Systematic computer aided methods and tools for lipid process technology

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Publication date:
2018

Document Version
Publisher's PDF, also known as Version of record

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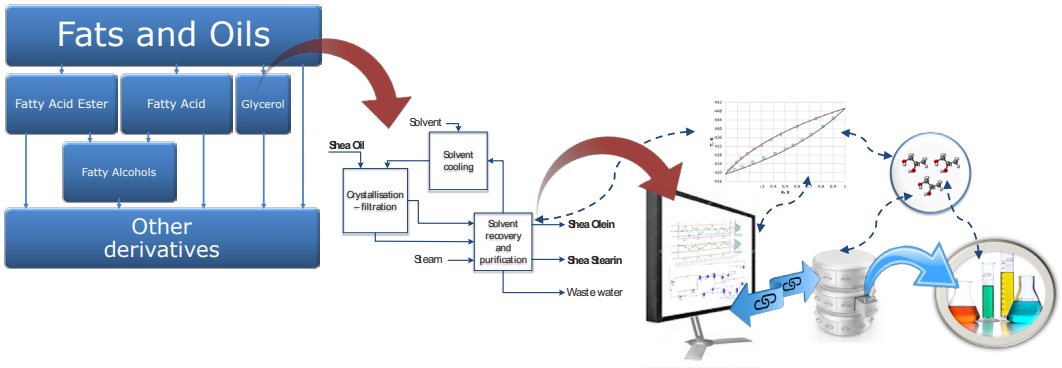

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PhD Thesis

2018

DTU Chemical Engineering
Department of Chemical and Biochemical Engineering

Systematic computer aided methods and tools for lipid process technology

Doctor of Philosophy Thesis

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October 2018

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ABSTRACT

Industrial use of lipids increased as a consequence of the rapid development in bio-based economies. In addition to food products applications, lipids are used by many other industrial sectors, like biodiesel, edible oil, health, personal care, oleochemicals to name a few. The lipid-based industry expansion led to new challenges regarding the design and development of better performing processes and products. Despite the advances in the currently available property modelling and product-process design techniques via different computer-aided methods and tools for the chemical and petrochemical industries, the lipid-based industry has not exploited this knowledge. Availability of pure compounds and mixture models is of high importance as they are the core of all methods and tools for process-product design. It is very difficult to provide a complete set of experimental data for developing pure compound and mixtures thermodynamic models to cover all of the lipid compounds. These issues justify the effort made to develop thermodynamic models that are able to predict the properties of lipid components and their mixtures from a minimum amount of experimental data. The models should also be able to be implemented within different tools, in order to achieve reduced time and cost when designing lipid related products and processes.

In this work, a systematic identification method for data analysis and phase equilibria modelling for lipid systems was developed. The aim of the method is to offer support for fast assessment and solution of the data selection and binary interaction parameter estimation for group contribution based models problem. The developed method covers the following aspects: (1) inclusion of a detailed algorithm for data selection, which complements personal judgment and available expertise; (2) use of an efficient calculation sequence, which can be further exploited for planning experimental data collection in order to fill in the gaps within the binary interaction matrix; (3) the regression problem formulation and solution for each regression step. The method utilised the *Lipids Database,* which provided the pure compound information, and the data for lipid mixtures. The method was applied for different UNIFAC model variants, and the new lipid-based parameters were validated and tested for predictive abilities. This thesis shows that for the VLE description, the lipid-based parameters for all the UNIFAC variants provide the best performances when compared with published parameters for the same models. The extrapolation of the lipid-based parameter to SLE description show similar performances as the published parameters.

The Lipids Database containing the new parameters for Original UNIFAC model was used to study the solvent fractionation process of Shea oil. The process design, modelling and analysis were performed using well-known methods and tools. The analysis results of the base case provided the opportunity to bring improvements to the process economics. The process retrofit involved heat integration and led to a decrease in utility consumption by 50%. The use of the *Lipids Database* with the new lipid-based parameters for Original UNIFAC allowed a faster implementation and evaluation of the process. This highlights the importance of having such a database with necessary thermodynamic models for developing and improving processes within lipid-based industry.

RESUMÉ

Som følge af den øgede udvikling i forbindelse med bio-baserede økonomier har den industrielle anvendelse af lipider været stigende. Ud over fødevareindustrien anvendes lipider i mange andre industrisektorer som biodiesel, spiseolie, sundhed, personlig pleje, oleokemikalier og andre. Udvidelsen af lipidindustrien førte til nye udfordringer for at designe og udvikle bedre processer og produkter. Der er sket store fremskridt inden for modellering af stoffers egenskaber. Desuden er der kommet nye produkt-procesdesign teknikker via forskellige computer-støttede metoder og værktøjer i den kemiske og petrokemiske industri. Den lipid-baserede industri har blot ikke udnyttet denne viden. Tilgængelighed af modeller for rene forbindelser og blandinger er af stor betydning, fordi de udgør kernen i alle metoder og værktøjer til proces-produktdesign. Det er meget vanskeligt at levere et komplet eksperimentelt datasæt til udvikling af termodynamiske modeller for rene komponenter og blandinger, der dækker alle lipidforbindelserne. Derfor er det retfærdiggjort at der udvikles termodynamiske modeller, der kan forudsige egenskaberne af rene lipider og deres blandinger ved anvendelse af en minimums mængde eksperimentelle data. Modellerne skal implementeres inden for forskellige værktøjer for at opnå reduceret tid og omkostninger ved design af lipidprodukter og lipidprocesser.

En systematisk identifikationsmetode til dataanalyse og fase-ligevægtsmodellering for lipidsystemer blev udviklet i dette arbejde. Formålet med metoden er at opnå en hurtig vurdering og fastsættelse af dataudvælgelsen for bestemmelsen af binære interaktionsparametre for gruppebidragsmodeller. Den udviklede metode dækker følgende aspekter: (1) inddragelse af en detaljeret algoritme til dataudvælgelse som supplement til personlig vurdering og tilgængelig ekspertise; (2) anvendelse af en effektiv beregningssekvens som kan udnyttes til planlægning af yderligere eksperimentel dataindsamling for at udfylde hullerne inden for den binære interaktionsmatrix og for at muliggøre trin for trin estimering af de binære gruppe- interaktionsparametre; (3) formulering og løsning af regressionsproblemet for hvert regressionstrin. Metoden anvender *Lipids Database*, som leverer informationen om rene forbindelser og for lipidblandinger. Metoden blev anvendt i forbindelse med forskellige UNIFAC modelvarianter. De nye *lipidbaserede* parametre blev valideret og testet for ekstrapolering. Det blev vist, at for VLE-beskrivelsen giver de lipidbaserede parametre for alle UNIFAC-varianterne de bedste resultater, når de sammenlignes med offentliggjorte parametre for de samme modeller. Ekstrapoleringen af de lipidbaserede parametre til SLE-beskrivelse giver resultater som er sammenlignelig med resultaterne fra de offentliggjorte parametre.

Desuden blev den oprindelige UNIFAC-model med de lipidbaserede parametre brugt til at udføre procesdesign, modellering og analyse af Shea-olie solventfraktionering. Det foreslåede base-case design blev forbedret gennem retrofit ved at anvende varmeintegration.

PREFACE

This thesis is submitted as fulfilment of the requirements for the degree of Doctor of Philosophy in Chemical Engineering at the Technical University of Denmark (DTU). The research project has been carried out at KT Consortium, at the Department of Chemical and Biochemical Engineering, from September 2015 to October 2018 under the supervision of Professor John M. Woodley, Professor Georgios M. Kontogeorgis and Dr. Bent Sarup. The project was founded by DTU and Alfa Laval Copenhagen A/S.

I would like to express my special appreciation and gratitude to my supervisors Professor John Woodley, Professor Georgios Kontogeorgis and Dr Bent Sarup for all their support, guidance trust and encouragements throughout this project. I would like to also express my gratitude to Professor Rafiqul Gani, who gave me the opportunity to take this project and for his supervision and guidance.

I would like to thank to my former and current colleagues at KT Consortium, CERE and PROSYS. I wish to extend a special thank you for the support, discussions and help in times of need to: Seyed, Sawitree, Daniela, Spardha and Nipun. A special thanks also to Francois, Teresa, Zacharias, Eva and Christian. Special acknowledgments are expressed to Professor Kaj Thomsen for the Danish translation of the abstract.

I would like to express my gratitude to Professor Valentin Pleșu for all his support throughout my chemical engineering years, who always believes in me.

I would like to thank to all my friends for their care and support. Big thanks for help, patience and fun times to Abeni, Voica, Elena and Paula.

I would like to thank the one person that has shared this journey and supported me through the struggles. Rafa, I am grateful for all your encouragements and care.

Last but not least, my deep recognition is addressed to my beloved parents, Aurora and Carmelino, for their warm care, endless support and unlimited love.

Olivia Ana Perederic

November 2018
Kongens Lyngby, Denmark

CONTENTS

ABSTRACT I

RESUMÉ III

PREFACE V

CONTENTS VII

NOMENCLATURE IX

1 INTRODUCTION 1

1.1 BACKGROUND AND MOTIVATION 2
1.2 PROJECT OBJECTIVES 4
1.3 THESIS STRUCTURE 5

2 LIPID PHASE EQUILIBRIA: DATA AND MODELS 7

2.1 DATA AVAILABILITY AND QUALITY 8
2.2 PHASE EQUILIBRIA CALCULATION MODELS FOR LIPID SYSTEMS 16

3 SYSTEMATIC IDENTIFICATION METHOD: DESCRIPTION 33

3.1 DATA COLLECTION AND ANALYSIS 37
3.2 DATA ORGANIZATION AND SELECTION 37
3.3 PARAMETER ESTIMATION AND VALIDATION 38
3.4 ALGORITHM A: DATA ORGANIZATION 39
3.5 ALGORITHM B: DATA SELECTION ALGORITHM 41
3.6 METHOD APPLICATION EXAMPLE 42
SUMMARY 47

4 SYSTEMATIC IDENTIFICATION METHOD: APPLICATION AND VALIDATION 49

4.1 DATA COLLECTION AND ANALYSIS 50
4.2 DATA ORGANIZATION AND SELECTION 51
4.3 PARAMETER ESTIMATION AND VALIDATION 52
4.4 OTHER UNIFAC MODELS 70
SUMMARY 72

5 SYSTEMATIC IDENTIFICATION METHOD: PREDICTIVE ABILITIES 73

5.1 VLE PREDICTION 74
5.2 SLE PREDICTION 76
5.3 NEED FOR NEW DATA 82
SUMMARY 85

6 LIPID THERMODYNAMIC MODELS APPLIED TO LIPIDS PROCESSING: SOLVENT FRACTIONATION 87

6.1 PROCESS IMPORTANCE AND DESCRIPTION 88
6.2 PROCESS MODELLING, SIMULATION AND ANALYSIS 94
6.3 PROCESS IMPROVEMENTS 102
SUMMARY 109

FINAL REMARKS 111

CONCLUSIONS 112
FUTURE WORK 113
APPENDIX A LIPIDS DATABASE STRUCTURE 115
APPENDIX B VLE DATASETS 117
APPENDIX C SLE DATASETS 137
APPENDIX D LLE DATASETS AND MODELLING 141
APPENDIX E DSC EXPERIMENTAL RESULTS 145
APPENDIX F SHEA OIL FRACTIONATION SIMULATION RESULTS 157
REFERENCES 165

NOMENCLATURE

List of Abbreviations

A	association
AP	acidification potential
ASOG	Analytical Solution of Groups
ATP	aquatic toxicity potential
CAPEX	capital expense
CBE	cocoa butter equivalents
CBEX	cocoa butter extenders
CBI	cocoa butter improvers
CBR	cocoa butter replacement
CBS	cocoa butter substitute
CI	connectivity indices
CPA	Cubic Plus Association
CR-1	combining rule
CW	cooling water
ECR	Elliot combining rule
EoS	equation of state
FH	Flory-Huggins
GC	group contribution
GCA	group contribution-associating
GLY	constitutive group for glycerol molecule in lipid-based parameter matrix for different UNIFAC model variantss
GWP	global warming potential
HI	heat integration
HTC	human toxicity carcinogenic
HTPE	human toxicity by exposure
HTPI	human toxicity potential by ingestion
ICAS	Integrated Computer Aided System
IL	ionic liquids
Lip	lipids
LLE	liquid-liquid equilibria
LP	low pressure steam
MHV1	modified Huron–Vidal first order
MHV2	modified Huron–Vidal second order
min	minute (see Appendix E)
MoT	Modelling Testbed
NRTL	Non-Random Two Liquid
OPEX	operating expense
PCOP	photochemical oxidation potential
PFD	process flowsheet diagram

PPC	polar perturbed chain
PR	Peng-Robinson
Pub	published
RK	Redlich–Kwong
SAFT	Statistical Associating Fluid Theory
SH	Starvermann–Guggenheim
SLE	solid-liquid equilibria
SRK	Soave-Redlich-Kong
TDE	ThermoData Engine
UNIFAC	Universal Quasi-Chemical Functional Group Activity Coefficient
UNIQUAC	Universal Quasi-Chemical
VLE	vapour-liquid equilibria

Compounds abbreviation

C30-44	triacylglycerol with 30-44 carbon atoms
CHOLSTRL	cholesterol
DAG	diacylglycerol
FA	fatty acid
MAG	monoacylglycerol
MUFA	mono- unsaturated fatty acid
PUFA	poly-unsaturated fatty acid
SFA	saturated fatty acid
SITOSTRL	sitosterol
SMUT	symmetric monounsaturated triacylglycerol
STRC12.0	stigmasterol-dodecanoate ester
TAG	triacylglycerol
TOCO	tocopherol

Acylglycerol components abbreviation

A	arachidic
Li	linoleic
M	myristic
O	oleic
OH	hydroxyl
P	palmitic
S	stearic

List of Symbols

$A_{0,1,2}$	factor(s) within the general form of binary interaction parameter term in UNIFAC model (see Eq. 2.18)
A_k	van der Waals group surface area, cm^2/mol
a_{mk}	binary group interaction parameter for group m and n (related to Ψ_{mn} in Eq. 2.6)
$a_{mk}^{\ 0}$	initial value of binary group interaction parameter (see Eq. 4.4)
ARD_0	average relative deviation of a data set
$ARD_1(\%)$	average relative deviation in percent for all the data sets within a category-group
$ARD_2(\%)$	average relative deviation in percent for all data sets (VLE, SLE)
$B_{0,1,2,3}$	Parameters within temperature correction equation (see Appendix E)
C	correction temperature, °C (see Appendix E)
C_0	parameter for general equation form of combinatorial term in UNIFAC model
C_1	parameter for general equation form of volume fraction in UNIFAC model
$C_{1,..,10}$	parameters within DIPPR correlation (see Appendix A)
F_{obj}	objective function (see Eq. 4.2)
F_P	average relative deviation of calculated pressure, kPa(see Eq. 4.3)
F_R	regularization term within objective function (see Eq. 4.4)
g^E	Gibbs excess energy
H^E	excess enthalpy
M	number of pairs that need to be estimated (within category-group notation X.M.N)
M	number of phase equilibria (VLE, SLE, LLE) data sets within a category-group
N	number of applicable tests (see Eq. 2.3)
N	total phase equilibria (VLE, SLE) data points tests)
N	type of involved pair (within category-group notation X.M.N)
P_i^{sat}	pure compound saturation pressure of molecule i
q_i	pure component molecule surface area of compound i
Q_i	quality factor value of a VLE data set for one of the following tests: (Q_1)Herington, (Q_2) van Ness, (Q_3) Point, (Q_4) Infinite dilution, (Q_5)EOS test
Q_k	normalised group surface area parameter of group k
Q_{pure}	end point test quality factor value of a VLE data set
Q_{VLE}	overall quality factor value of a VLE data set
R	ideal gas constant
R	heating speed, °C/minute (see Appendix E)
r_i	pure component molecule volume parameter of molecule i
R_k	normalised group volume parameter of group k
T	Temperature, K
T	total data sets number (within $ARD_2(\%)$)
$\bar{T}$	average temperature, °C (see Appendix E)
T^*	shifted temperature (see Chapter 6)
T_0	reference temperature (see Table 2.3)

T_c	critical temperature, K (see Appendix A)
T_{ei}	onset temperature, °C (see Appendix E)
T_{er}	offset temperature, °C (see Appendix E)
T_{lit}	literature value of the melting point, °C (see Appendix E)
$T_{m,i}$	melting temperature of compound i
T_p	peak temperature, °C (see Appendix E)
T_r	reduced temperature (see Appendix A)
U_{mk}	interaction energy between group m and k
V	heating speed, K/minute (only in Appendix E)
V^E	excess volume
V_k	van der Waals group volume, cm^3/mol
x	liquid phase mol fraction of component i
X	number of involved group interaction parameters pairs (within category-group notation X.M.N)
X_k	group k concentration in the mixture
y	vapour phase mol fraction of component i
Z	lattice coordination number (it is equal to 10 for UNIFAC)
Γ_k	activity coefficient of group k in mixture
$\Gamma_{k,i}$	activity coefficient of group k in pure component i
ΔC_p	heat capacity
ΔH^f	fusion enthalpy of compound i

Greek letters

β	empirical term within objective function (see Eq. 4.4)
γ_i	activity coefficient of component i
θ_i	area fraction of component i
θ_k	area fraction of group k
Θ_m	surface area fraction of group m within the mixture
$\nu_{k,i}$	group k frequency in molecule i
Φ_i	molecular volume fraction contribution of compound i
φ_i	fugacity coefficient of component i
Ψ_{mk}	UNIFAC parameter (see Eq. 2.16)

Subscripts and superscripts

A	association
C	combinatorial
c	crystallization (see Appendix E)
$calculated$	calculated
DH	Debye–Huckel
$experimental$	experimental
fin	final (see Appendix E)
FV	Free-Volume
I	liquid phase one
II	liquid phase two

in	initial (see Appendix E)
m	melting (see Appendix E)
max	maxim
min	minim
R	residual (first order groups)
R'	residual (second order groups)

Indexes

i	components in mixtures
i	number of data points (within ARD_0 equation)
i	applied test number (see Eq. 2.3)
j	components in mixtures
j	number of data sets within a category-group (within $ARD_1(\%)$ equation)
k	group index in UNIFAC model
k	number of total data sets (within $ARD_2(\%)$ equation)
m	group index in UNIFAC model
n	group index in UNIFAC model

1
INTRODUCTION

The aim of this chapter is to familiarise the reader with the needs of the lipid industry, which give rise to the motivation of this project and subsequently the results presented in this thesis. The main objectives of the t and the approaches to achieve them are presented within the following chapters:

Chapter structure:

1.1 Background and motivation

1.2 Project objectives

1.3 Thesis structure

1.1 Background and motivation

Challenges such as raw material depletion, energy consumption and sustainability have plagued the chemical industry due to rapid population growth, globalization, societal and environmental requirements. Thus, the industry has evolved through the means of process systems engineering methods and tools in order to overcome these challenges.

