420E+07	1.01042E+05
MG-O-OH	-3.41380E+05	-1.45048E+06	-2.22080E+07	1.07883E+05
MO-O-OH	-2.64260E+05	-1.33448E+06	-2.20820E+07	1.05782E+05
P-A-OH	-4.09340E+05	-1.58728E+06	-2.29490E+07	1.12623E+05
S-S-OH	-4.09340E+05	-1.58728E+06	-2.29490E+07	1.12623E+05
S-O-OH	-3.32220E+05	-1.47128E+06	-2.28230E+07	1.10522E+05
O-O-OH	-2.55100E+05	-1.35528E+06	-2.26970E+07	1.08421E+05
S-LI-OH	-2.55100E+05	-1.35528E+06	-2.26970E+07	1.08421E+05
O-LI-OH	-1.77980E+05	-1.23928E+06	-2.25710E+07	1.06320E+05
LI-LI-OH	-1.61620E+05	-1.17148E+06	-2.23970E+07	1.06877E+05
O-LN-OH	-1.00860E+05	-1.12328E+06	-2.24450E+07	1.04219E+05
LI-LN-OH	-2.37400E+04	-1.00728E+06	-2.23190E+07	1.02118E+05
LN-LN-OH	5.33800E+04	-8.91280E+05	-2.21940E+07	1.00017E+05
P-BE-OH	-3.91020E+05	-1.62888E+06	-2.41780E+07	1.17901E+05
O-A-OH	-3.13900E+05	-1.51288E+06	-2.40520E+07	1.15800E+05
LI-A-OH	-2.36780E+05	-1.39688E+06	-2.39260E+07	1.13699E+05
O-GA-OH	-2.36780E+05	-1.39688E+06	-2.39260E+07	1.13699E+05
LI-GA-OH	-1.59660E+05	-1.28088E+06	-2.38000E+07	1.11598E+05
O-BE-OH	-2.95580E+05	-1.55448E+06	-2.52810E+07	1.21078E+05
LI-BE-OH	-2.18460E+05	-1.43848E+06	-2.51550E+07	1.18977E+05
O-ER-OH	-2.18460E+05	-1.43848E+06	-2.51550E+07	1.18977E+05
LI-ER-OH	-1.41340E+05	-1.32248E+06	-2.50290E+07	1.16876E+05

MAG	FORMATION (KJ/MOL)		ENERGY (KJ/MOL)	
	Gibbs	Enthalpy	Combustion	Fusion
CP-OH-OH	-4.81453E+05	-8.37320E+05	-6.15124E+06	4.05880E+04
C-OH-OH	-4.63133E+05	-8.78920E+05	-7.38029E+06	4.58660E+04
L-OH-OH	-4.44813E+05	-9.20520E+05	-8.60934E+06	5.11440E+04
M-OH-OH	-4.26493E+05	-9.62120E+05	-9.83839E+06	5.64220E+04
P-OH-OH	-4.08173E+05	-1.00372E+06	-1.10670E+07	6.17000E+04
Mg-OH-OH	-3.99013E+05	-1.02452E+06	-1.16820E+07	6.43390E+04
Mo-OH-OH	-3.21893E+05	-9.08520E+05	-1.15560E+07	6.22380E+04
S-OH-OH	-3.89853E+05	-1.04532E+06	-1.22960E+07	6.69780E+04
O-OH-OH	-3.12733E+05	-9.29320E+05	-1.21710E+07	6.48770E+04
LI-OH-OH	-2.35613E+05	-8.13320E+05	-1.20450E+07	6.27760E+04
LN-OH-OH	-1.58493E+05	-6.97320E+05	-1.19190E+07	6.06750E+04
A-OH-OH	-3.71533E+05	-1.08692E+06	-1.35260E+07	7.22560E+04
Ga-OH-OH	-2.94413E+05	-9.70920E+05	-1.34000E+07	7.01550E+04
Be-OH-OH	-3.53213E+05	-1.12852E+06	-1.47550E+07	7.75340E+04
Er-OH-OH	-2.76093E+05	-1.01252E+06	-1.46290E+07	7.54330E+04

FATTY ESTER	FORMATION (KJ/MOL)		ENERGY (KJ/MOL)	
	Gibbs	Enthalpy	Combustion	Fusion
MXHN	-2.94561E+05	-5.00581E+05	-	-
MEC7H14	-2.91590E+05	-5.25730E+05	-4.55686E+06	2.05490E+04
MEC8H16	-2.82430E+05	-5.46100E+05	-5.17182E+06	2.31880E+04
MEC9H18	-2.73270E+05	-5.66900E+05	-5.78634E+06	2.58270E+04
MDECOATE	-2.54700E+05	-5.73800E+05	-6.34850E+06	3.30000E+04
MEC11H22	-2.54950E+05	-6.08500E+05	-7.01539E+06	3.11050E+04
MLAURATE	-2.40000E+05	-6.12300E+05	-7.56680E+06	-
MEC13H26	-2.36630E+05	-6.50100E+05	-8.24444E+06	3.63830E+04
MEC14H28	-2.27470E+05	-6.70900E+05	-8.85896E+06	3.90220E+04
MEC14H26	-1.50350E+05	-5.54900E+05	-8.73315E+06	3.69210E+04
MEC15H30	-2.18310E+05	-6.91700E+05	-9.47348E+06	4.16610E+04
MEC16H32	-2.09150E+05	-7.12500E+05	-1.00880E+07	4.43000E+04
MEC16H30	-1.32030E+05	-5.96500E+05	-9.96219E+06	4.21990E+04
MEC16H28	-5.49100E+04	-4.80500E+05	-9.83638E+06	4.00980E+04
MEC17H34	-1.99990E+05	-7.33300E+05	-1.07030E+07	4.69390E+04
MEC17H32	-1.22870E+05	-6.17300E+05	-1.05770E+07	4.48380E+04
MEC18H36	-1.90830E+05	-7.54100E+05	-1.13170E+07	4.95780E+04
MOLEATE	-1.17000E+05	-6.26000E+05	-1.11000E+07	-
MEC18H32	-3.65900E+04	-5.22944E+05	-1.10650E+07	4.53760E+04
MEC18H30	4.05300E+04	-4.08535E+05	-1.09370E+07	4.32750E+04
MEC20H40	-1.72510E+05	-7.95700E+05	-1.25460E+07	5.48560E+04
MEC20H38	-9.53900E+04	-6.79700E+05	-1.24200E+07	5.27550E+04
MEC20H36	-1.82700E+04	-5.63700E+05	-1.22940E+07	5.06540E+04
MEC20H32	1.35970E+05	-3.31700E+05	-1.20430E+07	4.64520E+04
MEC22H44	-9.53900E+04	-6.79700E+05	-1.24200E+07	5.27550E+04
MEC22H42	-7.70700E+04	-7.21300E+05	-1.36490E+07	5.80330E+04
MEC24H48	-1.35870E+05	-8.78900E+05	-	6.54120E+04
MEC24H46	-5.87500E+04	-7.62900E+05	-1.48780E+07	6.33110E+04
EEC6H12	-2.91590E+05	-5.25300E+05	-4.55729E+06	2.05490E+04
EEC7H14	-2.82430E+05	-5.46100E+05	-5.17182E+06	2.31880E+04

FATTY ESTER	FORMATION (KJ/MOL)		ENERGY (KJ/MOL)	
	Gibbs	Enthalpy	Combustion	Fusion
EOCTNOAT	-2.82458E+05	-5.74865E+05	-	-
ENONNOAT	-2.75460E+05	-5.96514E+05	-	-
EEC10H20	-2.54950E+05	-6.08500E+05	-7.01539E+06	3.11050E+04
EEC11H22	-2.45790E+05	-6.29300E+05	-7.62991E+06	3.37440E+04
EEC12H24	-2.36630E+05	-6.50100E+05	-8.24444E+06	3.63830E+04
EEC13H26	-2.27470E+05	-6.70900E+05	-8.85896E+06	3.90220E+04
EEC14H28	-2.18310E+05	-6.91700E+05	-9.47348E+06	4.16610E+04
EEC14H26	-1.41190E+05	-5.75700E+05	-9.34767E+06	3.95600E+04
EEC15H30	-2.09150E+05	-7.12500E+05	-1.00880E+07	4.43000E+04
EEC16H32	-1.99990E+05	-7.33300E+05	-1.07030E+07	4.69390E+04
EEC16H30	-1.22870E+05	-6.17300E+05	-1.05770E+07	4.48380E+04
EEC16H28	-4.57500E+04	-5.01300E+05	-1.04510E+07	4.27370E+04
EEC17H34	-1.90830E+05	-7.54100E+05	-1.13170E+07	4.95780E+04
EEC17H32	-1.13710E+05	-6.38100E+05	-1.11910E+07	4.74770E+04
EEC18H36	-1.81670E+05	-7.74900E+05	-1.19320E+07	5.22170E+04
EEC18H34	-1.04550E+05	-6.58900E+05	-1.18060E+07	5.01160E+04
EEC18H32	-2.74300E+04	-5.42900E+05	-1.16800E+07	4.80150E+04
EEC18H30	4.96900E+04	-4.26900E+05	-1.15540E+07	4.59140E+04
EEC20H40	-1.63350E+05	-8.16500E+05	-1.31610E+07	5.74950E+04
EEC20H38	-8.62300E+04	-7.00500E+05	-1.30350E+07	5.53940E+04
EEC20H36	-9.11000E+03	-5.84500E+05	-1.29090E+07	5.32930E+04
EEC20H32	1.45130E+05	-3.52500E+05	-1.26570E+07	4.90910E+04
EEC22H44	-8.62300E+04	-7.00500E+05	-1.30350E+07	5.53940E+04
EEC22H42	-6.79100E+04	-7.42100E+05	-1.42640E+07	6.06720E+04
EEC24H48	-1.26710E+05	-8.99700E+05	-1.56190E+07	6.80510E+04
EEC24H46	-4.95900E+04	-7.83700E+05	-1.54930E+07	6.59500E+04