Lipid related industries[1], which involve animal fats and vegetable oils, gained importance as they expanded from local to large-scale production (Greyt, 2013), as well as the reorientation of the industry from petro-based towards bio-based renewable resources. In the last 25 years, the use of lipid feedstock has almost doubled, reaching a capacity of 212 x 10^6 tons in 2016/2017(OIL World Statistics, 2016). A significant contribution to this evolution comes from the increasing demand of biofuels. The evolution of fat and oil consumption from 1989 to 2017, presented in Figure 1.1, shows that the biofuel industry became significant in the last sixteen years, reaching almost 15% out of the total lipids consumption in 2016/2017. The remaining 85% is represented by food and other industries like cosmetics, paintings, and base chemicals (oleochemicals) production (Greyt, 2013; IHS).

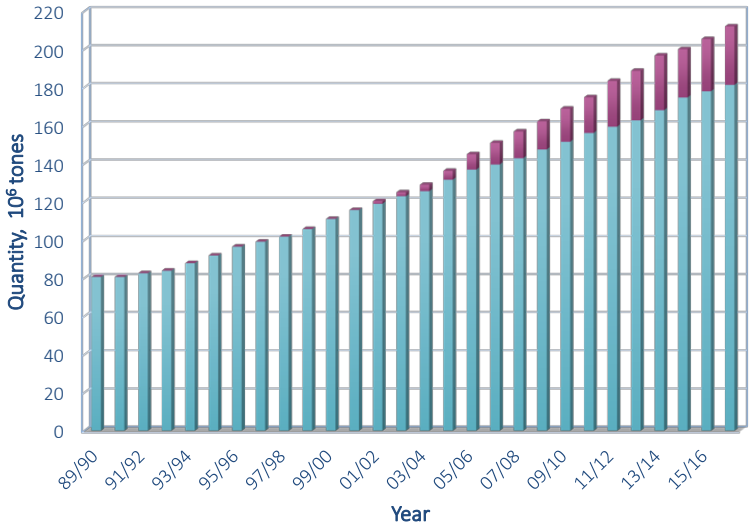


Figure 1.1. The evolution of lipids consumption between 1989 and 2017 (ISAT Mielke GmbH, 2016): blue indicates (■) food and other edible and non edible uses except biofules, magenta (■) indicates biofules uses

Such growths have led to new challenges regarding the design and development of better performing processes and products for the lipid related industry. Despite the advances in

[1] Lipid(s) are organic compounds which are belonging to different classes such as: fatty acids, fatty esters, mono-, di- and triglycerides, sterols, waxes, etc. (Fahy et al., 2009). In this work, all compounds that are usually found in vegetable oils and fats will be covered under the lipid(s) term.

property modelling and process design techniques available via different computer-aided methods and tools for the chemical and petrochemical industries, the lipid industry has yet to exploit this. This is due to the lack of experimental data and property models within commercial software applications, which are not able to accurately describe the phase behaviour of lipid systems. Over the past years, new methods and models for predicting single properties and temperature dependent properties for lipid pure compounds have been reported (e.g. critical properties (Marrero and Gani, 2001), viscosity (Ceriani et al., 2011), heat capacity (Ceriani et al., 2009), heat of vaporization (Ceriani et al., 2009), (Cunico et al., 2014), vapour pressure (Cunico et al., 2014). Another important modelling task is the phase equilibria prediction, which is directly related to process synthesis, modelling and simulation, as well as product design. Both experimental data and models, are highly important within each stage of the thermodynamic modelling - process design - process synthesis - product design framework.

Lipid-based industries employs processes such as, fat splitting, esterification, epoxidation, hydrogenation, amidation, sulfonation, and ethoxilation (Greyt, 2013), where different types of phase equilibria play important roles. An example of a lipid related process that involves all types of phase equilibria is fat splitting and its products separation (e.g. liquid-liquid equilibria (LLE) for fat hydrolysis process, vapour-liquid equilibria (VLE) and solid-liquid equilibria (SLE) for fatty acids separation and glycerol purification). In order to be able to design and improve lipid related processes, where several types of phase equilibria and properties are involved, a reliable set of thermodynamic models is required to be able to predict the correct phase behaviour of the involved compounds and mixtures.

Models, such as UNIQUAC and NRTL, have been used to predict LLE (Andrade et al., 2012; Basso et al., 2013) and VLE (Chen et al., 2014; Tang et al., 2013) for lipid systems involved in biodiesel purification, but for problems involving many compounds belonging to different classes, extensive property and equilibrium data are needed. Using equations of state such as SAFT (Corazza et al., 2016; Oliveira et al., 2014b) and CPA (Oliveira et al., 2014a, 2009; Tsivintzelis et al., 2016), for lipid-systems with strong associative interactions, like alcohol-ester, glycerol-alcohol, give suitable results. Unfortunately, their prediction is limited to a few compounds combinations (e.g. fatty acids-fatty acids, fatty esters with fatty esters or alcohol) and cannot be extrapolated to other type of lipid mixtures, which involve complex compounds (e.g. systems with TAG, DAG, MAG, etc.). As these models (UNIQUAC, NRTL as well as SAFT, CPA) need molecular interaction parameters that are usually regressed from binary molecular mixtures, they cannot be extrapolated to new systems since they need specific phase equilibria data for all involved compounds. Group contribution based methods can provide a wide range of properties for pure compounds and their mixtures, making them an indispensable tool for process design and related analyses when no data or only limited data are available. Therefore, these methods, which are able to predict the molecular interactions from the group interactions, are an option worth investigating when data availability is limited and there is a need for extrapolation beyond systems for which phase equilibria data are available.

1.2 Project objectives

The need for accurate and reliable models to predict phase equilibria for lipid systems is driven by the limited application of computer-aided methods and tools for process synthesis, modelling and simulation within the lipid related industries, along with the high cost associated with the separation processes. In addition, the work of developing property models is more challenging when it is required to predict the properties of new and complex lipid components and their mixtures, for which no data are available in the databases and literature. All of these issues justify every effort made for developing property models able to predict the behaviour of lipid components and their mixtures. Further, there is the need for the implementation of these property models within different tools in order to achieve reduced time and cost when designing lipid related products and processes.

The objective of this project is to develop, validate and apply systematic methods and tools for the lipid process technology. This covers the following: extension and maintenance of the *Lipids Database*, phase equilibrium property modelling and application to separation processes, separation process synthesis, design and analysis related to the use in lipid technology. The project objectives were fulfilled as follows:

- A systematic identification method for data analysis and phase equilibria modelling was proposed and tested. The method aim is to identify the best data for the regression of new binary interaction parameters for group contribution models like UNIFAC.
- The method was applied to different UNIFAC variants, and the new identified parameters were validated and tested for extrapolation features to other types of systems and phase equilibria.
- The Original UNIFAC model with the new lipid-based parameters is used within the process design and analysis of Shea oil solvent fractionation using acetone.

1.3 Thesis structure

This thesis consists of seven parts (six chapters and *Final Remarks*) which cover the introduction; experimental lipid data and models background; proposed method description, application and extrapolation abilities; the process modelling, design and analysis for a lipid process and the final remarks. A short description of each part is given below.

1. **Introduction**. The motivation of expanding the knowledge within lipid property modelling and process design is presented in this chapter along with the project objectives and the thesis structure.
2. **Lipid Phase Equilibria: Data and Models.** The availability of experimental data for lipid systems is discussed. The most applied models for lipid phase equilibria modelling are presented and their performance for such systems is discussed.
3. **Systematic Identification Method: Method Description.** The chapter presents the method structure as well as the involved algorithms. A few examples for a better understanding of the method and algorithms are given.
4. **Systematic Identification Method: Method Application and Validation.** Method application for regressing new parameters for Original UNIFAC model is presented along with the model performance using the lipid-based parameters set. A brief presentation of method application for other UNIFAC model variants and the results obtained are also discussed at the end of this chapter.
5. **Systematic Identification Method: Method extrapolation abilities.** The Original UNIFAC model and its variants using the lipid-based parameters are tested for extrapolation capabilities. In addition, the possibility to use the method to identify needed experimental data is covered under the *Need of new data* section.
6. **Lipid Thermodynamic Model(s) Applied to Lipid Processing: Solvent Fractionation.** The *Lipids Database,* which includes the lipid-based parameters for the Original UNIFAC model is used for modelling, design, simulation and analysis of Shea oil fractionation with acetone. The chapter presents the process importance and description, the workflow for design, modelling and analysis, as well as the results and process improvements.

Final Remarks. The conclusions and achievements are covered in this last part of the thesis, alongside future work suggestions.

2

LIPID PHASE EQUILIBRIA: DATA AND MODELS

Industries like biotechnology, pharmaceutical, agriculture, chemical, food, materials, and others utilise chemical engineering methods and tools for development and analysis of various processes. The thermodynamic properties of the involved chemicals and the models used to describe them are the foundation of all these methods and tools. This chapter aims to cover the lipids phase equilibria thermodynamics by analysing available data and by presenting, the most extensively used thermodynamic models for lipids phase equilibria modelling, with the final purpose of identifying the gaps that hinder the application of available chemical engineering methods and tools within the lipids processing field.

Chapter structure and contents:

2.1 Data availability and quality: highlight of lipid data importance; discussion and analysis of the availability and quality of the lipids data, and presentation of the *Lipids Database* structure and updates.

2.2 Phase equilibria calculation models for lipids: presentation of the most applied models used for lipids phase equilibria modelling along with their application and performances.

2.1 DATA AVAILABILITY AND QUALITY

Data importance for model and process development using CAPE methods and tools

Thermodynamic properties are needed in all stages of a process-product development: from design, optimisation, and economic analysis to control system design, plant operation and product lifecycle, often being used via computer-aided methods and tools. In Computer Aided Process-Product Engineering (CAPE), the thermodynamic insights and property values are used in the process-product model via properties models. Depending on what stage of a process-product design they are used, the property models can play different roles (Gani and O'Connell, 2001). The service role is represented by the ability of the property model to provide values upon request (e.g. calculation of vapour pressure of a compound and mixture at particular T, P, x conditions) and it is usually employed during the process simulation. For the service-advice role, the properties are used during decision-making process in the design stage (e.g. separation of an azeotropic binary mixture, solid-liquid separation feasibility, solvent design). The service-advice-solve role also known as the integration role (Gani and O'Connell, 2004) is given by the inclusion of the property model within CAPE methods which provide integrated solution strategies for different problems (e.g. McCabe-Thiele Method for distillation column design, Pinch Technology for heat integration). No matter which of the roles the property models are used for, it is very important that they are able to accurately describe the behaviour of the substance(s) under different operating conditions. Since all these property models are used within the CAPE tools as parameterized mathematical equations, the model parameter regression and tuning is an important problem. Getting a good set of parameters for a model depends directly on the experimental data availability and quality. Therefore, it is important that the experimental data published and used to develop models, should pass through a careful assessment from the collection activity to evaluation, quality assurance, and data process. For example, modelling of primary properties, defined as single value properties (e.g. critical properties, heat of fusion, etc.) use information on molecular structure. The modelling of secondary properties modelling are dependent on primary properties, while functional properties are dependent on primary and/or secondary properties plus on the intensive variables (temperature, pressure, composition) (Kontogeorgis and Gani, 2004). Therefore, if a functional property model is developed or reparametrized, it is very important that all the other properties models and data involved are accurate, resulting in the needs for a full set of reliable experimental data to be available for a class of compounds and mixtures.

A series of tools developed at the Thermodynamics Research Canter (TRC) of the U.S. National Institute of Standards and Technology (NIST) aims to help the user collect, select and assess data quality. The ThermoGlobe (Frenkel, 2015, 2009) platform integrates different tools applied for data collection (Guided Data Capture (Diky et al., 2003)), data accessing and analysing (ThermoData Engine (Diky et al., 2009)), data standardisation (ThermoML (Frenkel et al., 2011)), extensive data base access (TRC Source Database (Frenkel et al., 2001)) and others. Another series of tools are provided by DECHEMA (DECHEMA, 2018a): Data Preparation Package (DPP) for experimental/raw data processing, IK-Cape Thermodynamics for properties and their derivatives calculation, IK-CAPE-PPDX for standardisation of data and models

information transfer. Besides the software, DECHEMA provides also databases (DECHEMA, 2018b). DETHERM database is for thermophysical property data. CHEMSAFE provides safety parameters for flammable and explosive chemicals. DIPPR 801 database provides parameters for thermodynamic models (DIPR801)All of these tools play a crucial role within process systems engineering research advancements (Frenkel, 2011) giving the users fast access to collect and select thermodynamic data for further use in property and process modelling. Additionally, the availability of appropriate methods and tools for choosing good quality data for model development and/or parameterization in a systematic manner could prove to be very useful.

The industrial needs for properties, which aim to reduce time and cost of process development represent the main driving force within property models development. A good set of experimental properties values, which turns into high confidence and robust property models can lead to process innovation and improved process performances (Gupta and Olson, 2003). The industry highlights the needs for reliable experimental data for families of compounds that can be used for property and process modelling, but also the need for having reliable models with predictive capacities (Hendriks et al., 2010). These kinds of models should be further developed and improved to meet the industrial and academic demands.

Experimental measurements are non-trivial since data gathering over a wide range of pressures and temperatures can be very difficult. The substance purity can prove to be a major issue, especially in the case of lipids, when some of these compounds are obtained by separation from a lipid mixture (e.g. oil), which contains different isomers, or compounds with similar properties. Moreover, some of these compounds can be very sensitive with respect to temperature variation, making their separation even more difficult.

2.1.1 *Lipids Database*: structure and updates

The limited experimental data available in the literature for both pure lipid compounds and their mixtures has resulted in the need to develop predictive models to cover all the requirements during process-product development. Some of the pure compound models developed specifically for lipid compounds include: critical properties (Marrero and Gani, 2001), vapour pressure (Ceriani et al., 2013), heat of vaporization (Ceriani et al., 2013), heat capacity (Ceriani et al., 2009), viscosity (Ceriani et al., 2011), heat of fusion (Cunico et al., 2013), heat of formation (Cunico et al., 2013). Availability of such models, allowed for the development of the *Lipids Database*.