MINOR COMPOUND	FORMATION (KJ/MOL)		ENERGY (KJ/MOL)	
	Gibbs	Enthalpy	Combustion	Fusion
PL-PE	N/A	N/A	-2.7622E+07	N/A
PL-PI	-1.4389E+04	-7.6056E+05	-1.6697E+07	5.4194E+04
A-TOCOPH	-1.1889E+04	-7.2976E+05	N/A	5.3173E+04
B-TOCOPH	-9.3890E+03	-7.1049E+05	-1.5476E+07	5.2152E+04
D-TOCOPH	-1.1889E+04	-7.2976E+05	-1.6092E+07	5.3173E+04
G-TOCOPH	2.0654E+05	-3.9352E+05	N/A	5.4971E+04
A-TOCOTR	2.0904E+05	-3.6272E+05	N/A	5.3950E+04
B-TOCOTR	2.1154E+05	-3.4345E+05	N/A	5.2929E+04
D-TOCOTR	2.0904E+05	-3.6272E+05	N/A	5.3950E+04
G-TOCOTR	1.0351E+06	2.6009E+05	N/A	6.9356E+04
A-CAROTN	1.0463E+06	2.6486E+05	N/A	6.7896E+04
B-CAROTN	1.0504E+06	3.2454E+05	N/A	6.5756E+04
D-CAROTN	9.4962E+05	2.2267E+05	N/A	6.0701E+04
E-CAROTN	1.0779E+06	3.3490E+05	N/A	7.9699E+04
G-CAROTN	7.4140E+05	-9.6658E+04	N/A	7.8214E+04
LTEIN	1.1513E+06	4.2641E+05	N/A	8.3063E+04
LYCOPNE	6.2644E+05	-3.4170E+04	N/A	4.9296E+04
SQUALNE	7.4140E+05	-9.6658E+04	N/A	7.8214E+04
ZEAXNTN	8.9784E+04	-6.3704E+05	N/A	3.9444E+04
CAMPSTRL	8.0404E+04	-6.0615E+05	N/A	4.0289E+04

MINOR COMPOUND	FORMATION (KJ/MOL)		ENERGY (KJ/MOL)	
	Gibbs	Enthalpy	Combustion	Fusion
CHOLSTRL	9.1904E+04	-6.6495E+05	N/A	4.2083E+04
SITOSTRL	1.7414E+05	-5.4347E+05	N/A	4.1246E+04
STIGSTRL	1.1133E+05	-9.6417E+05	N/A	7.1350E+04
STRC12.0	2.4341E+05	-9.7297E+05	N/A	8.6347E+04
STRC18.1	-3.9931E+05	-1.7881E+06	N/A	1.2421E+05
AC-STRGL	-4.5989E+05	-1.3625E+06	N/A	7.9112E+04
FR-SRTGL	N/A	N/A	-2.7622E+07	N/A

E.
Case Studies Stream Summary

In this Appendix, a summary of the streams used in the development of the simulation model for each one of the selected Case Studies is presented. Due to the confidentiality agreement, and as did for the thermophysical model parameters, , it is not possible to disclose all the stream information. Hence, only information such as name of the temperature stream, phase, temperature, pressure, and mass fraction (or percentage) of the selected compounds is given.

E.1 Solvent Recovery Section Stream Summary Table

Table E.1 Stream Summary of the OIL EXTRACTION section of Case Study 1

Stream Name	**FEED_SEEDS**	**FEED_ MEAL**	**EXTCT_FEED**	**WATER _PREP**
Phase	Liquid	Solid	Mixed	Liquid
Temperature	20.00	20.00	20.00	20.00
Pressure	1.00	1.00	1.00	1.00
Weight Fraction				
WATER	0.0000	0.1375	0.1050	1.0000
HEXANE	0.0000	0.0000	0.0000	0.0000
GLUTAMIC	0.0000	0.8625	0.6939	0.0000
LILILI	0.9578	0.0000	0.1926	0.0000
CHOLESTE	0.0041	0.0000	0.0008	0.0000
ALFA-TOC	0.0010	0.0000	0.0002	0.0000
LINOLEIC	0.0371	0.0000	0.0075	0.0000
NC15	0.0000	0.0000	0.0000	0.0000
O2	0.0000	0.0000	0.0000	0.0000
N2	0.0000	0.0000	0.0000	0.0000

Table E.2 Stream Summary of the OIL EXTRACTION and DTC section of Case Study 1

Stream Name	MEAL	MISCELA	HEX_REC_ MEAL	SOLID_ OUT
Phase	Mixed	Liquid	Liquid	Mixed
Temperature	22.79	22.79	22.79	22.79
Pressure	1.00	1.00	1.00	1.00
Weight Fraction				
WATER	0.0913	0.0000	0.1544	0.0566
HEXANE	0.3000	0.7000	0.8456	0.0000
GLUTAMIC	0.6027	0.0000	0.0000	0.9341
LILILI	0.0056	0.2873	0.0000	0.0086
CHOLESTE	0.0000	0.0012	0.0000	0.0000
ALFA-TOC	0.0000	0.0003	0.0000	0.0000
LINOLEIC	0.0002	0.0111	0.0000	0.0003
NC15	0.0002	0.0000	0.0000	0.0003
O2	0.0000	0.0000	0.0000	0.0000
N2	0.0000	0.0000	0.0000	0.0000

Table E.3 Stream Summary of the OIL RECOVERY section of Case Study 1

Stream Name	HEX_REC	MISCELA _1EV	HEX_REC_2	MISCELA_ 2EV
Phase	Vapor	Liquid	Vapor	Liquid
Temperature	62.75	62.75	110.00	110.00
Pressure	0.56	0.56	0.31	0.31
Weight Fraction				
WATER	0.00000	0.00000	0.00000	0.00000
HEXANE	1.00000	0.34957	0.99986	0.02809
GLUTAMIC	0.00000	0.00000	0.00000	0.00000
LILILI	0.00000	0.62300	0.00000	0.92974
CHOLESTE	0.00000	0.00264	0.00000	0.00395
ALFA-TOC	0.00000	0.00062	0.00000	0.00093
LINOLEIC	0.00000	0.02416	0.00014	0.03730
NC15	0.00000	0.00000	0.00000	0.00000
O2	0.00000	0.00000	0.00000	0.00000
N2	0.00000	0.00000	0.00000	0.00000

Table E.4 Stream Summary of the OIL RECOVERY section of Case Study 1

Stream Name	**FEED_COND**	**HEX_REC_3**	**STEAM_ STRIP**	**CRUDE_OIL**
Phase	Mixed	Vapor	Vapor	Liquid
Temperature	35.02	120.31	72.00	124.26
Pressure	0.31	0.70	0.01	0.70
Weight Fraction				
WATER	0.00000	0.18475	1.00000	0.01890
HEXANE	0.99997	0.81504	0.00000	0.00002
GLUTAMIC	0.00000	0.00000	0.00000	0.00000
LILILI	0.00000	0.00000	0.00000	0.93852
CHOLESTE	0.00000	0.00000	0.00000	0.00398
ALFA-TOC	0.00000	0.00000	0.00000	0.00093
LINOLEIC	0.00003	0.00021	0.00000	0.03764
NC15	0.00000	0.00000	0.00000	0.00000
O2	0.00000	0.00000	0.00000	0.00000
N2	0.00000	0.00000	0.00000	0.00000

Table E.5 Stream Summary of the CONDENSATION SYSTEM section of Case Study 1

Stream Name	COND1_VAP	COND1_LIQ	COND2_VAP	COND2_LIQ
Phase	Vapor	Mixed	Vapor	Liquid
Temperature	35.02	35.02	35.02	35.02
Pressure	0.31	0.31	0.31	0.31
Weight Fraction				
WATER	0.0000	0.0000	0.0000	0.0000
HEXANE	1.0000	1.0000	1.0000	1.0000
GLUTAMIC	0.0000	0.0000	0.0000	0.0000
LILILI	0.0000	0.0000	0.0000	0.0000
CHOLESTE	0.0000	0.0000	0.0000	0.0000
ALFA-TOC	0.0000	0.0000	0.0000	0.0000
LINOLEIC	0.0000	0.0000	0.0000	0.0000
NC15	0.0000	0.0000	0.0000	0.0000
O2	0.0000	0.0000	0.0000	0.0000
N2	0.0000	0.0000	0.0000	0.0000

Table E.6 Stream Summary of the MOS section of Case Study 1

Stream Name	T1_FEED	T2_REC_OUT	T1_VAP_OUT	T1_REC_OUT
Phase	Mixed	Liquid	Vapor	Liquid
Temperature	20.00	93.07	25.00	24.50
Pressure	0.31	0.30	0.03	0.03
Weight Fraction				
WATER	0.68263	0.04945	0.29512	0.05248
HEXANE	0.07104	0.00000	0.00041	0.00039
GLUTAMIC	0.00000	0.00000	0.00000	0.00000
LILILI	0.00000	0.00000	0.00000	0.00000
CHOLESTE	0.00000	0.00000	0.00000	0.00000
ALFA-TOC	0.00000	0.00000	0.00000	0.00000
LINOLEIC	0.00065	0.00013	0.00000	0.00012
NC15	0.00000	0.95042	0.00117	0.94701
O2	0.05726	0.00000	0.16389	0.00000
N2	0.18842	0.00000	0.53941	0.00000

Table E.7 Stream Summary of the MOS section of Case Study 1

Stream Name	T2_STEAM_FEE	T2_OUT	COND_HEX	PURGE
Phase	Vapor	Vapor	Mixed	Mixed
Temperature	75.00	93.29	31.13	20.00
Pressure	0.01	0.30	0.31	0.30
Weight Fraction				
WATER	1.00000	0.95928	0.00279	0.95928
HEXANE	0.00000	0.00733	0.99717	0.00733
GLUTAMIC	0.00000	0.00000	0.00000	0.00000
LILILI	0.00000	0.00000	0.00000	0.00000
CHOLESTE	0.00000	0.00000	0.00000	0.00000
ALFA-TOC	0.00000	0.00000	0.00000	0.00000
LINOLEIC	0.00000	0.00000	0.00003	0.00000
NC15	0.00000	0.03338	0.00000	0.03338
O2	0.00000	0.00000	0.00000	0.00000
N2	0.00000	0.00001	0.00000	0.00001

Table E.8 Stream Summary of the Water-Hexane Separation section of Case Study 1

Stream Name	WET_HEX	DRY_HEX	VAP_MOS	MOS_WATER
Phase	Liquid	Liquid	N/A	Liquid
Temperature	28.89	28.89	0.00	28.89
Pressure	0.30	0.30	0.00	0.30
Weight Fraction				
WATER	0.08277	0.00016	0.00000	0.99880
HEXANE	0.91691	0.99958	0.00000	0.00001
GLUTAMIC	0.00000	0.00000	0.00000	0.00000
LILILI	0.00000	0.00000	0.00000	0.00000
CHOLESTE	0.00000	0.00000	0.00000	0.00000
ALFA-TOC	0.00000	0.00000	0.00000	0.00000
LINOLEIC	0.00002	0.00001	0.00000	0.00006
NC15	0.00031	0.00024	0.00000	0.00112
O2	0.00000	0.00000	0.00000	0.00000
N2	0.00000	0.00000	0.00000	0.00000

E.2 Crude Palm Oil Deodorization Process Streams Summary

Table E.9 Stream summary A table for Case Study 2

Stream Name	FEED	FINAL_OIL	ECON_OIL	STEAM_FH	MVC
Stream Phase	Liquid	Liquid	Liquid	Vapor	Vapor
Pressure	1000.00	2006.69	7000.00	2697.13	4.66
Temperature	105	40	214.05	130	210
Mass Fraction					
PPP	5.5000E-02	5.7230E-02	5.5000E-02	0.0000E+00	3.7897E-05
POP	3.6320E-01	3.7798E-01	3.6320E-01	0.0000E+00	1.3708E-04
POS	6.0900E-02	6.3384E-02	6.0900E-02	0.0000E+00	1.3731E-05
PLIP	9.9000E-02	1.0303E-01	9.9000E-02	0.0000E+00	2.2451E-05
POO	2.0800E-01	2.1648E-01	2.0800E-01	0.0000E+00	4.5412E-05
PLIO	9.5300E-02	9.9188E-02	9.5300E-02	0.0000E+00	1.1807E-05
P-P-OH	2.2500E-02	2.3143E-02	2.2500E-02	0.0000E+00	1.3850E-03
P-O-OH	4.4600E-02	4.5714E-02	4.4600E-02	0.0000E+00	1.6467E-03
P-LI-OH	1.0400E-02	1.0570E-02	1.0400E-02	0.0000E+00	4.0302E-04
P-S-OH	0.0000E+00	5.5823E-05	0.0000E+00	0.0000E+00	0.0000E+00
P-OH-OH	3.0000E-03	7.0097E-04	3.0000E-03	0.0000E+00	1.0548E-02
O-OH-OH	1.7000E-03	6.4098E-04	1.7000E-03	0.0000E+00	3.8487E-03
LI-OH-OH	4.0000E-04	1.2763E-04	4.0000E-04	0.0000E+00	1.0108E-03
PALMITIC	1.7500E-02	2.1876E-05	1.7500E-02	0.0000E+00	4.2713E-01
OLEIC	1.3250E-02	2.7610E-04	1.3250E-02	0.0000E+00	1.9721E-01
LINOLEIC	3.4000E-03	5.8426E-05	3.4000E-03	0.0000E+00	6.8287E-02
B-TOCOPH	4.0000E-04	2.5476E-04	4.0000E-04	0.0000E+00	5.3621E-04
B-TOCOTR	6.0000E-04	3.4173E-04	6.0000E-04	0.0000E+00	9.8831E-04
STIGSTRL	1.2500E-04	9.3702E-05	1.2500E-04	0.0000E+00	1.1189E-04
STRC18.1	2.5000E-05	2.6048E-05	2.5000E-05	0.0000E+00	9.5838E-09
SQUALNE	6.0000E-04	4.5313E-04	6.0000E-04	0.0000E+00	5.8056E-04
WATER	1.0000E-04	2.2589E-04	1.0000E-04	1.0000E+00	2.8605E-01

Table E.10 Stream summary B table for Case Study 2

Stream Name	FH_OIL	DEOD_DIST	DEACD_OIL	DEACD_ STEAM	STRIP_ STEAM
Stream Phase	Mixed	Vapor	Liquid	Mixed	Vapor
Pressure	4.66	4.66	6.69	6.692	2697.13
Temperature	250.00	247.13	245.90	170.56	130
Mass Fraction					
PPP	5.5153E-02	4.0338E-04	5.7262E-02	2.7792E-04	0.0000E+00
POP	3.6421E-01	1.6947E-03	3.7818E-01	1.1596E-03	0.0000E+00
POS	6.1069E-02	1.7212E-04	6.3416E-02	1.1771E-04	0.0000E+00
PLIP	9.9275E-02	4.4235E-04	1.0308E-01	2.9788E-04	0.0000E+00
POO	2.0858E-01	6.1990E-04	2.1659E-01	4.2205E-04	0.0000E+00
PLIO	9.5564E-02	2.6439E-04	9.9238E-02	1.7699E-04	0.0000E+00
P-P-OH	2.2557E-02	1.4709E-02	2.2796E-02	1.0099E-02	0.0000E+00
P-O-OH	4.4718E-02	1.9887E-02	4.5587E-02	1.3480E-02	0.0000E+00
P-LI-OH	1.0427E-02	5.1195E-03	1.0609E-02	3.4333E-03	0.0000E+00
P-S-OH	0.0000E+00	1.8442E-15	2.0626E-07	1.4942E-05	0.0000E+00
P-OH-OH	2.9685E-03	4.5498E-02	8.4802E-04	1.0693E-02	0.0000E+00
O-OH-OH	1.6902E-03	2.1290E-02	7.3857E-04	7.1061E-03	0.0000E+00
LI-OH-OH	3.9729E-04	5.4439E-03	1.4966E-04	1.6029E-03	0.0000E+00
PALMITIC	1.5935E-02	3.1606E-01	2.1918E-05	1.6765E-03	0.0000E+00
OLEIC	1.2542E-02	2.4880E-01	1.7861E-04	1.3196E-02	0.0000E+00
LINOLEIC	3.1515E-03	6.3017E-02	2.5179E-05	3.7767E-03	0.0000E+00
B-TOCOPH	3.9908E-04	3.0538E-03	2.7573E-04	1.5341E-03	0.0000E+00
B-TOCOTR	5.9793E-04	5.3380E-03	3.7559E-04	2.4721E-03	0.0000E+00
STIGSTRL	1.2492E-04	6.8962E-04	9.8961E-05	3.8624E-04	0.0000E+00
STRC18.1	2.5069E-05	1.6557E-07	2.6029E-05	1.1250E-07	0.0000E+00
SQUALNE	5.9947E-04	3.2428E-03	4.7799E-04	1.8265E-03	0.0000E+00
WATER	2.2384E-05	2.4425E-01	1.9029E-05	9.2625E-01	1.0000E+00

Table E.11 Stream summary C table for case study 2

Stream Name	HYDROLYSIS	HOLD_1ST_LIQ	HOLD_1ST_VAP	HOLD_2ND_LIQ	HOLD_2ND_VAP
Stream Phase	Mixed	Liquid	Vapor	Liquid	Vapor
Pressure	6.692121506	6.692121506	6.692121506	6.692121506	6.692121506
Temperature	245.3500671	245.3500671	245.3500671	135.321228	135.321228
Mass Fraction					
PPP	5.6942E-02	5.7242E-02	7.1969E-04	5.7230E-02	7.0402E-07
POP	3.7607E-01	3.7806E-01	3.0037E-03	3.7798E-01	1.6925E-06
POS	6.3063E-02	6.3397E-02	3.0491E-04	6.3384E-02	1.8328E-07
PLIP	1.0251E-01	1.0305E-01	7.7194E-04	1.0303E-01	2.7000E-08
POO	2.1538E-01	2.1653E-01	1.0934E-03	2.1648E-01	4.7094E-07
PLIO	9.8684E-02	9.9208E-02	4.5867E-04	9.9188E-02	1.1815E-08
P-P-OH	2.3164E-02	2.3148E-02	2.6161E-02	2.3143E-02	1.2755E-05
P-O-OH	4.5666E-02	4.5724E-02	3.4925E-02	4.5714E-02	1.2948E-05
P-LI-OH	1.0563E-02	1.0572E-02	8.8951E-03	1.0570E-02	2.9914E-06
P-S-OH	5.5744E-05	5.5835E-05	3.8709E-05	5.5823E-05	1.5861E-08
P-OH-OH	8.4436E-04	7.0129E-04	2.7678E-02	7.0097E-04	4.1645E-05
O-OH-OH	7.3538E-04	6.4119E-04	1.8400E-02	6.4098E-04	2.0001E-05
LI-OH-OH	1.4902E-04	1.2768E-04	4.1504E-03	1.2763E-04	4.5505E-06
PALMITIC	4.4808E-05	2.1946E-05	4.3324E-03	2.1876E-05	1.5807E-05
OLEIC	4.5608E-04	2.7668E-04	3.4102E-02	2.7610E-04	1.2519E-04
LINOLEIC	1.1004E-04	5.8592E-05	9.7586E-03	5.8426E-05	3.7078E-05
B-TOCOPH	2.7454E-04	2.5481E-04	3.9755E-03	2.5476E-04	1.1349E-08
B-TOCOTR	3.7396E-04	3.4180E-04	6.4064E-03	3.4173E-04	1.9732E-08
STIGSTRL	9.8533E-05	9.3722E-05	1.0009E-03	9.3702E-05	2.0173E-09
STRC18.1	2.5917E-05	2.6053E-05	2.9155E-07	2.6048E-05	7.3701E-12
SQUALNE	4.7593E-04	4.5325E-04	4.7293E-03	4.5313E-04	5.0980E-06
WATER	4.3104E-03	1.9199E-05	8.0910E-01	2.2589E-04	9.9972E-01