The *Lipids Database*, Figure 2.1, is structured in two parts: (1) pure compound properties and, (2) mixture properties. Each of these parts has associated experimental data and property models. The database is connected to the *Lipids toolbox*, which has different features, allowing for a better exploration of the database. The features of the toolbox are:

- Database search for pure compound experimental data or property models
- Optimization based data regression, which allows estimation of models parameters for new pure compound data
- Pure compound property data consistency check performed for classes of compounds by checking the trend of a property against the number of carbon atoms

- Database management, which allows the database connection to process simulators such as PRO II (Schneider Electric Software, 2016) and ICAS (Gani et al., 1997), and a product simulator (the Virtual Product-Process Design Laboratory (Kalakul, 2016; Kalakul et al., 2017) via XML files. The simulators can import these files as private user libraries, thereby allowing a wider use of the database.

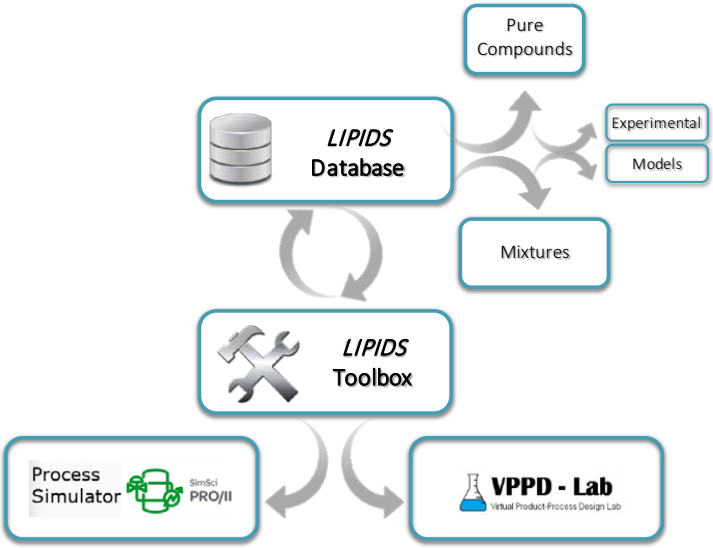


Figure 2.1. A schematic of the Lipids Database structure and connection to process-product computer-aided tools

The database has 335 compounds: 227 lipids or lipid related compounds and 8 non-lipid compounds (e.g. water, acetone, methanol, ethanol, 1 and 2-propanol, 1-butanol,hexane) classified in 18 categories (Kalakul, 2016; Perederic et al., 2018b). More details are presented in Appendix A. The experimental part of the pure compounds section of the database includes seven single value properties, which correspond to primary and secondary properties and six functional (temperature dependent) properties. Available experimental data covers around 15% of the compounds for single value properties, with most data belonging to normal melting and boiling points properties, and less than 10% for temperature dependent properties. It is important to note that none of the compounds has a full set of experimentally measured property data. The property models cover 14 single value properties and 10 temperature dependent properties. For each compound a full set of property models and parameters are available (Kalakul, 2016). The correlations used for the functional properties are standard DIPPR correlations (Thomson, 1996). These are selected for better use of the database with process simulators, where these correlations are readily available.

Phase equilibria data contain over 650 data sets for all type of phase equilibria including both binary and multicomponent data, as given in Table 2.1. The database developed by Cunico (Cunico, 2015) was updated with new data and the collection of source papers organized by phase equilibria type. A significant part of the LLE multicomponent data have been collected from Bessa and collaborators (Bessa et al., 2016). Among binary VLE data systems, 28.3%

correspond to fatty acids and fatty esters, while 56.5% of the data sets correspond to systems containing glycerol with alcohols and water. A few of the binary VLE data (Damaceno and Ceriani, 2018a, 2017a) are added later to the database, and are not used in the development of lipid related models, described in Chapters 3-4.

Regarding the LLE multicomponent data, over 70% of the data sets are related to biodiesel processing and most of the mixtures contain fatty esters with methanol, water and edible oils which are represented as pseudo-compounds. Among SLE binary data systems, 53.5% are fatty acids and fatty esters systems. Property models for phase equilibria calculations, as well as some mixture related properties are available in the database. More details are available in Appendix A Table A.4 (Kalakul, 2016; Perederic et al., 2018b). An extensive collection of parameters for different UNIFAC models applicable to lipid systems, as presented in the next section of the chapter (Table 2.4), is included in the database. The database is up to date with all the phase equilibria data published for lipids until the half of the year 2018. The quality factor is availabele in the database for all binary VLE data.

Table 2.1. List of available phase equilibrium data sets in the *Lipids Database*

Phase Equilibria Type	Binary		Multicomponent	
	Data sets*	Data points	Data sets	Data points
VLE	179 +	1786	12	64
SLE	86	929	22	335
LLE	12	187	368	2893
VLLE	-	-	7.0	72.0

* *Data set refers to the collection of data points for a system of two or more compounds measured at the same conditions and by the same authors.*

\+ *A few new datasets were recently added; current total number of binary VLE data is 209.*

2.1.2 Data quality and consistency tests

The consistency check of phase equilibria data aims to highlight the presence of errors within the data set, especially systematic errors, and to ensure data of the highest quality for experimental reference standards, which are further used to develop thermodynamic models and to perform process and equipment design (Olson, 2016).

VLE data analysis and evaluation is based on two thermodynamic constrains. First constrain results from the restrictions imposed by the Gibbs-Dunham equation, presented in Eq. 2.1. The second constrain results from the consistency between VLE data and pure compound vapour pressure (Kang et al., 2010). Some of the consistency tests used for VLE data analysis are described in detail in the following paragraphs. When it comes to SLE data, since most of the systems are eutectic rather than solid solutions, the solubility calculation can be done with Eq. 2.2. For this case, the data quality check is based on the limiting behaviour of the liquids line: SLE consistency with pure component melting point and agreement between experimental limiting slope and the solubility equation (Kang et al., 2014). Another SLE test, which is checking for the consistency between pure compound melting point and SLE data, and which includes the uncertainty factor of the pure compound melting point, was proposed by Cunico and collaborators (Cunico et al., 2013). Consistency of the LLE data is the most difficult to be

assessed. Gibbs-Duhem equation, in the form from Eq. 2.1 applied to both liquid phases, can be used for LLE data, but only if there is available information on excess enthalpy. Moreover, the equation cannot correlate for the composition of the two liquid phases. The only possibility to check for the quality of the data is the condition that at constant and near atmospheric pressure, the composition over the two liquid phases should be continuous. An algorithm based on this condition is used by NIST to assess the LLE data quality (Frenkel et al., 2005; Kang et al., 2014).

$$x_1 d\ln\gamma_1 + x_2 d\ln\gamma_2 - \frac{V^E}{RT}dp + \frac{H^E}{RT^2}dT = 0 \tag{2.1}$$

where x and γ are the molar fraction and activity coefficient of the two compounds from the mixture, V^E is the excess volume, H^E is the excess enthalpy, R and T are the ideal gas constant and temperature.

$$\ln\left(\frac{1}{\gamma_2 x_2}\right) = \frac{\Delta_c^1 H_m^\circ}{RT_m}\left(\frac{T_m}{T}-1\right) - \frac{\Delta C_p}{R}\left(\frac{T_m}{T}-1\right) + \frac{\Delta C_p}{R}\ln\left(\frac{T_m}{T}\right) \tag{2.2}$$

where x_2 and γ_2 are the mole fraction and activity coefficient of compound two in the liquid phase $\Delta^c{}_1H^0{}_m$ is the molar enthalpy of melting, T_m is the melting temperature, ΔC_p is the difference between heat capacity of the liquids and heat capacity of the solid at melting temperature.

The quality assessment algorithm (Kang et al., 2010) implemented in ThermoData Engine (TDE) from NIST (Diky et al., 2012) combines several tests based on: Gibbs-Duhem equation, Eq. 2.1, modelling capabilities, and vapour pressure consistency with pure components, as presented in Figure 2.1. The results from each consistency test (passed/not passed) are translated to numbers through the quality factor equation assigned within the algorithm for each test. All the individual quality factors, Q_i, are combined within the overall quality factor, Q_{VLE}, which is calculated using Eq. 2.3, and where N represents the number of applicable tests and Q_{pure} corresponds to end point test.

$$Q_{VLE} = Q_{pure} \cdot \frac{1}{N}\sum_{i=1}^{N} Q_i \,, \tag{2.3}$$

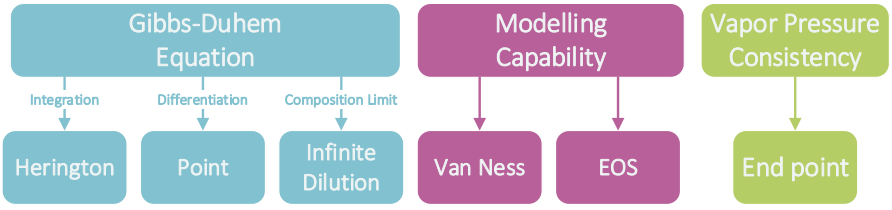


Figure 2.1. A schematic of the VLE consistency tests classification. Adapted from (Kang et al., 2014)

The overall quality of a data set includes the quality factor of six independent tests: Herington (Wisniak, 1994), van Ness (Van Ness et al., 1973), point (Kojima et al., 1990; Kurihara et al., 2004), Infinite dilution (Kojima et al., 1990; Kurihara et al., 2004) and equation of state (Van Ness et al., 1973; Voutsas et al., 2006). These tests are briefly described in following paragraphs. The overall quality factor, Q_{VLE}, is formulated that it can vary between zero and one. If a test, $test_i$, cannot be performed (e.g. the data are not suitable for that test), the respective test is skipped, and the quality factor is calculated only from the applicable tests (Diky et al., 2012). All test are formulated in such way that each individual test quality factor, Q_i, vary between zero and one. Except the end point test, which has the biggest influence within the overall quality factor, all the other test results are considered as an average value, Eq. 2.3.

The Herington or the integral test (Wisniak, 1994) also known as area test, is based on the Gibbs-Duhem equation and evaluates the area results from the integration of Eq. 2.1 over the composition range. The test is useful for nearly ideal systems, which can be found also in lipid systems, and the pass conditions of a VLE data set are based on the area value results from the integration (e.g. the ratio of above and below zero line area and maximum-minimum temperature ratio) (Kojima et al., 1990; Kurihara et al., 2004). The test shows compliance with the Gibbs-Duhem equation, and the results can be easily visualised in $ln(\gamma_1/\gamma_2)$ vs. x_1 plots. Some authors do not consider this test reliable (Wisniak, 2010), which can be true, if the data quality assessment is performed based only on this test. If the test is used alongside other tests, then it can be useful by providing visual information regarding the data overall quality.

The Point or the differential test is based on the excess Gibbs free energy differential, and it needs T-P-x-y data type for evaluation of activity coefficients (Kojima et al., 1990; Kurihara et al., 2004). The point test is not applied to isobaric data, which require more information to be provided (e.g. excess enthalpy H^E). The quality test results value is based on the deviation between experimental and calculated values of activity coefficients ratio.

The Infinite dilution test analyses the limiting behaviour of the Gibbs free energy and activity coefficients, and the pass/fail criteria is based on a deviation limit of experimental data (Kojima et al., 1990; Kurihara et al., 2004). The quality factor transposes the minimum requirements/values to pass the test and system deviation into a ratio.

The van Ness and equation of state (EoS) test are used for testing the modelling capabilities of a data set. The Van Ness test uses the NRTL model to predict the experimental data: p and y. T-P-x-y data sets are used to fit the model parameters (5 parameters) resulting in a minimum requirement of five data points. The sum of pressure and vapour composition deviation are normalized so they can be used within the quality factor. EoS test is applied for high pressure (P>1 MPa) isothermal T-P-x-y data. The quality factor is calculated using the pressure and vapour composition deviation (Diky et al., 2012). For the majority of lipid data sets this test is not performed since most of the data are at low or atmospheric pressure.

The aim of the end point or pure component consistency test (Kang et al., 2010) is to check if the vapour pressure at the endpoint of the system matches the pure component vapour pressure. The test can be used for different types of data (e.g. T-P-x-y, T-P-x or T-P-y). The condition to apply the test is to have experimental data for x within (0, 0.2) and (0.8, 1)

interval. The prediction and extrapolation of the data are performed with the NRTL model. The quality factor results from normalisation of the two pressures deviations.

Lipid VLE data quality

All the binary VLE data available in the *Lipids Database*, Table 2.1, are evaluated using the quality assessment algorithm (Kang et al., 2010) implemented in ThermoData Engine (TDE) from NIST (Diky et al., 2012). The extended list of binary VLE data sets is given in Appendix B.

For the Herington test, only 49 data sets have the requirements for the test to be performed where only 13 (26.5%) pass the test. The systems that pass the test are fatty acid-fatty acid systems (3 data sets), fatty ester-fatty ester systems (8 data sets) and glycerol-water system (1 data set). The point test was not applicable since all the isothermal data sets are T-P-X data, and the test requires T-P-X-Y data. The infinite dilution test is applicable for 46 systems, and all of them pass the test. The systems involve the following mixtures: fatty acid-fatty acid (14), fatty ester-fatty ester (24), glycerol-water (7), and fatty ester-alcohol (1).

The Van Ness test is applicable to 58 data sets, where only 6 (10.3%) pass the test. All the systems that pass the test are fatty acid-fatty acid types. The equation of state test is applicable to only 3 systems since the main request of the test is high-pressure data, and most of the lipid data is at atmospheric or sub-atmospheric pressures. The three datasets are fatty acid-alcohol systems and they fail this test.

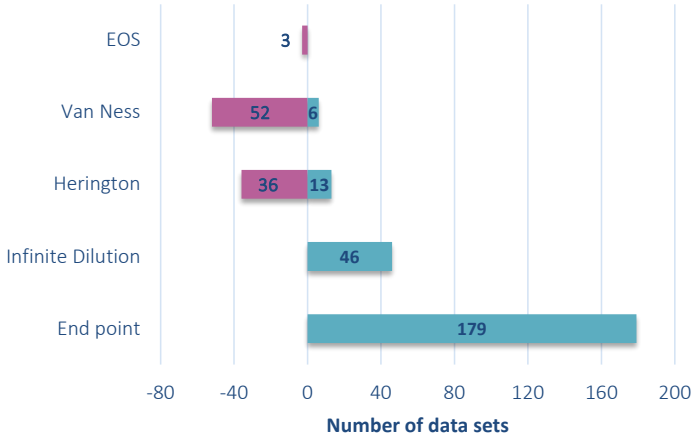


Figure 2.1. Passed-Failed overview of the Herrington, van Ness, Infinite dillution, End point and EoS consistency tests: ■ passed test, ■ failed test

The end point test is applied to all the data sets. All the data sets include pure compound data or mixture data in the intervals 0-0.2 and 0.8-1 of composition, as required by the test. Almost 40% of the data have a quality factor higher or equal to 0.5. 25% of the data pass the test with a quality factor of 0.25 up to 0.5, while the remaining data has a low quality factor (less than 0.25). For the overall quality factor, Q_{VLE}, most of the data are within 0-0.25 interval (53%), around one third (35%) of the data has a quality factor between 0.25 and 0.5, and only 12% of

the data has a quality factor higher than 0.5. The pass-fail and quality test factor results are presented in Figures 2.1 and 2.2.

If the data does not pass one of the tests, this does not mean that it is inconsistent and should be disregarded for further applications. The performance of all proposed tests should be analysed and the overall quality factor should be consider. Failing Herington, point or infinite dilution tests means that the data are not respecting the excess properties constraints resulted from Gibbs-Duhem equation. An example can be given for a few datasets which are fatty acid-fatty acid type (see Appendix B), which pass Infinite dilution test and the end point test quality factor is higher than 0.5, but they fail the Van Ness test. This can indicate a low quality (high deviations) of vapour phase composition.

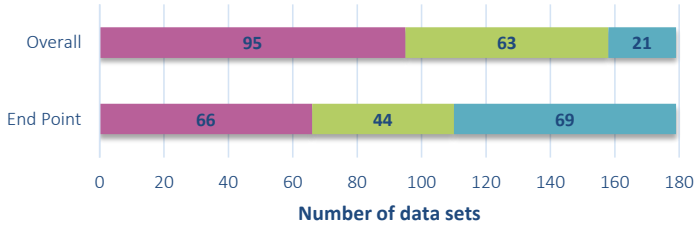


Figure 2.2. End point and overall quality factor overview:
■ Q=[0, 0.25), ■ Q=[0.25, 0.5), ■ Q=[0.5, 1]

2.2 Phase Equilibria Calculation Models for Lipid Systems

Research on the phase equilibria modelling of lipid systems have been carried out extensively during the last years, especially for biodiesel related systems (e.g. alcohol, glycerol, water esters systems). Several types of models are used to describe such systems: from equations of state to activity models and combined methods like EoS-g^E or associative-GC/EoS.

The analysis of the lipid phase equilibria modelling include around 150 papers, published during 1911-2018 (See Appendix B). The analysis conclusions are as follows: over 85% of the papers were focused on activity models for lipid systems, around 10% applied EoS with classic mixing rules (including here the CPA model) and around 3% of the papers applied EoS-g^E models. Within the activity coefficient models, NRTL was the most extensively used model (over 35%), followed by UNIQUAC (around 30%) and UNIFAC (around 25%). Less applied is the Wilson model, due to its limitation regarding LLE modelling. Most of the work on phase equilibria prediction is performed for systems involved in biodiesel production and separation, many involving LLE.

In the Section 2.2.1 of the chapter, the main types of models (equations of state and activity models) used for lipid phase equilibria modelling are presented, while examples of lipid systems and their performance are given in the next section.

2.2.1 Description of the models

The most important and applied models for lipid phase equilibria calculations are presented in the following sections. The models are grouped into cubic EoS and EoS-g^E models (EoS with classical and advanced mixing rules), association models (EoS and group contribution models with association term), activity models (Wilson, NRTL and UNIQUAC) and UNIFAC group contribution model (e.g. Original model and its variants).

2.2.1.1 Cubic EoS and EoS-g^E

The most applied cubic equation of state (EoS) models for lipid systems are Peng-Robinson (PR) (Peng and Robinson, 1976) and Soave-Redlich-Kong (SRK) (Soave, 1972) models. The advantage of these models is that they can describe the phase equilibria in a wide pressure and temperature range including near and supercritical conditions, they are simple, easy to use and are capable of describing both liquid and vapour phase (Kontogeorgis and Folas, 2010a). The extension of the models from pure compounds to mixtures is done via classical mixing rules (e.g. van der Waals one fluid) or advanced mixing rules (e.g. Huron-Vidal, MHV1, MHV2). The EoS with the classical mixing rules reports a good performance for ideal or slightly non-ideal systems, but they have poor performance for complex systems involving polar compounds (Kontogeorgis and Folas, 2010b; Oliveira et al., 2011). Usually the models predict positive deviation from ideality (e.g. $\gamma > 1$) for many of the systems that have negative deviation (e.g. $\gamma < 1$). In addition, the model does not correlate very well with the LLE of immiscible systems (e.g. many cases for lipid related systems) and they do not give a very good extrapolation to multicomponent systems. The biggest practical problem for these models is the availability of the binary interaction parameters, which are fitted from experimental data. The binary parameters do not correlate very well with molecular weight or other molecular

characteristics of the involved compounds, and therefore it is difficult to generalise them (Kontogeorgis and Folas, 2010a). Hence the need for experimental data to be available for all the binary systems, which can be time and resource consuming, especially in the case of lipid systems where many compounds are involved.

The extension of the EoS to polar systems can be done via EoS-g^E mixing rules by coupling the EoS with activity models. The EoS-g^E models have the advantages of both EoS (e.g. wide temperature and pressure application) and g^E (e.g. polar and non-polar compounds) models. These mixing rules incorporate the activity coefficient model within the EoS through the energy parameter. One limitation of the EoS-g^E models is the poor description of systems with asymmetric compounds (Kontogeorgis and Folas, 2010b), which for the lipid systems can be an important issue (e.g. many lipid related systems are asymmetric: acylglycerols, fatty acids and/or esters with water, methanol, ethanol or other solvents).

2.2.1.2 Association equations of state

Association EoS models are designed to describe self and cross-associating molecules. The advantage of these models is that they include a term, which describes the hydrogen bonding between the molecules, such that it is able to describe polar and non-polar systems in a wide range of pressures and temperatures. The main association models used for lipid phase equilibria investigation are: CPA (Kontogeorgis et al., 1996), GCA-EOS (Gros et al., 1996) and different SAFT variants. Association UNIFAC (A-UNIFAC) is also used, and it is discussed in the section dedicated to activity coefficient models. Compared to EoS-g^E models, CPA and SAFT based models have binary parameters that can be correlated to predict trends within specific/homologues series systems (e.g. water-fatty acid/ester) (Grenner et al., 2007; Tsivintzelis et al., 2016).

CPA

Cubic Plus Association EoS (CPA) (Kontogeorgis et al., 1996) combines the SRK EoS with the association term from SAFT EoS (Chapman et al., 1990; Huang and Radosz, 1990). The model uses different mixing rules and the most common are Elliot (ECR) and CR-1. The model is able to describe multicomponent mixtures involving polar and non-polar compounds for different type of phase equilibria based on binary interaction parameters fitted from binary data (Kontogeorgis and Folas, 2010c).

Other association models

GCA-EOS model is the extension of GC-EOS (Skjold-Jørgensen, 1984) by including the association term in a group contribution manner within the model.

GC-PPC-SAFT (Tamouza et al., 2004) is based on PC-SAFT EoS combined with group contribution approach for polar systems. The pure compounds segment parameters (dispersive energy, segment diameter and chain length) are defined as geometric and arithmetic averages of each group contribution.

2.2.1.3 Activity coefficient models

In this section, the Wilson (Wilson, 1964), NRTL (Renon and Prausnitz, 1968) and UNIQUAC (Abrams and Prausnitz, 1975) models are discussed. UNIFAC (UNIQUAC Functional-group

Activity Coefficients) (Fredenslund et al., 1975) model and its variants are presented in more detail in Section 2.2.1.4.

The activity coefficient models like Wilson, NRTL, UNIQUAC are based on local composition concept, unlike the cubic EoS with classic mixing rules which are based on random mixing or overall composition. This approach enables an improved and broader description of phase behaviour. The models provide better correlation of VLE compared to random mixing rules based models. With the exception of the Wilson model, the models are able to describe VLE, LLE, VLLE and SLE. The models with parameters fitted to binary data, provide good extrapolation to multicomponent data. As it is the case of cubic EoS with classical mixing rules, all the binary interaction parameters need to be fitted to experimental data, which therefore require large amounts of available experimental data (Kontogeorgis and Folas, 2010d). As previously stated for lipids, many of these experimental data are missing, which are the main shortcomings of these types of models.

The limitations of the models come from theoretical and practical aspects. Some of these limitations are related to coordination number, normalized size parameters (UNIQUAC) and parameters interrelation. These limitations have the following effects: (1) higher non-randomness correction which, if it is changed, results in the needs for binary interaction parameters refitting; (2) experimental fitting of size parameters for certain systems (UNIQUAC method limitation); (3) LLE multicomponent representation is highly dependent on the parameters, which are on their own highly dependent on the data they are fitted to (e.g. data quality influence parameters values and therefore the LLE representation) (Kontogeorgis and Folas, 2010d).

Wilson

The Wilson (Wilson, 1964) model is generally giving very good VLE prediction especially when compared to EoS with classical mixing rules for systems involving polar compounds (Kontogeorgis and Folas, 2010d). The model is able to correlate excess enthalpy when temperature dependent parameters are used. The main drawback of the Wilson model is its incapacity to model LLE.

NRTL

The Non-Random Two Liquid Model (Renon and Prausnitz, 1968), NRTL, has three parameters (versus two for other activity coefficient local composition models) to be adjusted. The third parameter accounts for non-randomness, and it is sometimes fixed based on theoretical considerations, but in most of the cases, it is fitted from experimental data for a better correlation. NRTL is the only local composition model that does not have an entropic term, which makes it an enthalpic model, thus NRTL can represent the excess enthalpy well. However, it is not able to represent excess Gibbs energy. The model is able to simultaneously represent VLE and LLE for both binary and multicomponent systems (Kontogeorgis and Folas, 2010d).

UNIQUAC

The Universal Quasi-Chemical model (Abrams and Prausnitz, 1975), UNIQUAC, can correlate VLE, LLE and SLE for a wide range of compounds (e.g. polar, non-polar, association). It is the only model accounting for compounds size and shape (through van der Waals surface and

volume parameters resulted from Bondi's method) within the entropic/combinatorial term. One limitation of the model related to the surface and volume parameters is that for some molecules (e.g. water, methanol) the model can predict false immiscibility between phases. For these cases, the parameters are fitted to experimental data. The coordination number, which accounts for the non-randomness is over-estimated (e.g. Z=10); if its value is changed, then all the binary parameters need a new estimation. The model gives a good representation of the excess enthalpy. The LLE representation is highly dependent on the data the model is fitted to, as it is the case for the NRTL model (Kontogeorgis and Folas, 2010b).

2.2.1.4 UNIFAC model

The Universal Quasi-Chemical Functional Group Activity Coefficient model (UNIQUAC Functional-group Activity Coefficients) (Fredenslund et al., 1975), UNIFAC, is the extension of the UNIQUAC model to a group contribution predictive model. The development of the model is based on the group contribution models for pure compounds properties. The aim of this model is to use a small number of functional groups in order to describe a very large number of mixtures, as it is the case of lipids, which can be described by a few (8-10) groups, as presented in Chapter 4.

The model formulation is presented in detail in the following section, followed by a review of model variants and their application.

Original UNIFAC model

The Original UNIFAC model with the first set of binary interaction parameters was published in 1975 (Fredenslund et al., 1975). After several updates to the parameters table (revision and expansion), new variants of the model (to increase model performance and applicability) and new methods to perform the parameters estimation were published. The model with the original set of binary interaction parameters can predict VLE between 300-425 K and pressures up to few atmospheres for non-polar compounds (Fredenslund et al., 1977b).

The model describs the activity coefficient equation for a compound, i, within a mixture (Eq. 2.4) as the the sum of two contributions: a combinatorial (enthalpic) part (γ_i^C), which accounts for the size and shape of the molecules, and a residual (entropic) part (γ_i^R), which accounts for the interaction energy.

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \tag{2.4}$$

In the original model, the combinatorial contribution, γ_i^C, defined in Eq. 2.5, is the same as for UNIQUAC model. The first three terms correspond to Flory-Huggins (FH) contribution corrected for the molecular shape using a Starvermann–Guggenheim (SG) correction (last term of Eq. 2.5). In the Original UNIFAC model, as presented in Eqs. 2.5-2.7 the molecular volume fraction contribution (Φ, Φ') is the same within FH and SG term. The general form of the Eq. 2.5 and Eq. 2.7 by using C_0 and C_1 parameters is given for later representation of other UNIFAC model variants, and they are listed in Table 2.3. For the Original UNIFAC model, C_0 and C_1 are equal to 1. The correction term considers the non-randomness factor resulting from the molecular coordination (Z). As it is the case for UNIQUAC model, the value for Z is considered 10 and it represents an average between the hexagonal packing (Z=12) and cubic packing (Z=6) of the liquid phase. The term $Z/2$ results from the model derivation from the two fluid

theory and it is supposed to appear in both combinatorial and residual contribution (Eq. 2.4), but it is kept only for the combinatorial term since the non-randomness correction is too strong within the energy contribution. In fact, the term is incorporated within the binary interaction parameters. The molecular area fraction (θ) is used in the correction term of combinatorial contribution. Both area and volume fractions are calculated using the van der Waals volume (V_k) and surface area (A_k) of the groups. These values are calculated using Bondi's method (Bondi, 1968) from molecular and structure data. The values of the volume and surface area normalized to the volume and surface area of a CH_2 unit from a polyethylene molecule[2]. The combinatorial term has a significant contribution to the activity coefficient value for asymmetric mixtures where molecules are very different in size and shape (e.g. triacylglycerol-methanol).

$$\ln \gamma_i^C = 1 - \frac{\Phi'}{x_i} + \ln\left(\frac{\Phi'}{x_i}\right) - \frac{Z}{2} q_i C_1 \left[1 - \frac{\Phi}{\theta} + \ln\left(\frac{\Phi}{\theta}\right)\right] \tag{2.5}$$

$$\Phi_i = \frac{x_i r_i}{\sum_j x_j r_j} \tag{2.6}$$

$$\Phi'_i = \frac{x_i r_i^{C_0}}{\sum_j x_j r_j^{C_0}} \tag{2.7}$$

$$\theta_i = \frac{x_i q_i}{\sum_j x_j q_j} \tag{2.8}$$

$$r_i = \sum_k v_{k,i} R_k \tag{2.9}$$

$$q_i = \sum_k v_{k,i} Q_k \tag{2.10}$$

$$R_k = \frac{V_k}{15.17} \tag{2.11}$$

$$Q_k = \frac{A_k}{2.5 \cdot 10^9} \tag{2.12}$$

The residual contribution accounts for the excess enthalpy caused by the energetic interactions between the groups. The term is similar to the one used in UNIQUAC model, except that the molecular fraction and molecular interaction are exchanged with groups fractions and groups interactions. The residual contribution is defined as the sum of individual contribution of each group, k, within the mixture (Γ_k) less the individual contribution of the group, k, in a reference solution containing only molecule i (Γ_k^i). In Eq. 2.12, v_k^i is the number

[2] V_k, A_k and normalization values have following units of measure: cm^3/mol and cm^2/mol.

of groups k in molecule i. The residual activity coefficient of group k in both the mixture and reference solution (Γ_k, Γ_k^i) is assumed to be a function of surface area fraction (Θ_m) (calculated from group concentrations (X_k) and surface area (Q_k)), interaction parameters (a_{mk}) and temperature (T). The interaction parameter (a_{mk}) measures the difference between interaction energy of group m and group k (U_{mk}) and interaction energy of two groups k (U_{kk}), Eq. 2.17. In the Original UNIFAC model, the interaction parameter is considered independent of temperature. The equation for the binary interaction parameter, Eq. 2.18, is presented in a general way to account for other UNIFAC variants presented later in the chapter, which considers a_{mk} temperature dependent. For Original UNIFAC A_0=1, A_1=0, and A_2=0 (see also Table 2.3) for Eq.18.

$$\ln \gamma_i^R = \sum_k v_k^i \cdot \left[\ln \Gamma_k - \ln \Gamma_k^i\right] \tag{2.12}$$

$$\ln \Gamma_k = Q_k \cdot \left[1 - \ln\left(\sum_m \Theta_m \Psi_{mk}\right) - \sum_m \frac{\Theta_m \Psi_{mk}}{\sum_n \Theta_n \Psi_{nm}}\right] \tag{2.13}$$

$$\Theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \tag{2.14}$$

$$X_m = \frac{\sum_i v_m^i x_i}{\sum_j \sum_n v_n^j x_j} \tag{2.15}$$

$$\Psi_{mk} = \exp\left(\frac{-a_{mk}}{T}\right) \tag{2.16}$$

$$a_{mk} = U_{mk} - U_{kk} \tag{2.17}$$

$$a_{mk} = A_0 a_{mk,0} + A_1 a_{mk,1} + A_2 a_{mk,2} \tag{2.18}$$

Variants of the Original UNIFAC model

Several papers presenting modified versions of the Original UNIFAC model were published in the literature since the model was first reported. The new versions of the UNIFAC can be classified based on different aspects: activity coefficient equation modifications, updated or special parameters tables for spcific phase equilibria or applications (which can include new groups and new binary interaction parameters) and binary interaction parameters estimation methods. A general activity coefficient formulation to account for all UNIFAC variants is described in Eq. 2.19. The UNIFAC variants are presented in Table 2.2 based on this formulation. Small differences in the last four terms between different models variants are available, but these are not discussed here. The first three terms in Eq. 2.19 describe the short-range interactions, which are a result of molecules size and shape (γ_i^C), and energetic interactions between first (γ_i^R) and second order groups ($\gamma_i^{R'}$). The fourth term introduces mid-

range interactions, which are a result of dipole interactions or indirect charge effects ($\gamma_i^{2ndvirial}$). The fifth term stands for the long range interactions and it is as a result of direct charge effect of ionic interaction (γ_i^{DH}). The sixth term is related to hydrogen bonding (association (γ_i^{A})) interaction, and the last term is specific to free volume effects (γ_i^{FV}). Other particularities of the combinatorial term (more precisely the volume contribution) and residual term (the binary interaction parameter temperature dependence) for some of the models are given in Table 2.3 and they are based on Eq.2.7 and Eq. 2.18.

$$\ln \gamma_i = B_0 \ln \gamma_i^C + B_1 \ln \gamma_i^R + B_2 \ln \gamma_i^{R'} + B_3 \ln \gamma_i^{2^{nd}\,virial} + B_4 \ln \gamma_i^{DH} + B_5 \ln \gamma_i^A + B_6 \ln \gamma_i^{FV} \quad (2.19)$$

Table 2.2 UNIFAC variants based on activity coefficient formulation differences (Eq. 2.19)

Model	Reference	B_0	B_1	B_2	B_3	B_4	B_5	B_6
Polar and non-polar UNIFAC								
(1) Original, (2) Linear/KT-1st order, (3) Modified Lyngby, (4)Modified Dortmund UNIFAC	(1) (Fredenslund et al., 1975), (2) (Hansen et al., 1992), (3) (Larsen et al., 1987), (4) (Weidlich and Gmehling, 1987)	1	1	0	0	0	0	0
KT-UNIFAC	(Kang et al., 2002)	1	1	1	0	0	0	0
Electrolyte UNIFAC								
(1) LIFAC, (2) e-KT-UNIFAC (1st and 2nd approach)	(1) (Mohs and Gmehling, 2013; Yan et al., 1999) (2) (Kim et al., 2016)	1	1	0	1	1	0	0
UNIFAC-Debye-Hückel	(Pinho et al., 1994)	1	1			1		
Association UNIFAC								
(1) UNIFAC-AG, -AM, (2) A-UNIFAC	(1) (Fu et al., 1996) (2) (Mengarelli et al., 1999)	1	1	0	0	0	1*	0
Polymer UNIFAC								
UNIFAC-FV	(Mengarelli et al., 1999)	1*	1	0	0	0	0	1
UNIFAC-YA	(Iwai and Arai, 1989)	1*	1	0	0	0	0	1
(1) ENTROPIC-FV, (2) ENTROPIC-FV/ GK-FV, (3) ENTROPIC-FV1.2	(1) (Elbro et al., 1990) (2) (Kontogeorgis et al., 1993) (3) (Kouskoumvekaki et al., 2002)	0	1	0	0	0	0	1*
UNIFAC-ZM	(Zhong et al., 1996)	1*	1	0	0	0	0	
UNIFAC-Liu	(Liu and Cheng, 2005)	1	1	0	0	0	0	1*

* Each of the variants has a different formulation of the term compared to first proposed model including the specific term.