C.3 Crude Soybean Oil Deacidification Process Streams Summary

Table E.12 Stream summary A table for Case Study 3

Stream Name	Bleached oil	Product Oil	ECON_OIL	FH_OIL
Temperature	90.00	40.00	220.00	260.00
Pressure	1200.00	1900.00	3700.00	3700.00
Phase	Liquid	Liquid	Liquid	Liquid
% Weight				
OOO	4.5000E+01	4.5470E+01	4.5000E+01	4.5000E+01
POS	4.2250E+01	4.2687E+01	4.2250E+01	4.2250E+01
PPP	8.5980E+00	8.6824E+00	8.5980E+00	8.5980E+00
O-O-OH	2.4800E+00	2.4134E+00	2.4800E+00	2.4800E+00
O-OH-OH	1.0000E-01	2.3969E-02	1.0000E-01	1.0000E-01
OLEIC	6.5000E-01	2.4732E-02	6.5000E-01	6.5000E-01
B-TOCOPH	1.2000E-01	5.7884E-02	1.2000E-01	1.2000E-01
STIGSTRL	4.0000E-01	2.3477E-01	4.0000E-01	4.0000E-01
STRC18.1	4.0000E-01	4.0395E-01	4.0000E-01	4.0000E-01
SQUALNE	2.5000E-03	1.4767E-03	2.5000E-03	2.5000E-03
WATER	0.0000E+00	1.1092E-03	0.0000E+00	0.0000E+00

Table E. Stream summary B table for Case Study 3

Stream Name	FH_OIL	FEED_DEOD	STRIP_STEAM	DEAC_DIST
Temperature	260.00	260.00	130.00	259.31
Pressure	3700.00	3700.00	2697.13	3.30
Phase	Liquid	Liquid	Vapor	Vapor
% Weight				
OOO	4.5000E+01	4.5002E+01	0.0000E+00	5.7038E-01
POS	4.2250E+01	4.2252E+01	0.0000E+00	7.3519E-01
PPP	8.5980E+00	8.5985E+00	0.0000E+00	3.6402E-01
O-O-OH	2.4800E+00	2.4801E+00	0.0000E+00	4.4818E+00
O-OH-OH	1.0000E-01	1.0001E-01	0.0000E+00	3.7123E+00
OLEIC	6.5000E-01	6.5004E-01	0.0000E+00	3.0440E+01
B-TOCOPH	1.2000E-01	1.1401E-01	0.0000E+00	2.7606E+00
STIGSTRL	4.0000E-01	4.0002E-01	0.0000E+00	8.1615E+00
STRC18.1	4.0000E-01	4.0002E-01	0.0000E+00	1.5713E-02
SQUALNE	2.5000E-03	2.5001E-03	0.0000E+00	5.0556E-02
WATER	0.0000E+00	0.0000E+00	1.0000E+02	4.8708E+01

Table E.13 Stream summary C table for Case Study 3

Stream Name	DEAC_OIL	ECON_DEAC_OIL	TOC_SCRUB	TOCO_FLOW
Temperature	258.89	132.51	171.03	170.00
Pressure	4.89	2200.00	3.15	1700.00
Phase	Liquid	Liquid	Liquid	Liquid
% Weight				
OOO	4.5470E+01	4.5470E+01	3.0967E+00	3.0967E+00
POS	4.2687E+01	4.2687E+01	3.9912E+00	3.9912E+00
PPP	8.6824E+00	8.6824E+00	1.9757E+00	1.9757E+00
O-O-OH	2.4134E+00	2.4134E+00	2.4126E+01	2.4126E+01
O-OH-OH	2.3969E-02	2.3969E-02	7.3315E+00	7.3315E+00
OLEIC	2.4732E-02	2.4732E-02	7.9949E+00	7.9949E+00
B-TOCOPH	5.7884E-02	5.7884E-02	1.2081E+01	1.2081E+01
STIGSTRL	2.3477E-01	2.3477E-01	3.9154E+01	3.9154E+01
STRC18.1	4.0395E-01	4.0395E-01	8.5305E-02	8.5305E-02
SQUALNE	1.4767E-03	1.4767E-03	1.5964E-01	1.5964E-01
WATER	1.1092E-03	1.1092E-03	3.9346E-03	3.9346E-03

Table E.14 Stream summary D table for Case Study 3

Stream Name	LT_FEED	FFA_SCRUB	FFA_FFLOW	STEAM
Temperature	170.02	132.51	65.00	65.04
Pressure	3.00	2200.00	1200.00	2.10
Phase	Vapor	Liquid	Liquid	Vapor
% Weight				
OOO	3.2600E-05	4.5470E+01	8.2203E-05	2.5307E-13
POS	8.2953E-05	4.2687E+01	2.0914E-04	6.6719E-13
PPP	1.4900E-04	8.6824E+00	3.7560E-04	6.3626E-12
O-O-OH	4.5146E-02	2.4134E+00	1.1372E-01	9.2385E-09
O-OH-OH	2.8721E+00	2.3969E-02	7.1958E+00	5.0182E-04
OLEIC	3.5584E+01	2.4732E-02	8.8530E+01	1.1888E-01
B-TOCOPH	4.7822E-01	5.7884E-02	1.1729E+00	9.5038E-09
STIGSTRL	1.1226E+00	2.3477E-01	2.8265E+00	2.1444E-08
STRC18.1	1.0377E-06	4.0395E-01	2.6169E-06	1.4350E-14
SQUALNE	2.5384E-02	1.4767E-03	6.3744E-02	3.6529E-07
WATER	5.9872E+01	1.1092E-03	9.6658E-02	9.9881E+01

F.

VLE & SLE Analysis of Lipid Systems Through the Original UNIFAC & UNIFAC-CI Models

In this Appendix, the predictive accuracy of the Original UNIFAC and UNIFAC-CI for VLE and SLE of lipid systems is, to some extent, discussed. As it has been widely discussed in Chapter 2 and Chapter 3 of this thesis, experimental data on lipid systems is, in the best case, scarce. Consequently, the systems addressed in this Appendix are mainly involving fatty esters, free fatty acids, fatty alcohols, and glycerols. Unfortunately, experimental data on VLE or SLE of triglycerides are not available in the open literature.

Two sections constitute this Appendix: In the first section the VLE analysis of twelve binary systems takes place. Six of these systems are composed by a fatty methyl ester and methanol; six systems are composed by a fatty alcohol and glycerol; and one composed by water and glycerol. In the second section, the SLE analysis of five FFA-FFA systems is performed.

F.1 Vapor-Liquid Equilibria of Lipid Systems

The selected lipid systems to be analyzed are: 1) Methyl Laurate-Methanol, 2) Methyl Myristate-Methanol, 3) Methyl Oleate-Methanol, 4) Methyl Laurate-Ethanol, 5) Methyl Myristate-Ethanol, 6) Methyl Oleate-Ethanol, 7) Methanol (1)-Glycerol (2), 8) Ethanol (1)-Glycerol (2), 9) 1-Propanol (1)-Glycerol (2), 10) 2-Propanol (1)-Glycerol (2), 11) 1-Butanol (1)-Glycerol (2), 12) Water (1)-Glycerol (2).

From the VLE predictions (see Figures F.1-F.12) it is possible to observe that for the binary systems 1-6 both experimental data and predictions (predicted by both UNIFAC models) show negative deviations (see the T-x line) from ideality. To be highlighted that for systems 1-3 a better prediction is obtained through the Original UNIFAC model; while for systems 4-6 systems are better prediction is obtained through the UNIFAC-CI model.

For system 7, the predictions obtained through both UNIFAC models show a positive deviation from ideality whereas the experimental data shows that the system is ideal. However, for system 8 predictions are almost the same as ideality whereas the data show a negative deviation from ideality. In the case of systems 9-11 experimental and predicted data show a negative deviation from ideality. For system 12 the data show positive deviation from ideality.

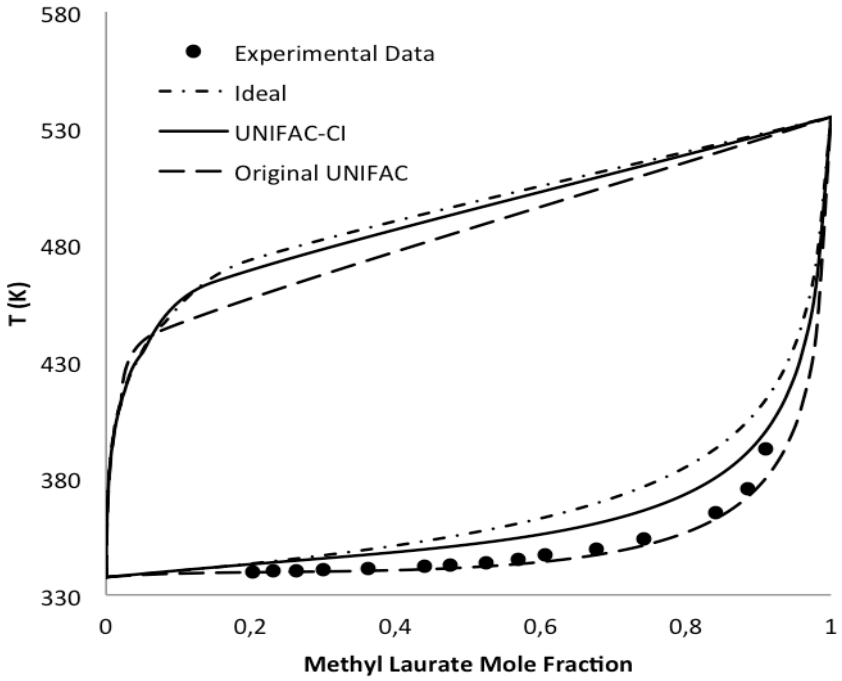


Figure F. 1 Lipid System Methyl Laurate (1)-Methanol (2)

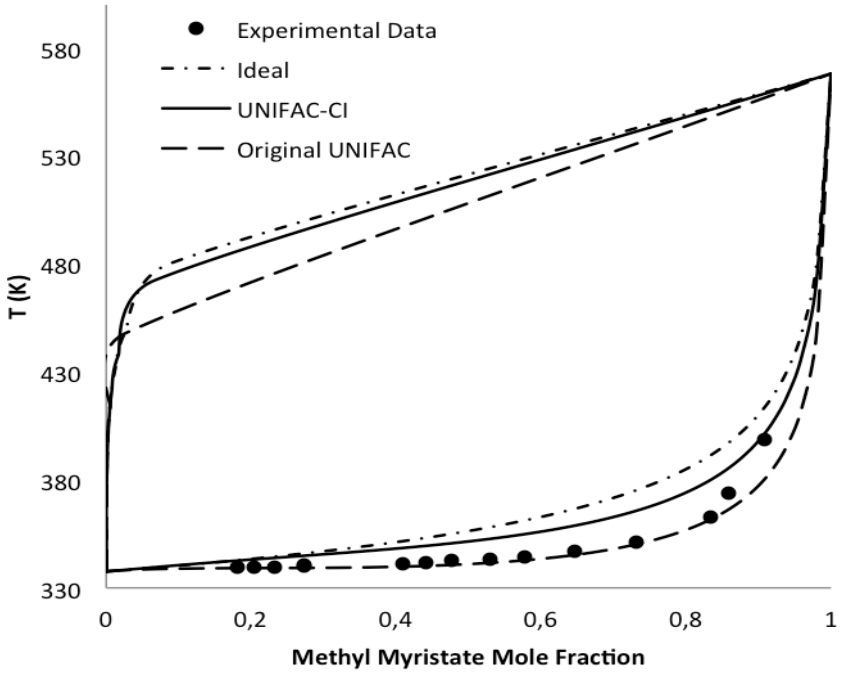


Figure F. 2 Lipid system Methyl Myristate (1)-Methanol (2)

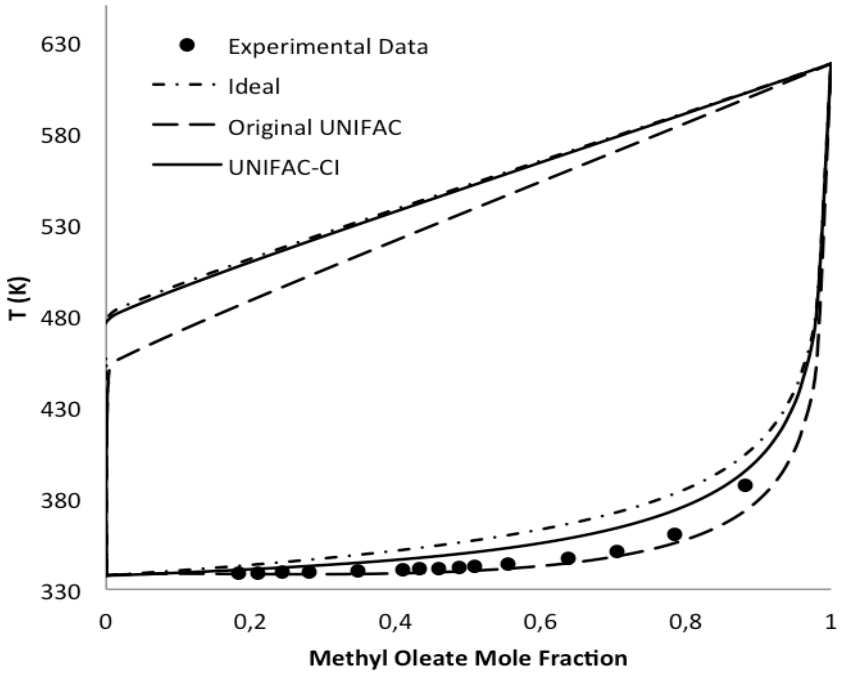


Figure F. 3 Lipid system Methyl Oleate (1)-Methanol (2)

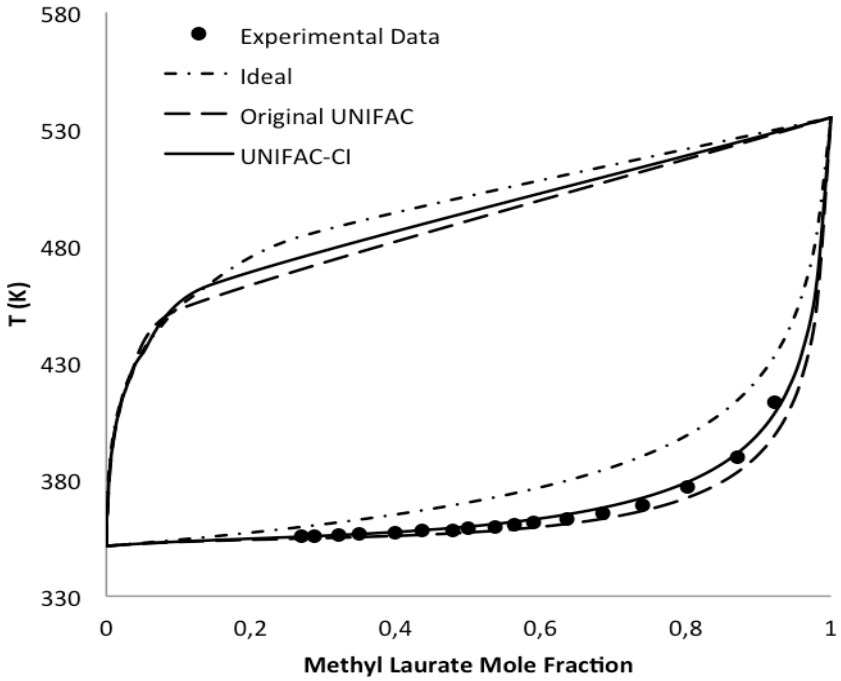


Figure F. 4 Lipid System Methyl Laurate (1)-Ethanol (2)

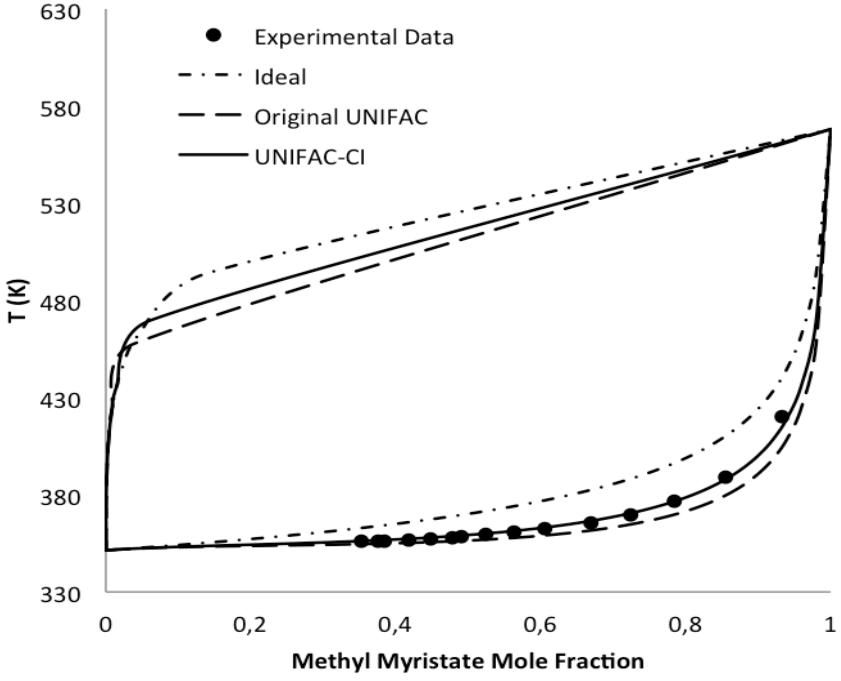


Figure F. 5 Lipid system Methyl Myristate (1)-Ethanol (2)

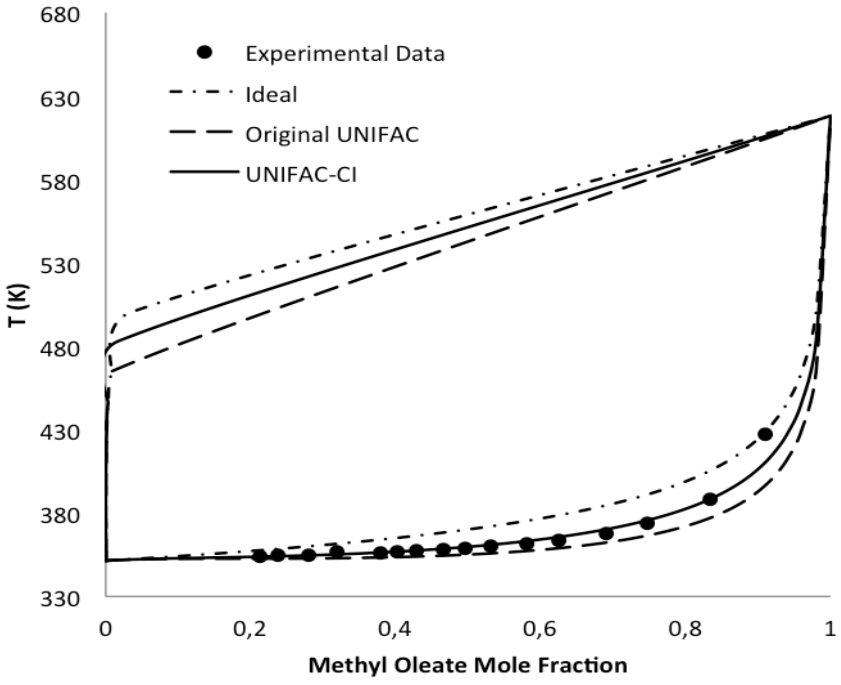


Figure F. 6 Methyl Oleate (1)-Ethanol (2)