Besides the UNIFAC models with clear dedication to general classes of compounds presented in Table 2.2 (e.g. electrolytes, polymers), other UNIFAC variants have been adapted to special classes of compounds, applications or phase equilibria. This implies introduction of new/ specific groups within the model, new sets of binary interaction parameters estimated from specific data (e.g. compound specific or phase equilibria/type of data specific). A brief overview

of these models is presented in Table 2.4, showing the high flexibility of the UNIFAC model(s), and its expanded range of applications.

Attempts to improve and expand the model applications were done by proposing new methods for binary interaction parameters estimation by different authors. The UNIFAC-CI model provides binary interaction parameters based on atom connectivity indices. The other methods proposed are focused on data selection and parameter regression approach. Each of these methods and their particularities are presented in Table 2.5.

Table 2.3 UNIFAC variants based on combinatorial volume fraction contribution and activity coefficient temperature dependence

Model	A_0	A_1	A_2	C_0	C_1
Original UNIFAC	1	0	0	1	1
Linear UNIFAC/ KT-UNIFAC 1st order	1	$T-T_0$	0	1	1
Modified Lyngby UNIFAC	1	$T-T_0$	$T \ln(T_0/T) + T - T_0$	2/3	0
Modified Dortmund UNIFAC	1	T	T^2	3/4	1
KT-UNIFAC 2nd order	1	$T-T_0$	0	1	1
LIFAC	1	0	0	1	1
e-KT-UNIFAC (1st and 2nd approach)	1	$T-T_0$	0	1	1
UNIFAC-AG,- AM, A-UNIFAC	1	0	0	1	1
ENTROPIC-FV	1	0	0	1	1
ENTROPIC-FV/ GK-FV	1	$T-T_0$	0	-	-

*If the model is not mentioned here it means that the combinatorial term and binary interaction parameters have the form of Original UNIFAC model.

**T_0 is a fixed value; for all models presented in this table T_0=298.15 K.

Table 2.4 Different UNIFAC variants based on their application

Application	Modifications	UNIFAC variant	Reference
Phase Equilibria			
VLE	Several sets of parameters fitted only from VLE data	Original UNIFAC	(Fredenslund et al., 1977a, 1975; Gmehling et al., 1982; Hansen et al., 1991; Macedo et al., 1983; Skjold-Jørgensen et al., 1979; Tiegs et al., 1987; Wittig et al., 2003)
LLE	Several sets of parameters fitted only from LLE data	Original UNIFAC	(Magnussen et al., 1981)
VLE, LLE, H^E, γ^∞	Several sets of parameters fitted from VLE, LLE, H^E, γ^∞	Dortmund UNIFAC	(Constantinescu and Gmehling, 2017; Gmehling et al., 2002, 1993a; Jakob et al., 2006; Lohmann et al., 1998; Weidlich and Gmehling, 1987)
Class of compounds			
Weak electrolytes (Amino acids)	Specific groups and parameters fitted from amino acids solubility data	UNIFAC-Debye-Hückel	(Pinho et al., 1994)
Ionic Liquids (IL)	Specific groups and parameters fitted from IL data	(1) Original UNIFAC, (2) Modified Dortmund UNIFAC	(1) (Lei et al., 2009; Liu et al., 2018) (2) (Kato and Gmehling, 2005; Paduszyński and Domańska, 2013)
Polymers	Specific groups and parameters fitted from polymer solubility data	UNIFAC-FV	(Elbro et al., 1990)
Glycoles, Polyols	New CH_2 definition, new parameters fitted from activity data	Original UNIFAC	(Marcolli and Peter, 2005)
Polyphenols	new parameters and new groups fitted to polyphenols solubility data	Dortmund UNIFAC	(Méndez Sevillano et al., 2014)
Sugars	new parameters and new groups fitted to different data (VLE, SLE, solubility)	(1) Original UNIFAC, (2) Modified Lyngby UNIFAC	(1) (Spiliotis and Tassios, 2000) (2) (Peres and Macedo, 1999, 1997)

Table 2.4 Different UNIFAC variants based on their application (Continued)

Application	Modifications	UNIFAC variant	Reference
Alkyl methanoates	new parameters and new groups	Dortmund UNIFAC	(Fernández et al., 2015, 2014)
Refrigerants	new parameters and new groups fitted from refrigerants (1) VLE and (2) LLE data	(1) Original UNIFAC, (2) Modified Dortmund UNIFAC	(1) (Kleiber, 1995) (2)(Kleiber and Axmann, 1999)
Lipids			
(1) LLE parameters (biodiesel)	updated parameters in the UNIFAC-LLE parameter set	Original UNIFAC	(Batista et al., 1999)
(2) LLE parameters (biodiesel)- 2 sets	new groups and new parameters fitted to LLE data	Original UNIFAC	(Hirata et al., 2013)
(3) LLE parameters (biodiesel) - 2 set	updated parameters; and new groups and parameters fitted to LLE data	Original UNIFAC	(Hirata et al., 2013)
(4) LLE parameters (biodiesel)	updated parameters fitted to LLE data	UNIFAC-FV	(Noriega et al., 2016)
(5) LLE parameters	updated parameters fitted to LLE data	Original UNIFAC	(Roosta, 2018)
(6) VLE parameters	new parameters involving CH_2, OH, CCOO, COOH groups fitted to acylglycerols VLE	Original UNIFAC	(Cunico et al., 2015)

Table 2.5 Different UNIFAC methods to estimate the binary interaction parameters

Name	UNIFAC variant	Method details	Reference
UNIFAC CI	Original UNIFAC	Atom connectivity indices are used to calculate binary interaction parameters	(González et al., 2007; Mustaffa et al., 2011)
NIST UNIFAC, NIST-modified UNIFAC, NIST KT UNIFAC	Original UNIFAC, KT 1st order UNIFAC	Weighted adequacy function and critically evaluated data are used in regression procedure	(Kang et al., 2011)
NIST-modified UNIFAC, NIST-KT UNIFAC	Dortmund UNIFAC, KT 1st order UNIFAC	Uses quality factors binary VLE data as weighting factors within fitting procedure. Note: NIST-KT UNIFAC is based on KT 1st order UNIFAC and T_0=0 in Eq.2.18	(Kang et al., 2015)
Hirata method	Original UNIFAC	Ternary LLE data and compounds weight fraction are used in the fitting procedure	(Hirata et al., 2013)

2.2.2 Models performance for lipid systems

The performance of lipid phase equilibria for all the models presented in Section 2.2.1 are presented and discussed in this section.

2.2.2.1 Cubic EoS and EoS-g^E

Peng-Robinson (PR) and Soave-Redlich-Kwong (SRK) are used for lipid VLE and LLE evaluation using both conventional and EOS-g^E mixing rules. The lipid systems for which the models were used are following: methanol/ethanol - glycerol - water systems (Soujanya et al., 2016), methanol/ethanol - ester/triacylglycerol (Glišić et al., 2007; Shimoyama et al., 2008; Tang et al., 2006), and several systems involved in biodiesel production which includes fatty acids (Oliveira et al., 2011). SRK with conventional mixing rules does not provide good description of VLE containing polar compounds (e.g. glycerol-water), with the exception of glycerol – methanol/ethanol systems, which are close to ideal behaviour (Oliveira et al., 2011). Regarding the LLE modelling, SRK does not give suitable results for solubility of water in fatty acids (Glišić et al., 2007), but the model can represent the methyl oleate – methanol – glycerol system quite well (Oliveira et al., 2011). PR with conventional mixing rules gives good predictions for ethyl esters-ethanol systems (Shimoyama et al., 2008) and similar results as SRK for ester solubility in fatty acids. The model is used to describe triolein - methanol system at elevated pressure and temperature and gives satisfactory results (Tang et al., 2006).

The SRK-g^E (MHV2 mixing rules with Lyngby UNIFAC) presents good VLE prediction for polar systems (e.g. ester – ethanol/methanol/water), but it is not able to describe glycerol-water system (Oliveira et al., 2011). The PR- g^E (MHV2 and Lyngby UNIFAC) presents same trends in prediction of VLE as SRK-g^E, but with slightly better results. PR-ASOG (Tochigi, 1995) has good performance for VLE evaluation of methyl ester-methanol systems (Shimoyama et al., 2009). Very high deviations are obtained for both SRK-g^E and PR-g^E models for water solubility modelling. Satisfactory results are given for LLE description of several tertiary systems involving a fatty ester, alcohol and glycerol (Oliveira et al., 2011). Compared to other methods (e.g. CPA), the EoS-g^E presents lower performances. This can be explained by the high asymmetry of the lipid systems (large difference in size between molecules – e.g. fatty esters-methanol), for wich these models are well known to provide poor description. It is shown in different studies that the EoS-g^E fail to describe asymmetric systems (Voutsas et al., 1996), and this fact can be explained by the big differences in the combinatorial terms (gamma combinatorial from the g^E model and the one of the EoS) of the combined model (Kontogeorgis and Vlamos, 2000).

2.2.2.2 Association models

CPA

CPA is used to describe lipid VLE and LLE. Most of the systems analysed with the CPA model are related to biodiesel production and purification and cover water, ethanol/methanol, glycerol and esters (biodiesels related systems) compound classes. Two extensive studies regarding CPA application for biodiesel related systems are presented by the group of Oliveira and Coutinho (Oliveira et al., 2011), where the CPA performance are compared to other models (e.g. activity models, EoS and EoS-gE), and Tsivintzelis and Kontogeorgis (Tsivintzelis et al., 2016), which describe trends of CPA parameters for biodiesel related compounds and systems, giving a predictive feature to the model. Pure compounds CPA parameters are

available for fatty acids, methyl and ethyl esters, alcohols and glycerol. Correlations of binary interaction parameters with carbon number for phase equilibria modelling prediction are available for following systems: glycerol-methyl/ethyl esters, glycerol-alcohol, methanol/ethanol-methyl-ethyl esters, water-methyl/ethyl esters, water-fatty acids. Based on these parameters, the model is extrapolated to multicomponent systems and a good agreement with experimental data can be found (Tsivintzelis et al., 2016). CPA is used to model most of the compounds and phase equilibria related to biodiesel processing, but no information on other classes of lipid are available (e.g. mono, diacylglycerols and triacylglycerols, other solvents than methanol and ethanol, like acetone). The analysis of VLE and LLE modelling for several biodiesel related system using different models showed that CPA gives the best results (Oliveira et al., 2011).

Other association models

GCA-EOS is used for modelling LLE and VLLE for the methanol-glycerol-methyl oleate system and it gives good results (Andreatta et al., 2010). The performances for LLE prediction are similar with the ones of A-UNIFAC, described in Section 2.2.2.3 under UNIFAC variants.

GC-PPC-SAFT is able to describe the LLE for methanol-glycerol-methyl oleate system (Barreau et al., 2010). Another contribution compares the phase equilibria prediction performances of two different SAFT variants along with RK-ASPEN, and shows that the SAFT methods are more robust compared to RK-ASPEN. The author highlights that more research needs to be done for the improvement and expansion of the models (Silva et al., 2016). It is to be mentioned that extensive work on lipid pure compounds (e.g. fatty acids, triacylglycerols, methyl and ethyl esters) parameters for PC-SAFT combined with GC model is reported by Cunico (Cunico, 2015), and this work could be further extended to phase equilibria modelling.

2.2.2.3 Activity coefficient models

Wilson

The Wilson model is successfully applied to VLE and SLE modelling for different types of lipid systems. Alongside classical biodiesel related systems (e.g. fatty acid-fatty acid, ester-ester, glycerol-alcohol/water) some new systems are investigated monoacylglycerol-monoacylglycerol/fatty alcohol/fatty acid, n-alkane-ester/fatty alcohol/fatty acid (Benziane et al., 2013; Damaceno and Ceriani, 2017b). The Wilson model is able to correlate all afore mentioned systems. In most of the cases, the performances of the model are compared to NRTL and UNIQUAC, giving similar results. The Wilson model gives the best description for the system glycerol-isopropanol (Soujanya et al., 2016) when compared to NRTL (10 times better) and UNIQUAC (100 times better)). The model is used for SLE correlation as well. Some of the systems described with the Wilson model are: alkanes-fatty acids (Wei et al., 2014, 2013), fatty acids-esters (Goff et al., 2005) and fatty acids-solvents (Calvo et al., 2009, 2008).

A modified version of the model for LLE prediction, Wilson-NRF (Pazuki et al., 2007), is used for modelling biodiesel-glycerol-methanol system (Hakim et al., 2014). The model correlates to the experimental data well.

NRTL

NRTL model is the most extensively used model for lipid related systems phase equilibria modelling. The model is able to correlate with the experimental data very well. The general

trend is that the model is slightly better in representing the phase equilibria than UNIQUAC and Wilson models. NRTL is used to model VLE data which includes both highly polar (e.g. glycerol-ethanol/methanol/isopropanol (Coelho et al., 2011; Soujanya et al., 2016)) and non-polar (e.g. ester-ester (Chen et al., 2014)) systems. NRTL gives a good representation for SLE, where systems used in other applications than biodiesel are investigated (e.g. fatty acid-fatty ester (Goff et al., 2005), fatty acids-triacylglycerols (Costa et al., 2011) fatty acids/fatty alcohols-alkanes (Wei et al., 2014)). Extensive work has been done in the area of multicomponent LLE modelling related to biodiesel production and purification, for which the NRTL model is able to give a good correlation to the experimental data (Andrade et al., 2012; Ardila et al., 2013; Ferreira et al., 2015). NRTL gives a good representation of LLE modelling of systems involved in other applications than biodiesel as well (e.g. vegetable oil deacidification (Shiozawa et al., 2015)), lipid separation and purification for other applications (Damaceno and Ceriani, 2017a)).

UNIQUAC

As mentioned earlier, UNIQUAC model is almost as applied as NRTL model, and it is used to describe the same type of lipid systems as NRTL. The model is able to correlate experimental data for VLE, LLE and SLE very well. NRTL and UNIQUAC are the only models used to correlate systems with tocopherols for oil deacidification (Gonçalves et al., 2007; Rodrigues et al., 2005). UNIQUAC proved to give the best correlation compared to NRTL for following systems: fatty acids -ethanol-water-glycerol, triacylglycerol (Gonçalves and Meirelles, 2004; Kanda et al., 2013), ester-methanol-glycerol, water (Lee et al., 2010).

UNIFAC variants

The UNIFAC model under its many variants is the most extensively applied predictive model. The model is used for VLE, SLE and LLE prediction.