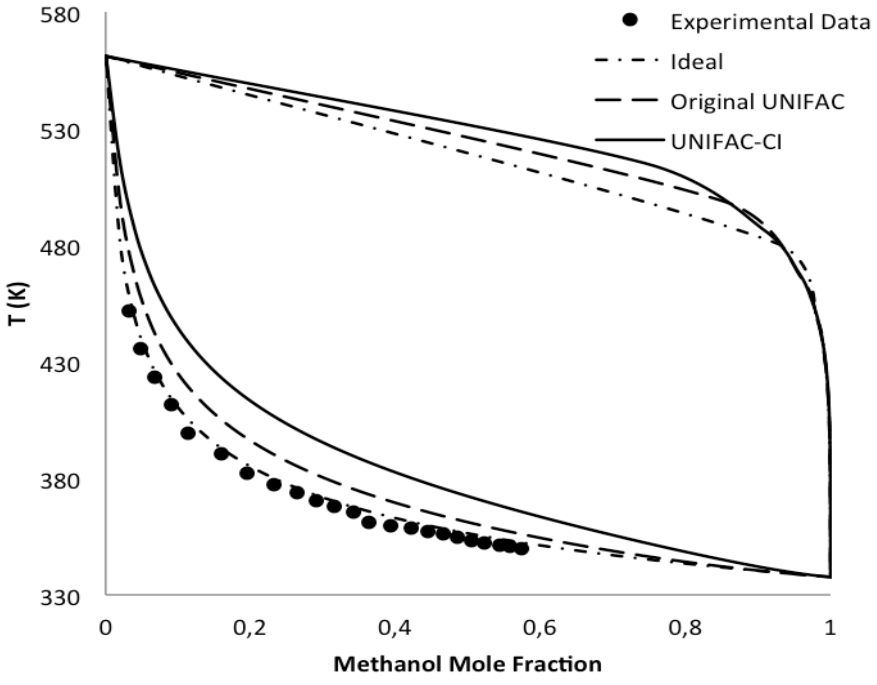


Figure F. 7 Lipid System Methanol (1)-Glycerol (2)

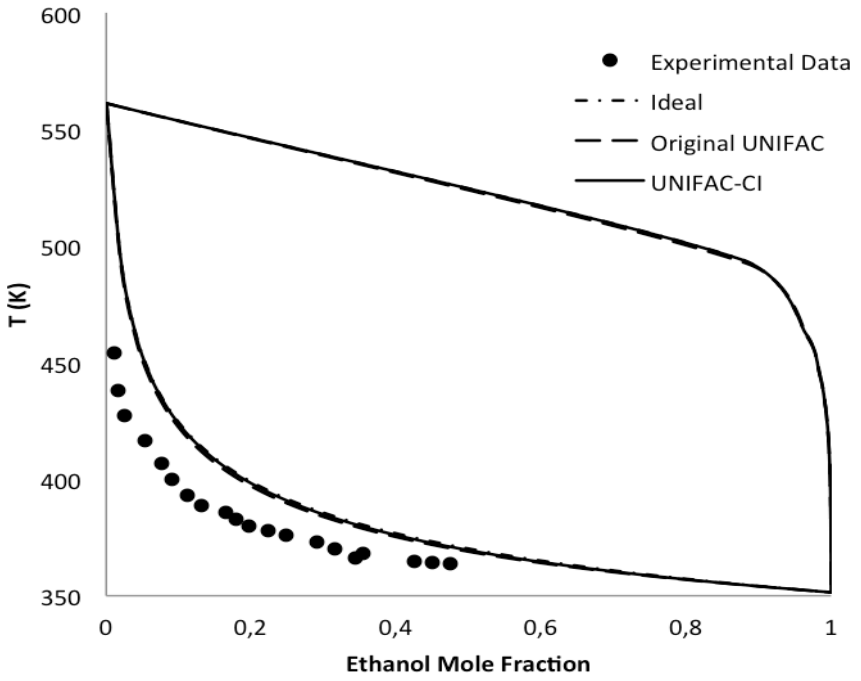


Figure F. 8 Lipid system Ethanol (1)-Glycerol (2)

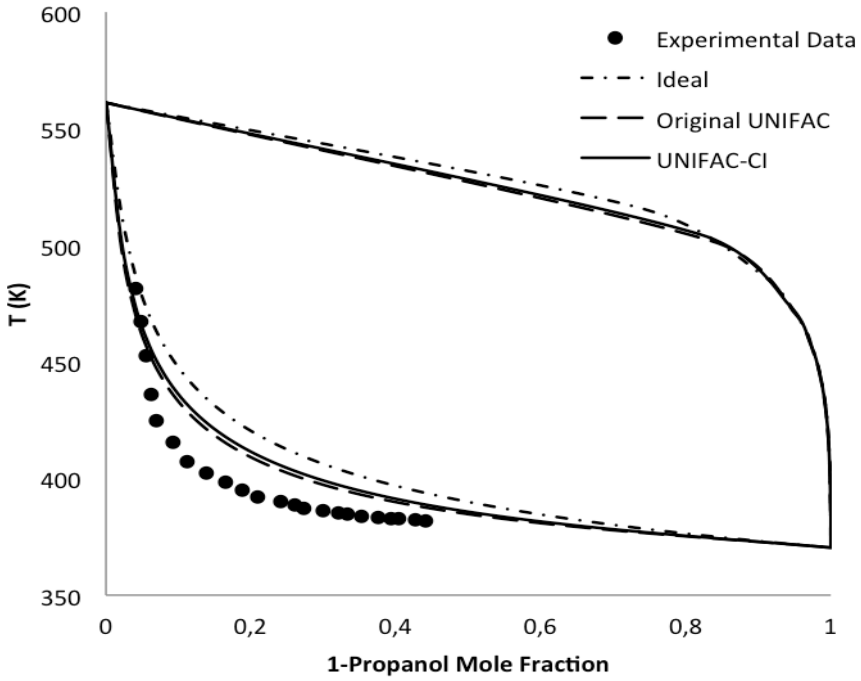


Figure F. 9 Lipid system 1-Propanol (1)-Glycerol (2)

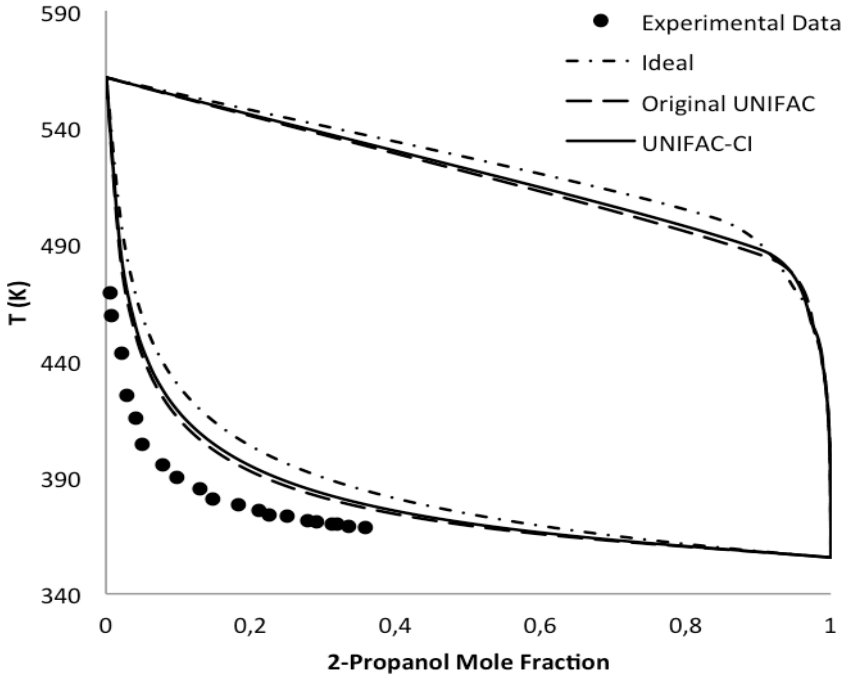


Figure F. 10 Lipid system 2-Propanol (1)-Glycerol (2)

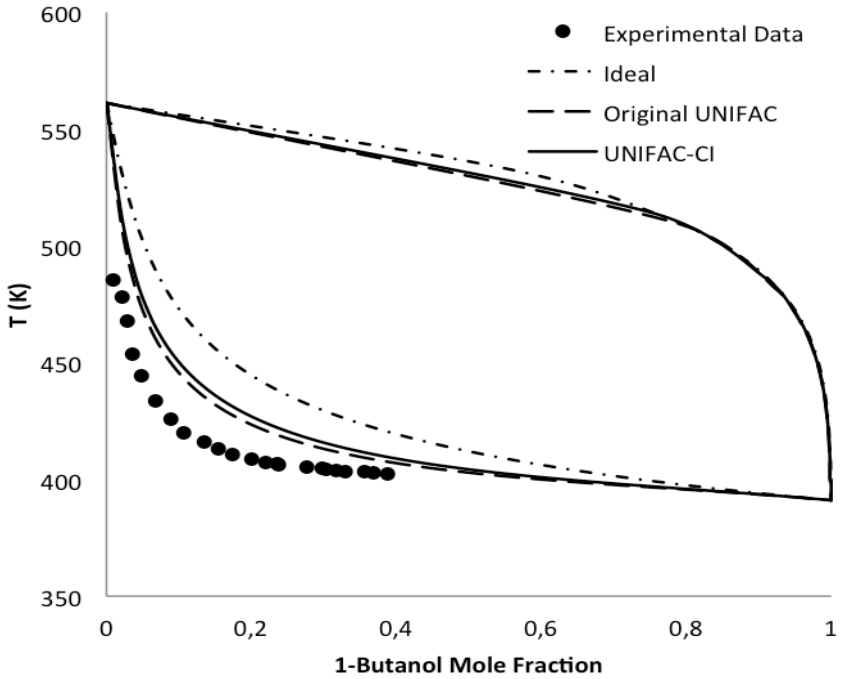


Figure F. 11 Lipid system 1-Butanol (1)-Glycerol (2)

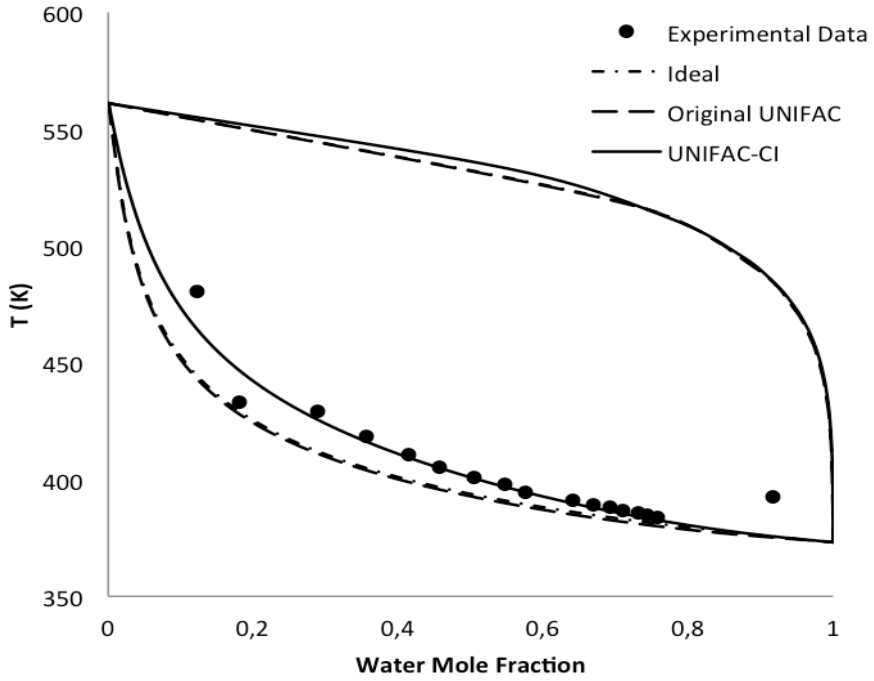


Figure F. 12 Lipid system Water (1)-Glycerol (2)

F.2 Solid-Liquid Equilibria of Lipid Systems

As can be seen in Figures F.13-F.17, the experimental data has a complex behavior. This is a result of having not only eutectic point/temperature but also peritectic and/or metatectic points/temperatures. Unfortunately, when using the UNIFAC models, it is only possible to capture some of the data but it is not possible to capture the complexity of the systems.

Hence, special calculations need to be set up and most likely tailor-made parameters need to be regressed. It is to be mentioned that this kind of complex system has been predicted using CPA for non-ideality systems. In the systems analyzed, an ideal behavior is observed as the species involved are chemically the same (acids).

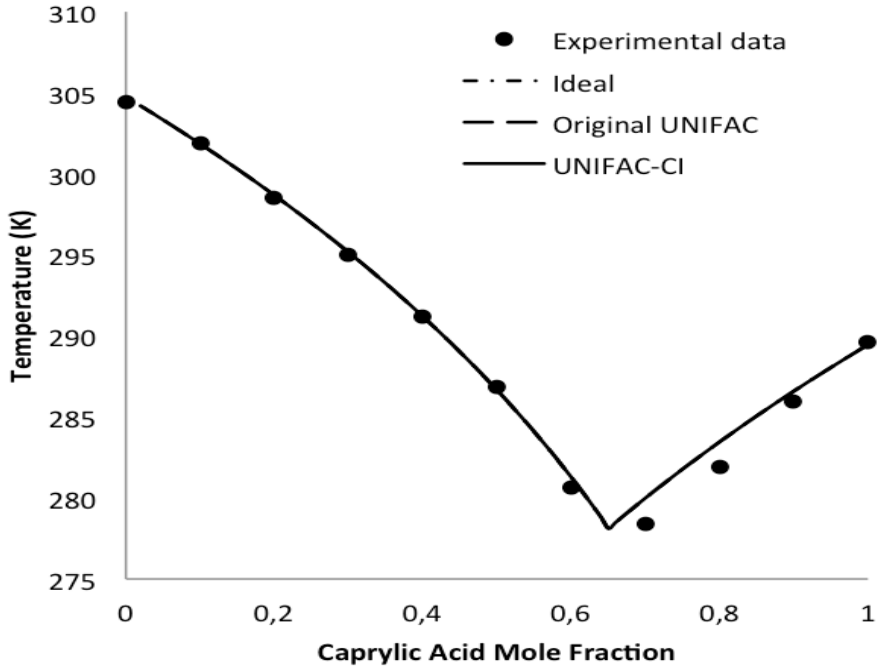


Figure F. 13 Lipid system Caprylic Acid (1)-Capric Acid (2)

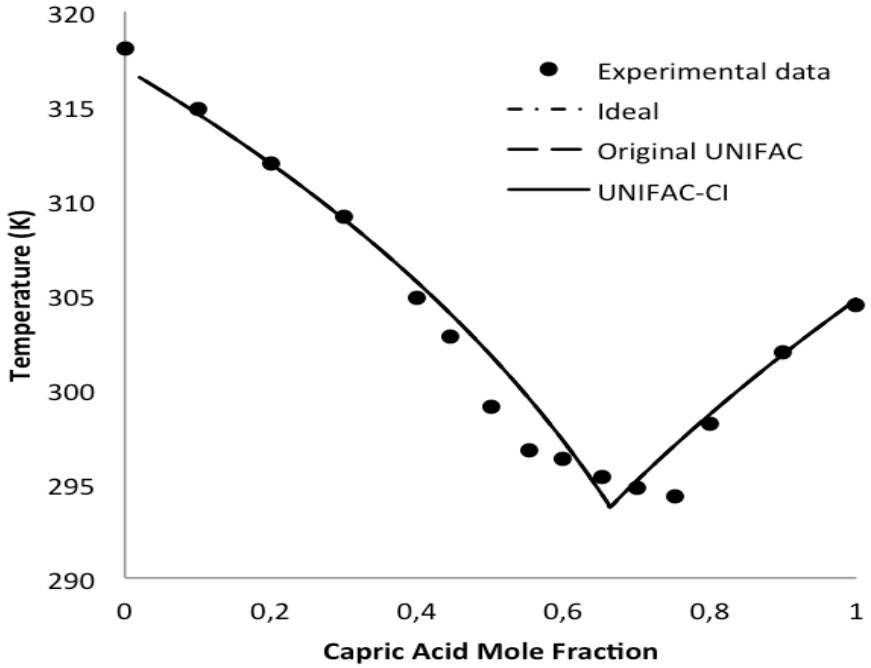


Figure F. 14 Lipid system Capric Acid (1)-Lauric Acid (2)

1.

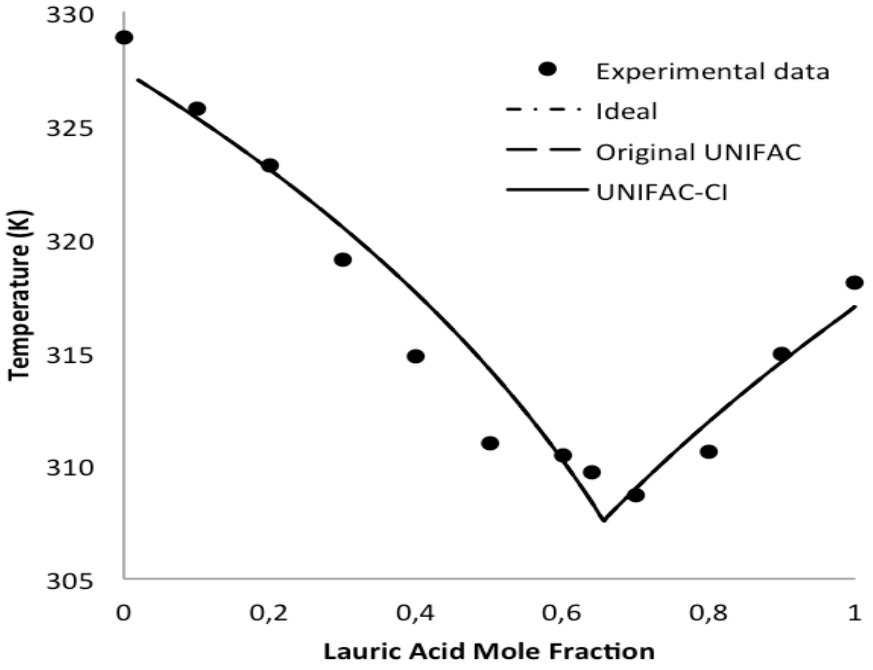


Figure F. 15 Lipid system Lauric Acid (1)-Myristic Acid (2)