Before analysing the UNIFAC predictive capacity, one important aspect to mention is that in some works, the reagents used in the experimental determination of phase equilibria are not of high purity (e.g. purity can vary between 50-97 wt.%). Some of these compounds are: oleic acid (Batista et al., 1999), methyl oleate (Andreatta et al., 2008), ethyl oleate (Robustillo et al., 2014), triolein (Costa et al., 2010). For the correlation models, the purity does not affect the model correlation ability (since the model parameters are regressed and tested from the same data), but it still can have effects when the parameters are extrapolated to multicomponent systems. In the case of the predictive methods, like UNIFAC, the model will not be able to properly describe the investigated system, unless all the impurities from the regent are considered within the model. Even though the impurities found in the reagent are also lipids with similar structure (same groups and binary interaction parameters, but with different concentrations/frequencies), their pure component properties like melting point and vapour pressure are different and they can affect the phase equilibria prediction. In the majority of the papers where the purity represents an issue, it is not clearly stated how the low purity compounds are treated in the systems. The only paper found to explain the modelling approach for phase equilibria data with low purity of a reagent, is within the work of Costa and collaborators (Costa et al., 2010) for the SLE modelling of palmitic acid –triolein (purity 50 wt.%), where the impure component is treated as a mixture.

The Original UNIFAC model using both the first parameters published (Fredenslund et al., 1975) as well as the updated ones (Hansen et al., 1991) gives a good prediction for esters systems (Chen et al., 2014), performing better than Dortmund UNIFAC (Weidlich and Gmehling, 1987). The Original UNIFAC model (Fredenslund et al., 1975) is tested for oil and non-polar solvent VLE prediction by using different combinatorial terms in the activity coefficient equation (Fornari et al., 1994), where improvements are achieved for some of the terms. Dortmund UNIFAC (Gmehling et al., 1993b) does not provide a good description for systems alkane-esters (Benziane et al., 2013). When Original UNIFAC (Fredenslund et al., 1975) is used for VLE prediction of polar systems (e.g. glycerol-water, glycerol-alcohol) higher deviations are observed compared to non-polar systems. The model gives reasonable results for glycerol - water system and glycerol-methanol/ethanol systems (Zaoui-Djelloul-Daouadji et al., 2014), but it is not able to predict glycerol-isopropanol-water system with a high accuracy (Soujanya et al., 2016). The performance of Dortmund UNIFAC with both initial and updated parameter matrix (Gmehling et al., 1993b; Weidlich and Gmehling, 1987) gives higher deviations to the systems glycerol-water/methanol/ethanol representation compared to the Original UNIFAC. When it comes to other lipid related systems (e.g. monoacylglycerol-ester) the Original UNIFAC (Fredenslund et al., 1975) predicts a unreal phase split for some of these systems (Cunico et al., 2015). Damaceno and Ceriani (Damaceno and Ceriani, 2017a) compared different UNIFAC variants performances for VLE prediction of new lipid systems involving monoacylglycerols (e.g. monoacylglycerol-monoacylglycerol, monoacylglycerol-fatty acid, monoacylglycerol-fatty alcohol) and concluded that best predictions are given by Original UNIFAC (Fredenslund et al., 1975) followed by Original UNIFAC model with NIST parameters (Kang et al., 2015), Original UNIFAC with parameters proposed by Cunico (Cunico et al., 2015), Dortmund UNIFAC with updated parameters (Gmehling et al., 1993b) and Lyngby UNIFAC (Larsen et al., 1987). The same models were tested by the authors for systems involving mono- and diacylglycerols with fatty esters, alcohols and alkanes and none of the models proved to be the best (Damaceno and Ceriani, 2018a) concluding that there is a lack of experimental data and more data are needed for the improvement of UNIFAC models.

Only Original UNIFAC with VLE (Fredenslund et al., 1975) and LLE parameters (Magnussen et al., 1981) and Dortmund UNIFAC with revised parameters (Gmehling et al., 1993b; Lohmann et al., 1998) are used for SLE prediction. The model variations are able to describe SLE of lipid-systems (e.g. fatty acids-triacylglycerol (Costa et al., 2010; Nishimura et al., 2011)). The models performance was compared for triolein-fatty alcohol systems, and Original UNIFAC (Fredenslund et al., 1975) which proved to give better predictions than Dortmund UNIFAC (Gmehling et al., 1993b). For complex systems involving fatty alcohols, the Dortmund model does not give a very good prediction. (Carareto et al., 2011).

All of the available LLE data and modelling is related to biodiesel production and purification. Since the process involves many polar compounds (e.g. methanol, ethanol, glycerol), a UNIFAC variant involving an associative term within the activity coefficient equation, associative UNIFAC (Mengarelli et al., 1999), was tested. The analysed systems are methyl oleate-glycerol-methanol, and ethanol. The model is not able to describe the miscibility of the methanol-methyl oleate system. This result could be due to the association and/or binary interaction parameters used in the model, but it can be, as well, due to the methyl oleate regent used in

the experiments, which has a purity of 70%. The Original UNIFAC with VLE (Fredenslund et al., 1975) and LLE (Magnussen et al., 1981) parameters and Dortmund UNIFAC with updated parameters (Gmehling et al., 1993b) have low performances for the methanol-methyl oleate-glycerol system (Lee et al., 2010; Negi et al., 2006): the two liquids phases compositions are not well predicted. The methyl oleate reagent purity is less than 0.99. The prediction of LLE for systems involving fatty acids, methanol/ethanol, water and oil is better for the Original UNIFAC using the parameters proposed by Hirata (Hirata et al., 2013) compared to the model using LLE parameters (Magnussen et al., 1981), but none of these two model variants are able to describe LLE involving other type of lipid compounds like mono- and diacylglycerols (Bessa et al., 2015). The systems involving mono- and diacylglycerols (Ferreira et al., 2015) are best described by the Original UNIFAC model with the parameters proposed by Bessa (Bessa et al., 2016).

Summary and why it is necessary to expand the UNIFAC model to lipid models

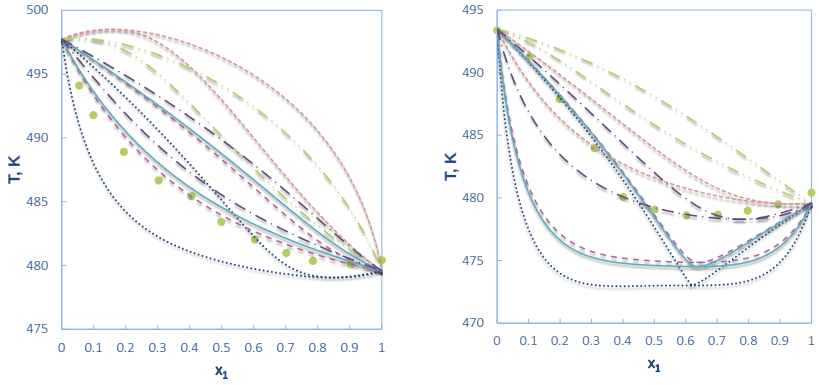
At the beginning of this chapter importance of the data used within the development of the models was highlighted. Lipid phase equilibria data has expanded over the last years and it was collected within the *Lipids Database*. The majority of the data corresponds to LLE and are related to a few systems involved in the biodiesel industry. VLE data quality is analysed through a series of consistency-quality tests within the method proposed by Kang and collaborators (Kang et al., 2010), which helps to identify best data for specific systems. Detailed results for each test of lipid VLE are presented and show that the majority of the data sets are in good agreement with the pure compound data.

Different models, from EoS to activity and combined models are used to describe lipid phase equilibria. The activity models proved to give better results compared to EoS with classical mixing rules and EoS-g^E. The general trend for increasing deviation of VLE correlation using different activity coefficient models is: NRTL ≈ Wilson <UNIQUAC. The SLE trend for increasing deviation is: UNIQUAC<Wilson ≈ NRTL. For LLE, NRTL and UNIQUAC prove to have similar performances and both can be used to describe lipid LLE. The differences in correlation between the two models are very small and these can be attributed to experimental data quality and fitting procedure. When it comes to association models, CPA proves to give the best overall prediction (Oliveira et al., 2011), but there can be some exceptions as well (see VLE results from (Oliveira et al., 2011)). Unfortunately, the prediction of these models is limited to a few combinations of compounds (e.g. fatty acids-fatty acids, fatty esters with fatty esters or alcohol) and it cannot be extrapolated to other types of lipid mixtures involving more complex compounds (e.g. systems with TAG, DAG, MAG) since their parameters are regressed for each binary pair. For lipid compounds this represents a major drawback due to the high number of compounds, and difficulty with measurements (e.g. purity, thermal stability). Therefore, group contribution models that are able to predict the phase equilibria based on group interactions are the best option to be considered taking into account the limited availability of lipid-data and the need for extrapolation beyond the systems for which phase equilibria data are available.

Available UNIFAC variants are tested on all types of phase equilibria involving lipids, proving that they are able to predict such systems. Several sets of model parameters for the Original

UNIFAC model that are dedicated for lipid LLE prediction have been proposed, showing that improvements in model prediction can be achieved if the right data are included in the binary interaction parameters regression. Performances of Original UNIFAC model using VLE parameters and NIST parameters, Linear UNIFAC, Lyngby Modified UNIFAC and Dortmund Modified UNIFAC, do not give adequate predictions especially for systems involving mono- and diacylglycerols. As presented by Damaceno and collaborators (Damaceno and Ceriani, 2017b), Original UNIFAC gives the best prediction overall. An example of the mentioned model variants performance for VLE prediction of a monoacylglycerol-fatty acid/fatty ester system is presented in Figure 2.3 (e.g. Original UNIFAC predicts a false immiscibility for monocaprylin-methyl hexanoate, and the other models prediction presents large deviations from the experimental data) (Perederic et al., 2018b).

UNIFAC model variants prove to have a high degree of flexibility with its different variants and sets of binary interaction parameter, which showed that the model predictive performances could be improved over a wide spectrum of compounds. As presented in Figure 2.3 and also concluded by some authors, available models do not give a good prediction for certain lipid systems. The models performance for lipid systems needs to be improved and it can be done by using a systematic approach for data selection and parameter estimation.



(a) (b)

Figure 2.3 VLE prediction using different UNIFAC models for monocaprylin (1) – hexanoic acid (2) system (a) and monocaprylin (1) – methyl hexanoate (2) system (b) at 2.50 kPa (Cunico et al., 2015): ● experimental data, — Original UNIFAC, — Modified UNIFAC, - - Linear UNIFAC, - - NIST-KT UNIFAC, — — Dortmund UNIFAC, — — NIST-modified UNIFAC

3

SYSTEMATIC IDENTIFICATION METHOD: DESCRIPTION

As presented in the previous chapter, group contribution models represent a good option for lipids phase equilibria prediction. It is shown that UNIFAC model has a high flexibility and if the right data are used within parameter regression, good phase equilibria prediction can be achieved for lipids systems. The aim of this chapter is to present a systematic identification-regression method developed for data analysis and model parameter regression applied for phase equilibria modelling. The method provides a detailed approach for data selection and a regression procedure for binary interaction parameter estimation for GC based models. The aim of the method is to offer support for a faster assessment and solution of the identification-regression problem.

The chapter is structured in six parts: the first three sections (3.1-3.3) follow the method, where each involved step is described. The algorithms involved are presented in Sections 3.4 and 3.5. At the end of the chapter, Section 3.6, an example of method application to a smaller problem is given for better understanding on how the method works.

Chapter structure:

3.1 Data collection and analysis
3.2 Data organization and selection
3.3 Parameter estimation and validation
3.4 Algorithm A
3.5 Algorithm B
3.6. Method application example

The work form the basis of following publications: *Perederic, O.A., Cunico, L.P., Kalakul, S., Sarup, B., Woodley, J.M., Kontogeorgis, G.M., Gani, R., 2018. Systematic identification method for data analysis and phase equilibria modelling for lipids systems. Journal of Chemical Thermodynamics 121, 153–169* and in *Perederic, O.A., Cunico, L.P., Sarup, B., Woodley, J.M., Gani, R, 2017. A Systematic Identification Method for Thermodynamic Property Modelling. Antonio Espuña, Moisès Graells, Luis Puigjaner (Editors), Proceedings of the 27th European Symposium on Computer Aided Process Engineering – ESCAPE 27, Computer Aided Chemical Engineering, Elsevier, 40, 205-210.*

A systemathic identification method is applied to estimate binary group interaction parameters for different UNIFAC models dedicated to lipid systems. The objective is that the new set of parameters must be able to improve the performance of the UNIFAC models (e.g. Original UNIFAC (Fredenslund et al., 1975)) with published parameters (e.g. VLE parameters (Fredenslund et al., 1975)) quantitatively as well as qualitatively by eliminating the prediction inaccuracies and/or uncertainties. This method aim is to fit the model parameters in a systematic, thermodynamically consistent and numerically efficient way. The *Lipids Database*, described in Chapter 2, is the source for experimental data and models for estimation of lipid pure compound properties (e.g. vapour pressure of pure compounds). The method is presented in (Perederic et al., 2018b).

As presented in the previous chapter, Original UNIFAC and other of its variants, use binary group interaction parameters, a_{mk}, for liquid phase activity coefficients calculations (see Eq. 2.5-2.18) needed for phase equilibria computations (Fredenslund et al., 1975). The difficulty with the estimation of binary group interaction parameters, in general and with prediction of phase equilibria in particular, is the selection and evaluation of the experimentally measured data used for the regression step. The proposed identification method aims to complement available expertise and personal judgment regarding data selection by providing a clear data selection algorithm as described in Section 3.2 and Section 3.5.

Problem size represents another issue regarding the regression of binary group interaction parameters. Estimation of all parameters in one step for different types of chemical systems can prove to be difficult (Kang et al., 2015). One-step regression of all parameters is impractical due to the large space of the optimization problem involving a high number of parameters, data, and local (sub-optimal) solutions. Long convergence times may also become problematic. The identification method provides a clear step-by-step procedure for model parameter estimation based on available data. The complete data set is organized into sub-sets from which only the associated parameters are regressed. For this reason, the binary lipid systems are classified into categories, each one containing a sub-set of data. In this way, the full set of parameters can be regressed efficiently and quickly. Fine-tunning o fthe parameters can be performed through a final optimisation strep at the end if it is necessary.

The identification method is tested for the regression of the Original UNIFAC model binary group interaction parameters (Perederic et al., 2018b), and further applied to Linear, Modified and Dortmund UNIFAC (Damaceno et al., 2018a). It is well-known that the Original UNIFAC model and its variants do not provide good predictions with the same set of binary group interaction parameters for VLE, LLE and SLE (Kontogeorgis and Folas, 2010d). Therefore, in this

work, the binary group interaction parameters are regressed only with VLE data. The extrapolation capabilities of the parameters are tested afterwords for other types of phase equilibria (e.g. SLE, LLE) or other type of systems not included within the regression. Only binary VLE data are considered for parameter regression since multicomponent data may not give a unique match of the VLE compositions. The data used for regression are selected based on the quality factor, as presented in Section 2.1 of Chapter 2 and it is described in Section 3.2 of this chapter.

The identification method consists of three hierarchical parts: (I) data collection and analysis, (II) data organization and selection, and (III) parameter estimation and validation, as highlighted in Figure 3.1. The steps and algorithm involved in each part are presented in the following sections of the chapter. The method has the following characteristics: (I) inclusion of a detailed algorithm for data selection, which complements personal judgment and available expertise; (II) use of an efficient calculation sequence, which can be further exploited for planning experimental data collection in order to fill in the gaps within the binary interaction matrix and to make possible the step by step estimation of the parameters; (III) the regression problem formulation and solution for each regression step.

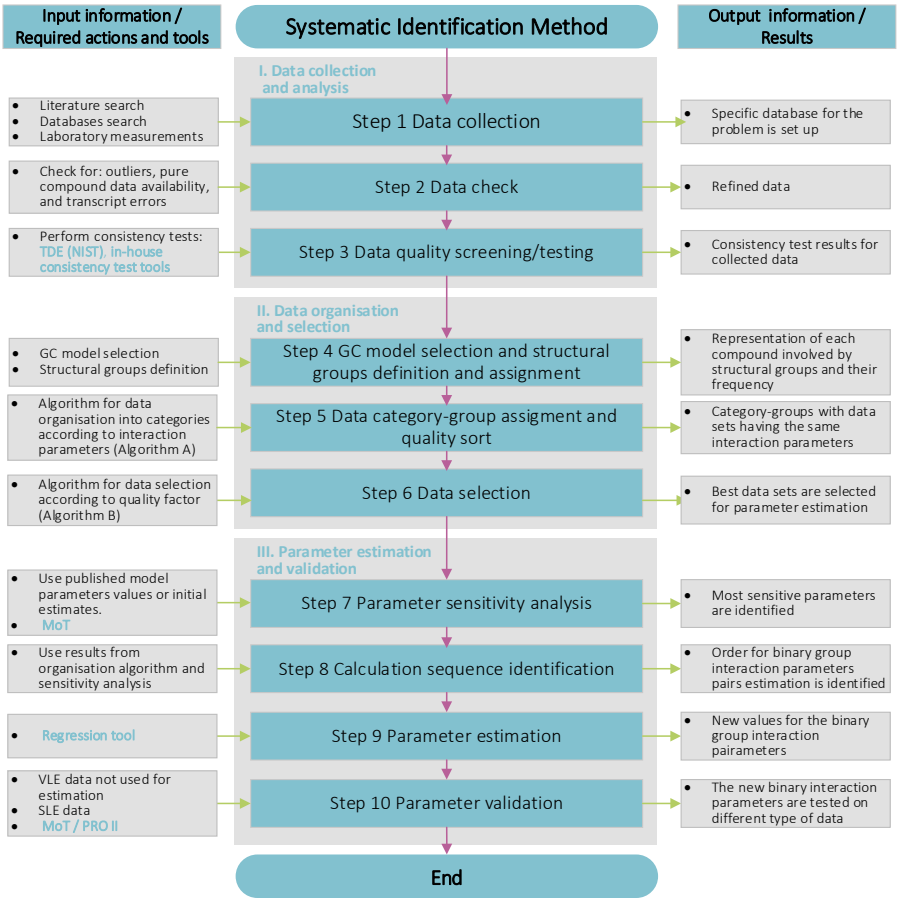


Figure 3.1 Flow-diagram for Systematic Phase Equilibria Modelling Method. Note: the required tools for each step are indicated by bold text in the input information column on the left hand side; the output information and/or results from each step are highlighted in the column on the right hand side

3.1 Data collection and analysis

The objective of Part I is to retrieve-collect all available data (***Step 1***) for the defined problem, to analyse the data in terms of physical check of errors (***Step 2***) and to determine the data quality (***Step 3***).

Step 1 - Data Collection: Binary VLE and SLE data for lipid systems are collected and/or retrieved from databases containing phase equilibria data (e.g. ThermoData Engine software (TDE) from NIST (Diky et al., 2012), DECHEMA database (Westhaus et al., 1999), *Lipids Database* (Cunico et al., 2013; Perederic et al., 2018b)), papers, or from laboratory measurements.

Step 2 -Data check: Collected VLE and SLE data sets are checked for outlier errors, transcript errors, and availability of pure compound data (e.g. vapour pressure, melting point). If the pure component data points are missing, these are added to the data sets. The values are taken from literature or databases if available; otherwise they are estimated by using property models for pure compounds available in *Lipids Database*.

Step 3 - Data quality testing: Thermodynamic consistency test are applied to the datasets checked in ***Step 2.*** VLE data evaluation is performed with ThermoData Engine (TDE) software from NIST (Kroenlein et al., 2011), which assigns a quality factor to each data set according to Eq.2.3, using the same consistency tests as presented in Chapter 2.

3.2 Data organization and selection

The GC model selection is done in Part II of the method, and the compounds present in the selected data sets are represented by the model defined groups (***Step 4)***. The aim of this part is to assign the available VLE data to corresponding category systems and prepare the data sub-sets according to a pre-established order determined by ***Algorithm A***, so that the model parameters can be regressed sequentially and efficiently (***Step 5***). The data sets to be included in each sub-sets need to pass the quality selection algorithm (***Algorithm B***) which is introduced at ***Step 6***.

Step 4 - GC model selection and molecular structure group definition and assignment: The main groups and subgroups of the selected GC model are identified and assigned to represent the compounds found in the VLE data sets. All the compounds found in the VLE data sets must be represented by the selected model groups. The set of binary group interaction parameters are then identified. An example of application of this step is given in Section 3.6 of the chapter.

Step 5 - Data category-group assignment and quality sorting: The data organization algorithm (***Algorithm A***) is used to sort the data into different category-groups according to the involved binary group interaction parameters. The aim of the algorithm is to identify the category-groups and their order in such a manner that, in the estimation step, only a small set of additional binary group interaction parameters is estimated, keeping the previously estimated parameters unchanged. An example for data sorting is given in in Section 3.6 of the chapter.

Step 6 - Data selection: The objective of the data selection algorithm (***Algorithm B***) used in this step is to remove low quality data. The algorithm tries to consider binary systems coming from different references, if their quality factor is higher than 0.1, in order to avoid systematic errors of the data. The algorithm is explained in Section 3.5 and an example of its application is given in Section 3.6.

3.3 Parameter estimation and validation

The parameter regression problem is formulated as a least squares optimization problem and it is solved with the Harwell subroutine VA07AD (Hopper, 1973). The regressed binary group interaction parameters are tested on retrieved VLE data. The parameters are extrapolated to other systems and phase equilibria (e.g. SLE).

Step 7 - Parameter sensitivity analysis: The parameter sensitivity analysis is performed for the category-groups where more than one binary interaction pair needs to be estimated. Original UNIFAC model published parameters are used as the reference point when available; otherwise a preliminary estimation of the parameters is performed in order to be able to do the sensitivity analysis.

Step 8 - Calculation sequence identification: The calculation order of binary group interaction pairs is determined from the available category-groups and from the sensitivity analysis. The estimation starts with the most sensitive pairs.

Step 9 - Parameter estimation: The parameter estimation is performed according to the determined calculation sequence from the previous step. For given surface area, Q_k, and volume, R_k, of each group, the binary group interaction parameters, a_{mk}, are regressed to match the corresponding VLE data. The objective function is given by Eq. 4.2. Other objective functions may also be used, but the performance of the objective functions or numerical solvers is beyond the scope of this work. The objective function used, presented in Eq. 4.2, was however selected after a number of tests.

Step 10 - Parameter validation: The validation of the parameters is done against all the VLE data retrieved and checked. The predictive power of the binary group interaction parameters is tested with the retrieved SLE data. ICAS-MoT (Sales-Cruz and Gani, 2003) and PRO II (Schneider Electric Software, 2016) are used to perform the validation tests. Multicomponent VLE or SLE data can be used as well for validation, but care should be taken, since the probability of errors regarding the composition is higher.

3.4 Algorithm A: Data organization

The algorithm aims to organize the data within category-groups, with general notation X.M.N that corresponds to the number of involved binary group interaction parameters pairs, a_{mk} and a_{km} (called further pairs and noted X), the number of pairs that need to be estimated (M), and type of involved pairs (N). For example, the category-group 3.2.1 (given in Table 3.1 in the category-group column) which involves 3 structure groups (CH_2, CH_3OH, CH_2COO) has the following meaning of the category-group numbers. The number 3 corresponds to X and stands for the number of available binary group interactions parameters pairs given by the data sets from this category-group (CH_2-CH_3OH, CH_2-C H_2COO, and CH_3OH-CH_2COO). The number 2 corresponds to M, which gives the number of binary interaction pairs that will be estimated from the data sets available in this category-group. In the list of category-groups one can notice that the CH_2-C H_2COO binary group interaction parameters pair is already identified for regression in category-group 1.1.2, which comes before 3.2.1 (see Section 3.6). While performing the regression, when one reaches category-group 3.2.1, the CH_2-CH_2COO binary pair interaction is already known, meaning that only CH_2-CH_3OH and CH_3OH-CH_2COO need to be regressed. The last number in the category-group is 1 which corresponds to N and denotes the type of the pair. The role of the last number is to differentiate between category-groups having the same number of involved and estimated binary group interaction parameters pairs. Another set of data involving 3 pairs with 2 needed to be identified, will get another value for N (e.g. 3.2.2, 3.2.3, 3.2.4, 3.2.5, and 3.2.6). The algorithm flow diagram is showed in Figure 3.2.

Algorithm steps:

Step A.1: X, M, and N are initialized to zero. All pairs are considered as unknown/ unidentified.

Step A.2: Category (X) iteration loop starts

Step A.3: All the systems with X pairs are identified and selected.

Step A.4: Sub-category (M) loop starts

Step A.5: All the systems with M unknown/unidentified pairs are identified, selected and organized according to their type (N).

Step A.6: All the pairs identified in Step A.5 are considered as known/identified.

Step A.7: Check remaining systems in X category for unknown /unidentified pairs. Are in the X category systems with M or less than M unknown pairs? If Yes, go to Step A.5. If No, go to Step A.8.

Step A.8: Check remaining systems in (X) category for unknown /unidentified pairs. Are in the (X) category systems with more than M unknown pairs? If Yes, go to Step 4. If No, go to Step A.9.

Step A.9: Are there systems with more than X pairs? If Yes, go to Step A.2. If No, go to END of the algorithm.

END: End the algorithm and go to Step 4 of the method.

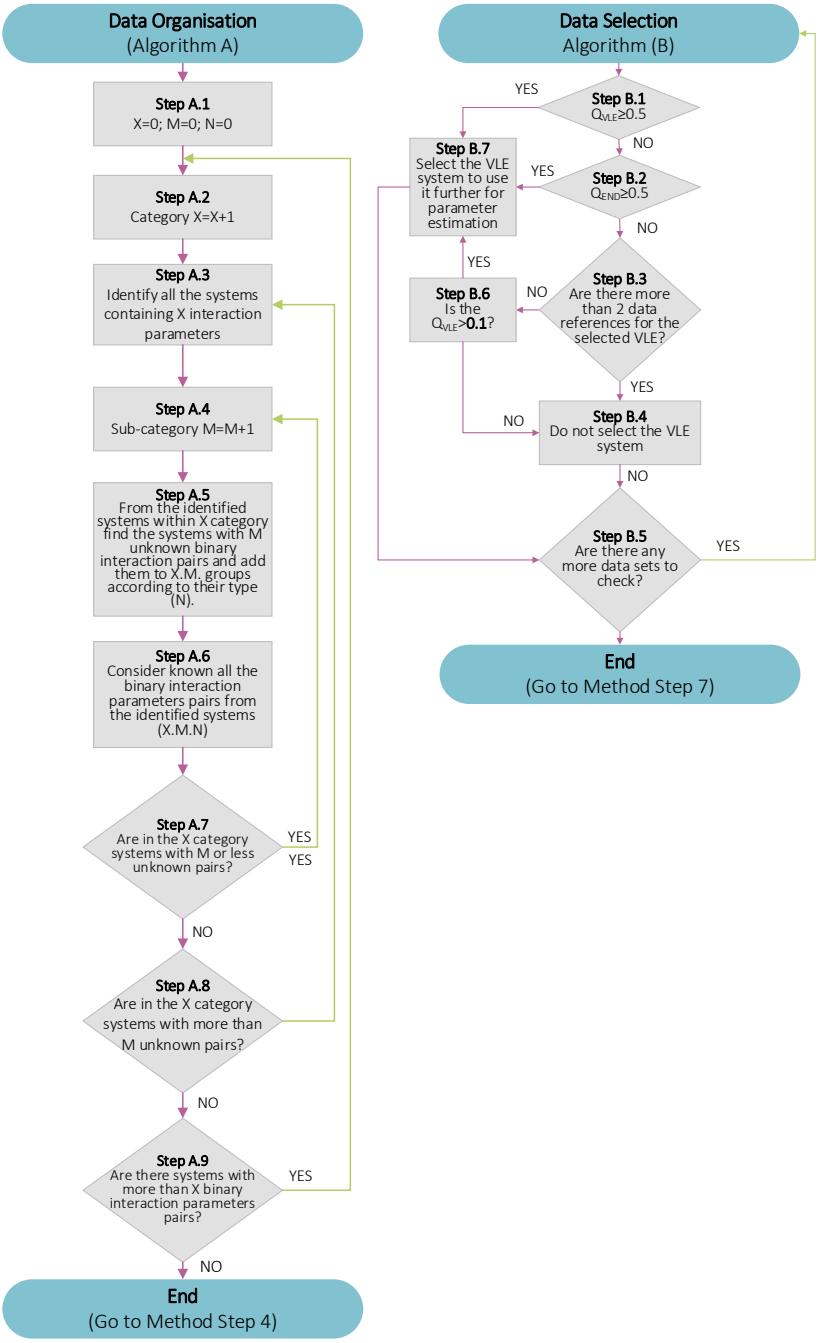


Figure 3.2 Data organization (Algorithm A) and data selection (Algorithm B) algorithms

3.5 Algorithm B: Data selection algorithm

The aim of the algorithm is to select the best data to be used for regression. The algorithm tries to eliminate experimental uncertainty and systematic errors by requesting to select at least two different sources for estimating certain interaction parameter(s), but only if these data sets have a minimum required quality value. The algorithm is applied individually to each category-group identified in Step 5 of the identification method. The algorithm consists of seven steps as presented below. The flow diagram for algorithm B is presented in Figure 3.2.

Algorithm steps:

Step B.1: Data set is checked for quality. If $Q_{VLE} \geq 0.5$, go to Step B.7. If $Q_{VLE} < 0.5$, go to Step B.2.

Step B.2: If $Q_{END} \geq 0.5$, go to Step B.7., If $Q_{END} < 0.5$, go to Step B.3.

Step B.3: If the selected VLE data sets come from more than two different references, go to *Step B.4.* If no go to Step B.6.

Step B.4: The VLE data set is not selected. Go to Step B.5.

Step B.5: If there are more data sets to be checked, go to Step B.1. If no, go to END of the algorithm.

Step B.6: If the $Q_{VLE} > 0.1$ go to Step B.7. If $Q_{VLE} \leq 0.1$, go to Step B.4.

Step B.7: Select the VLE data set for parameter estimation. Go to Step B.5.

END: End the algorithm for current category-group. Proceed to apply the algorithm to another category-group if available. Otherwise, go to Step 7 in the methodology.

3.6 Method application example

This chapter section presents a few examples for the most important parts of the method: Step 4 and the two algorithms introduced at Step 5 and Step 6 of the method. The examples consider a particular case and/or a smaller problem in order to make the user more familiar with the method and its algorithms, as well as to make the method results presented in Chapter 5 easier to understand and to follow.

3.6.1 Group definition and assignment (Method Step 4) example

In Step 4 the structural groups are defined and assigned to each compound from all the datasets. The example is built for methyl laurate – lauric acid system. The two molecules are presented in Figure 3.3.

- Methyl laurate: subgroup structure: CH_3 x 2, CH_2 x 9, CH_2COO x 1; involved main groups: CH_2, CH_2COO
- Lauric acid: subgroup structure: CH_3 x 1, CH_2 x 10, COOH x 1; involved main groups: CH_2, COOH
- System group interactions: CH_2-CH_2COO, CH_2-COOH, CH_2COO-COOH

Detailed representation of the groups, subgroups and interaction parameters are given for the main problem in Chapter 4, Tables 4.1 and 4.2.

(a) (b)

Figure 3.3 Chemical structure of (a) Lauric acid ($C_{12}H_{24}O_2$) and (b) Methyl Laurate ($C_{13}H_{26}O_2$). (Structure draw with MolView)

3.6.2 Algorithm A application example

For a better understanding of how the algorithm works, an example is presented. It is assumed that the whole database to be used for parameter estimation is composed of the VLE data sets given in Table 3.1.

For each of the 5 datasets, the structure group and available binary group interaction parameters are known from Step 4 of the method and they are given in the Table 3.1. Application of Algorithm A will yields the following results:

Step A.1 The category group descriptors X, M and N are initialised with zero.

Iteration I.a

Step A.2 X get the value X=1

Step A.3 The systems with one interaction are 1, 3, 4 and 6.

Iteration I.b

Step A.4 M get the value M=1

Step A.5 The systems that will be in category group X.M = 1.1 are 1, 3, 4 and 6. The type (N) of interactions available in the identified systems is CH_2-COOH (N=1) for systems 1 and 6, CH_2-CH_2COO (N=2), for system 4, and GLY-CH_3OH (N=3) for system 3. Note that the order of the system type is random and it does not affect in any way the calculation sequence.

Step A.6 All the binary pairs for the category groups X.M.N: 1.1.1, 1.1.2, and 1.1.3 are considered as known. This will help at identifying new binary group interaction parameters further when the algorithm is applied.

Step A.7 When X=1, the only possible value for M is 1, so no more systems are available. The option *No* is selected.

Step A.8. Similar as for the Step A.7, no more systems are available. The option *No* is selected.

Step A.9. There are systems with more than one binary interaction pair. The option *Yes* is selected.

Iteration II.a

Step A.2 X get the value X=1+1=2

Step A.3 There are no systems with two binary interaction parameters, therefore nothing will happen in *Steps A.4* to *A.6.*

Step A.7. No more systems to be identified. The option *Yes* is selected.

Iteration III.a

Step A.2 X get the value X=2+1=3

Step A.3 Two systems presents 3 binary interaction parameters: system 2 and 5.