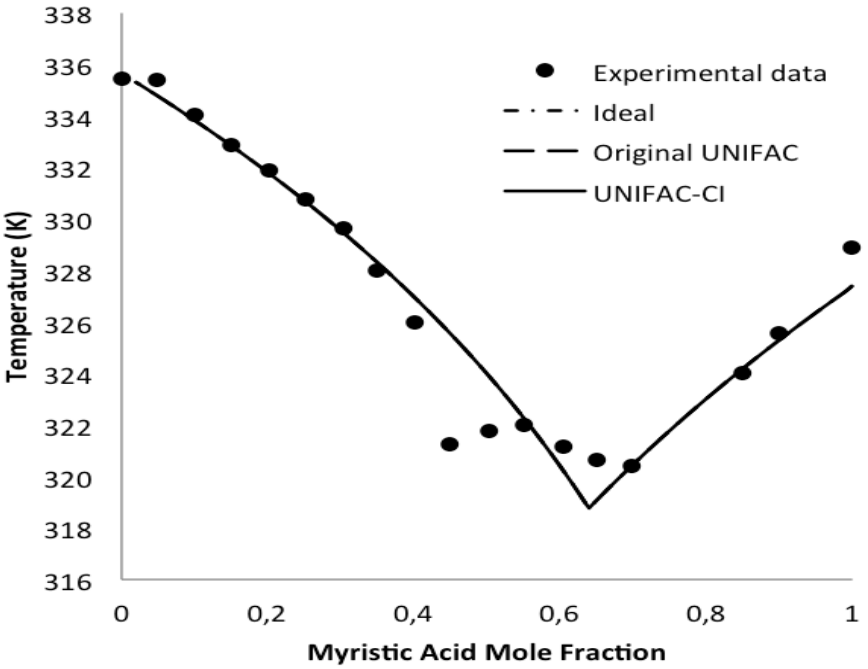


Figure F. 16 Lipid system Myristic Acid (1)-Palmitic Acid (2)

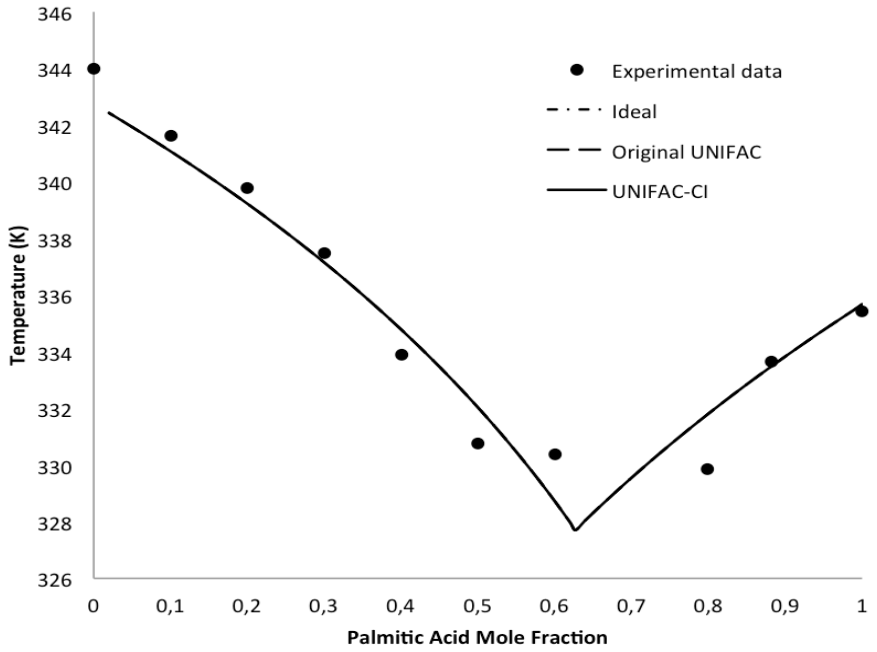


Figure F. 17 Lipid system Palmitic Acid (1)-Stearic Acid (2)

Final Remarks

Although the predictive accuracy of the selected UNIFAC models has proven to be sufficient in most of the cases, it is still necessary to fine-tune the model parameters in order to obtain a better prediction of the behavior of the VLE and SLE. Furthermore, for these lipid systems, the aim would be to collect suitable amount of lipid data and regress the parameters for systems no previously discussed and under temperature conditions that could match those present in typical lipid-related processes (*i.e* deodorization process). Finally, it is necessary to highlight that one of the advantages of using the UNIFAC-CI model is that through the regression of atom interactions parameters, missing group contribution/interaction parameters for any lipid system can possibly be generated.

Nomenclature

ABSPC	=	adsorption column in Case Study 1
ARD	=	average relative deviation
a_1, a_2, a_3	=	coefficients of Eq.(3.2)
A_{1k},...,D_{1k},	=	constants of Eq. (3.2)
A_{2k},...,D_{2k}	=	constants of Eq. (3.2)
$B_{1,A}$,$B_{2,A}$	=	temperature dependency correlation parameters of fragment *A* in Eq. (3.21)
b_1, b_2, b_3	=	coefficients of Eq. (3.2)
C_r	=	contribution of first-order group of type *r*
CCFA	=	chemical constituent fragment approach
C_{Pi}	=	liquid heat capacity of component *i* in J/molK
COND1	=	first condenser in Case Study 1
COND2	=	first condenser in Case Study 2
COND3	=	first condenser in Case Study 3
c_1, c_2	=	coefficients of Eq. (3.2)
DAGs	=	diglycerides
Deod_Oil	=	deodorized oil stream
DOE	=	design of experiments
D_s	=	contribution of second-order group of type *s*
DTDC	=	desolventiser–toaster–drier–cooler
DV	=	design variables
d_1, d_2, d_3	=	coefficients of Eq. (3.4)
D/A	=	Design/Analysis
Enriched_FFA	=	enriched free fatty acid stream
Enriched_TOC	=	enriched tocopherol stream
EoS	=	equation of state
E_t	=	contribution of third-order group of type *t*
EVAP1	=	first evaporator of Case Study 1
EVAP2	=	first evaporator of Case Study 1
E1, E2,..., E10	=	heat exchangers in Case Study 1
F	=	number of factorial points
FAME	=	fatty acid methyl ester

F_c	=	correction factor in Eq. (3.13)
FFA	=	free fatty acids
f_0, f_1	=	constants of Eq. (3.5)
f(X)	=	simple function of the target property X in Eq. (3.2)
GC	=	group contribution
G_f	=	standard Gibbs energy at 298K
G_{f0}	=	additional adjustable parameter of the estimation models of Eq.(3.1)
GTD	=	general temperature dependent
H_f	=	standard enthalpy of formation at 298K
H_{fus}	=	standard enthalpy of fusion at 298K
H_{f0}, H_{v0}, H_{fus0}	=	additional adjustable parameters of the estimation models of Eq.(3.1)
HT_Scrubber	=	high temperature condensing zone in Case Study 3.
H_{vap}	=	standard enthalpy of vaporization at 298K
LLE	=	liquid-liquid equilibria
LT_Scrubber	=	low temperature condensing zone in Case Study 3.
MAGs	=	monoglycerides
MG	=	Marrero and Gani
MOS	=	mineral oil system
M_r	=	number of first-order group *r* in the molecule
MW_i	=	molecular weight compound *i*
MW_{oil}	=	molecular weight oil
N	=	number of runs
N_C	=	number of carbon atoms
N_{CS}	=	number of carbon atoms in the alcohol chain
$N_{frag,A}$	=	number of fragments A in the component
N_k	=	number of group *k* in the molecule
NLP	=	non-linear programming
NOL	=	neutral oil loss
N_s	=	number of second-order group *s* in the molecule
O_t	=	number of third-order group *t* in the molecule

PB	=	Plackett-Burman
P_{ci}	=	critical pressure of compound *i* in K or °C
$P_{c,mix}$	=	critical pressure of the mixture in K or °C
P_{c1}, P_{c2}	=	additional adjustable parameters of the estimation models of Eq.(3.1)
P_i^{sat}	=	vapor pressure of compound *i* in Pa
PP	=	process parameters
Q	=	correction term of Eq. (3.2)
q	=	constant of Eq. (3.4)
R	=	universal gas constant
RSM	=	Response Surface Methodology
SLE	=	solid-liquid equilibria
STP1	=	first stripping column in Case Study 1
s_0, s_1	=	constants of Eq.**Error! Reference source not found.**
T	=	temperature in K or °C
TAGs	=	triglycerides
T_b	=	normal boiling point in K
T_{ci}	=	critical temperature of compound *i* in K or °C
$T_{c,mix}$	=	critical temperature of the mixture in K or °C
T_m	=	normal melting point in K
T_{ri}	=	reduced temperature of compound *i*
T_{m0}, T_{b0}, T_{c0}	=	additional adjustable parameters of the estimation models of Eq.(3.1)
V_c	=	critical volume
V_{c0}	=	additional adjustable parameter of the estimation models of Eq.(3.1)
V^l	=	liquid molar volume
V^{lm}_A	=	liquid molar volume of fragment *A*
V^v	=	vapor molar volume
w	=	parameter of Eq. (3.1)
x_i	=	mol fraction of compound *i*
x_i^{exp}	=	experimental/plant value

x_i^{sim}	=	value obtained through the simulation
z	=	parameter of Eq. (3.1)
Z_{RAi}	=	Rackett parameter of compound *i*
$Z_{RA,mix}$	=	Rackett parameter of mixture
1ST_EVAP	=	first effect evaporator in Case Study 1
2ND_EVAP	=	second effect evaporator in Case Study 1

Greek Symbols

α, β, γ, δ	=	constants of Eq.(3.4)
ΔH_i^{vap}	=	enthalpy of vaporization in (kJ/mol)
ξ_1, ξ_2	=	constants of Eq. (3)
ρ_i^l	=	liquid density of compound *i*
ρ_{ref}	=	reference density at a given temperature
μ_i^l	=	liquid viscosity of compound *i*
σ_i	=	surface tension of compound *i*

Subscripts

ci	=	critical of compound *i*
c,mix	=	critical of the mixture
i	=	component
k	=	group of compound *i*
r	=	first-order group
ref	=	reference
ri	=	reduced of compound *i*
oil	=	oil
s	=	second-order group
t	=	third-order group

Superscripts

l	=	liquid
v	=	vapor

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