Iteration III.b (1)

Step A.4 M get the value M=1

Step A.5 The systems with one unknown binary interaction parameter are identified. The only system available with one unknown binary interaction pair is System 2. For this system, 2 out 3 binary interactions were identified in the previous iteration (CH_2-CH_2COO and CH_2-COOH), meaning that the only unknown binary interaction parameter is CH_2COO-COOH. System 2 will be part of 3.1.1 category group.

Step A.6 All the binary interaction parameters (from previous and current iteration) are consider as identified.

Step A.7 No more systems with one unknown parameters are available. The option *No* is selected.

Step A.8 In the X=3 category there is still one more system remaining. The option *Yes* is selected.

Iteration III.b (2)

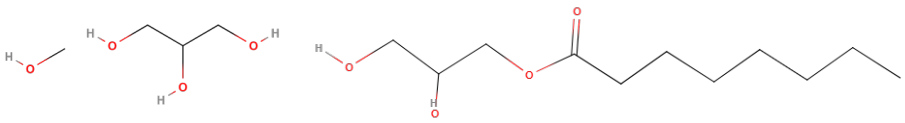
Step A.4 M gets the value M=1+1=2

Step A.5 The systems with two unknown binary interaction parameters are identified: system 5. For system 5 only CH_2-CH_2COO interaction is known from before (CH_2-OHacyl, CH_2COO-OH_{acyl} are unknown). This system will be part of the category group 3.2.1.

No more systems are available. Five category groups are identified (1.1.1, 1.1.2, 1.1.3, 3.1.1, 3.2.1). The algorithm ends, and the user returns to Step 6, after the data in each category group is sorted according to the quality factor.

Table 3.1. Example of VLE datasets organized within category groups with Algorithm A

No.	VLE dataset components		Identified structure groups	Identified binary interaction parameters	Category Group (X.M.N)
1	Saturated fatty acid (e.g. Myristic acid)	Saturated fatty acid (e.g. Stearic acid)	CH_2, COOH	CH_2-COOH	1.1.1
2	Saturated fatty ester (e.g Methyl laurate)	Saturated fatty acid (e.g. Myristic acid)	CH_2, CH_2COO, COOH	CH_2-CH_2COO, CH_2-COOH, CH_2COO-COOH	3.1.1
3	Glycerol	Methanol	GLY, CH_3OH	GLY- CH_3OH	1.1.3
4	Saturated fatty ester (e.g Methyl stearate)	Saturated fatty ester (e.g. Methyl laurate)	CH_2, CH_2COO	CH_2-CH_2COO	1.1.2
5	Saturated MAG (e.g. Monocaprylin)	Saturated fatty ester (e.g. Methyl palmitate)	CH_2, CH_2COO, OH_{acyl}	CH_2-CH_2COO, CH_2-OH_{acyl}, CH_2COO-OH_{acyl}	3.2.1
6	Saturated fatty acid (e.g. Palmitic acid)	Saturated fatty acid (e.g. Stearic acid)	CH_2, COOH	CH_2-COOH	1.1.1



(a) (b) (c)

Figure 3.4 Chemical structure of (a) Methanol (CH_4O), (b) Glycerol ($C_3H_8O_3$), (c) Monocaprylin ($C_{11}H_{22}O_4$) (Structure draw with MolView)

3.6.3 Algorithm B application example

The application of Algorithm B, used for data selection, is exemplified by applying it to three category groups, listed in Table 3.2. The algorithm is applied independently to each category group.

Category group 1.1.1

Iteration I

Step B.1 Q_{VLE} for dataset 1 is higher than 0.5. The option *Yes* is selected.

Step B.7. The VLE data set is selected.

Step B.5 There are more data sets in this category group. The option *Yes* is selected.

Iteration II

Same steps/path is follows for the second iteration when VLE dataset 2 is selected.

Iteration III

Step B.1 Q_{VLE} for dataset 1 is lower than 0.5. The option *No* is selected.

Step B.2 Q_{pure} for dataset is higher than 0.5. The option *Yes* is selected.

Step B.7. The VLE data set is selected.

Step B.5 There are more data sets in this category group. The option *Yes* is selected.

Iteration IV

Step B.1 Q_{VLE} for dataset 1 is lower than 0.5. The option *No* is selected.

Step B.2 Q_{pure} for is lower than 0.5. The option No is selected.

Step B.3 The selected datasets belong to only one reference. The option *No* is selected.

Step B.6 Q_{VLE} is higher than 0.1. The option *Yes* is selected.

Step B.7. The VLE data set is selected.

Step B.5 There are more data sets in this category group. The option *Yes* is selected.

Iteration V

Step B.1 Q_{VLE} for dataset 1 is lower than 0.5. The option *No* is selected.

Step B.2 Q_{pure} for dataset is lower than 0.5. The option No is selected.

Step B.3 The selected datasets belong to two references. The option *Yes* is selected.

Step B.4 The dataset is not selected.

Step B.5 There are no more data sets in this category group. The algorithm ends.

Category group 3.1.1

Step B.1 Q_{VLE} for dataset 1 is lower than 0.5. The option *No* is selected.

Step B.2 Q_{pure} for is lower than 0.5. The option No is selected.

Step B.3 There is no datasets previously selected (zero references). The option *No* is selected.

Step B.6 Q_{VLE} is higher than 0.1. The option *Yes* is selected.

Step B.7. The VLE data set is selected.

Step B.5 There are no more data sets in this category group. The algorithm ends.

Category group 6.1.3

Iteration I

Step B.1 Q_{VLE} for dataset 1 is lower than 0.5. The option *No* is selected.

Step B.2 Q_{pure} for is higher than 0.5. The option *Yes* is selected.

Step B.7. The VLE data set is selected.

Step B.5 There are more data sets in this category group. The option *Yes* is selected.

Iteration II

Step B.1 Q_{VLE} for dataset 1 is lower than 0.5. The option *No* is selected.

Step B.2 Q_{pure} for is lower than 0.5. The option No is selected.

Step B.3 There is no datasets previously selected (zero references). The option *No* is selected.

Step B.6 Q_{VLE} is lower than 0.1. The option *No* is selected.

Step B.4 The dataset is not selected.

Step B.5 There are no more data sets in this category group. The algorithm ends.

Table 3.2. Algorithm B application results to VLE datasets belonging to different category groups

Category Group (X.M.N)	No	VLE dataset components		Reference	Q_{VLE}	F_{pure}	Algorithm B
1.1.1	1	Caprylic acid	Caproic acid	(Rose and Supina, 1961)	0.65	0.93	Selected
	2	Caprylic acid	Caproic acid	(Rose and Supina, 1961)	0.56	0.93	Selected
	3	Caprylic acid	Caproic acid	(Rose and Supina, 1961)	0.49	0.76	Selected
	4	Lauric acid	Myristic acid	(Müller and Stage, 1961)	0.24	0.42	Selected
	5	Caprylic acid	Capric acid	(Akisawa Silva et al., 2011)	0.10	0.1	Not Selected
3.1.1	1	Methyl laurate	Lauric acid	(Monick et al., 1946)	0.03	0.11	Selected
6.1.3	1	Methyl oleate	Ethanol	(Oliveira et al., 2010)	0.25	0.5	Selected
	2	Triolein	2-Propanol	(Eduljee and Boyes, 1981)	0.01 <	0.01	Not Selected

Summary

In this chapter, a systematic-identification method for phase equilibria modelling and data analysis for group contribution type of models has been presented. The method consists of three hierarchical parts. The first part, data collection and analysis, consists of three steps and aims to build the collection of VLE data, which is checked for errors and tested for quality. In the second part, data organisation and selection, the group contribution model is selected and the structural groups are defined. The aim of this part is to organise the data set into subsets based on the binary interaction parameters by using the Organising Algorithm, and to select the best data to be used within regression by applying the Selection Algorithm. The last part, parameter estimation and validation, consist of four steps and aims to identify and apply the systematic calculation sequence for parameter regression, and to perform the parameters and model validation. The examples presented for method application help the reader and user understand easier how the method works. The aim of the method is to offer support within group contribution models (re)parametrisation.

4

SYSTEMATIC IDENTIFICATION METHOD: APPLICATION AND VALIDATION

The systematic identification method for data analysis and phase equilibria modelling presented in Chapter 3 is applied to lipid systems and Original UNIFAC model. The results for each part of the method are presented and discussed. Results from method application to Linear, Lyngby Modified and Dortmund Modified UNIFAC are briefly presented as well.

Chapter structure and contents:

4.1 Data collection and analysis: results presentation for the first part of the method.

4.2 Data organization and selection: results presentation for the second part of the method.

4.3 Parameter estimation and validation: estimation of Original UNIFAC binary group interaction parameter estimation, analysis and discussion of model validation performance.

4.4 Other UNIFAC models: results presentation and discussion for the method application to other UNIFAC models.

The work form the basis of following publications (1) *Perederic, O.A., Cunico, L.P., Kalakul, S., Sarup, B., Woodley, J.M., Kontogeorgis, G.M., Gani, R., 2018. Systematic identification method for data analysis and phase equilibria modelling for lipids systems. Journal of Chemical Thermodynamics 121, 153–169;* (2) *Perederic, O.A., Cunico, L.P., Sarup, B., Woodley, J.M., Gani, R, 2017. A Systematic Identification Method for Thermodynamic Property Modelling. Antonio Espuña, Moisès Graells, Luis Puigjaner (Editors), Proceedings of the 27th European Symposium on Computer Aided Process Engineering – ESCAPE 27, Computer Aided Chemical Engineering, Elsevier, 40, 205-210,* (3) *Damaceno, D.S., Perederic, O.A., Ceriani, R., Kontogeorgis, G.M., Gani, R., 2018. Improvement of predictive tools for vapor-liquid equilibrium based on group contribution methods applied to lipid technology. Fluid Phase Equilibria 470, 249–258.* For the last publication, the work for Linear, Lyngby Modified and Dortmund Modified UNIFAC models was performed in collaboration with Daniela Damaceno as follows: method, database and code for regression procedure (and its modifications) were done/provided by the author, the regression and validation of the parameters was performed by Daniela Damaceno, and SLE calculation with all the models and all the parameters were done by the author. The work is presented in detail in (Damaceno et al., 2018).

In this chapter the application of the identification method for estimation of Original UNIFAC model binary group interaction parameters dedicated to lipid systems is presented together with a discussion of the results obtained (Perederic et al., 2018b). In the last section of the chapter the method application results for Linear, Lyngby Modified and Dortmund Modified UNIFAC are presented (Damaceno et al., 2018b).

A clarification regarding the definition of the following two terms, validation, extrapolation and prediction is made, and it reflects the way the terms are used in this work:

- *validation* refers to applying the model with subsequent regressed parameters to binary VLE datasets which are the same type as the ones used within regression (the VLE datasets are of the same type as the ones available within the several categories)
- *extrapolation* refers to applying the model with subsequent regressed parameters to other type of binary VLE datasets (other classes of compounds combination, new compounds type), other type of phase equilibria (e.g. SLE, LLE), and/or multicomponent phase equilibria (e.g. VLE, SLE, LLE).
- *prediction* refers to model application with subsequent regressed parameters to other data than the one used for regression. It includes data covered from validation and extrapolation categories.

In the present chapter, only the model validation is presented, while the extrapolation capabilities of the model with the lipid- based parameters are presented in the next chapter.

4.1 Data collection and analysis

A total of 174 binary VLE data sets from the *Lipids Database* (Kalakul, 2016; Perederic et al., 2018b) are retrieved[3]. All the datasets and their references are given in Appendix B. If the data sets did not have the necessary pure compound property data, they are provided by using

[3] The 174 used for parameter regression represented all available binary VLE in the *Lipids Database* at the time when this part of the work was performed.

vapour pressure correlations for pure compounds from the *Lipids Database*. The consistency checks are performed with ThermoData Engine (Diky et al., 2009).

The quality of the datasets presents the following trends: around 12% of the datasets have an overall quality factor (Q_{VLE}) bigger than 0.5, while around 39% have the end point quality factor bigger than 0.5. Where applicable, all data sets fail EOS test, but all of them pass the infinite dilution test. For Van Ness around 10% of the data sets pass the tests, while for Herrington more than 25% of the data sets pass the test.

4.2 Data organization and selection

Initial attempts to represent the lipid compounds with the same published structural groups of the Original UNIFAC model resulted in poor predictions for systems containing acylglycerols. A new group OH_{acyl}, describing the OH from acylglycerols compounds is introduced as recommended by Cunico (Cunico, 2015). This group has also been used by Bessa et al. (Bessa et al., 2016) to describe LLE behaviour for lipid mixtures. Original UNIFAC with published parameters cannot describe VLE for glycerol-alcohol systems (Soujanya et al., 2016). For this reason a new group defining the whole glycerol molecule, GLY, is introduced with the aim of improving the glycerol-alcohol predictions. The complete list of structural main-groups and sub-groups used to represent all the lipid compounds in the selected VLE data sets along with their surface area, Q_k, and volume, R_k, parameters, as determined by Bondi's method (Bondi, 1968), are given in Table 4.1. For GLY, the R and Q parameters are calculated as sum of CH, CH_2 and OH contributions.

The application of Algorithm A to analysed collected data from Step 1-3 results in identification of 25 binary group interaction parameters. The data are organized in 18 category-groups, listed in Table 4.2, indicating the need to estimate several pairs together. Once the data are sorted according to the quality factor in each of the category-groups, the Algorithm for data selection (Algorithm B) is applied. A total of 70 data sets are selected from the 174 identified (see Table 4.2). The detailed list of binary VLE data is given in Appendix B.

Table 4.1 List of the structural groups, their area (Q_k) and volume parameters (R_k) used in this work for adapting the Original UNIFAC model for lipid systems

Main Group	Sub group	Q_k	R_k
CH_2	CH_3	0.8480	0.9011
	CH_2	0.5400	0.6744
	CH	0.2280	0.4469
C=C	CH=CH	0.8670	1.1167
OH	OH	1.2000	1.0000
CH_3OH	CH_3OH	1.4320	1.4311
H_2O	H_2O	1.4000	0.9200
CH_3CO	CH_3CO	1.4480	1.6724
CCOO	CH_2COO	1.4200	1.6764
COOH	COOH	1.2240	1.3013
OH_{acyl} [a]	OH_{acyl}	1.2000	1.0000
GLY_b	GLY	4.9080	4.7957

4.3 Parameter estimation and validation

In this section, the calculation sequence is presented along with the new set of binary group interaction parameters. The performance of the model with the new parameters is presented and discussed in the validation step.

4.3.1 Calculation sequence

For the category-groups where more than one binary group interaction parameters need to be regressed, the local differential sensitivity analysis is performed. The analysis aims to identify which of the parameters are more sensitive. Different trials showed that if the most sensitive binary group interaction parameters pair is estimated first, better performing parameters are found in the regression. The sensitivity analysis is performed in MoT (Sales-Cruz and Gani, 2006) by varying the initial values of the parameters within [-15%, +15%] interval with 5% increments. The order is retrieved based on the significance ranking values. The calculation sequence for category-groups identified with Algorithm A, and the sensitivity analysis is presented in Figure 4.1. The sensitivity within each category-group with more than one parameter decreases from left to right in the calculation scheme. The regression order of the binary group interaction parameters is from left to right and from top to bottom in the calculation sequence scheme. The relation between the parameters is shown in the calculation sequence with arrows. This information can be very useful when the user needs to re-estimate a certain parameter, allowing a fast identification of all the other parameters that are dependent on this one.

For a better understanding of the calculation sequence, two examples are presented:

- COOH/CCOO binary interaction is estimated from the systems available in category-group 3.1.1. In this category-group, the following binary group interaction parameters are involved: CH_2/COOH, CH_2/CCOO and COOH/CCOO. First the two binary pairs, CH_2/COOH and CH_2/CCOOH, are estimated from category-groups 1.1.1 and 1.1.2, and their new values are kept constant for the estimation of the COOH/CCOO pair.
- In group-category 3.2.1, the following binary group interaction parameters are involved: CH_2/CCOO, CH_2/CH_3OH, and CCOO/CH_3OH. In the first step, CH_2/CH_3OH pair is estimated by using and keeping fixed CH_2/CCOO, which is known from previous estimation, and CCOO/CH_3OH, which uses the Original UNIFAC as initial value. In the second step, CH_2/CCOO and CH_2/CH_3OH are kept constant and CCOO/CH_3OH is estimated. The values obtained for CH_2/CH_3OH in the first step are used now. Then a new regression is performed for the two binary pairs simultaneously, using the new values previously obtained. New values are stored and used in subsequent calculations/regression.

Table 4.2 List of VLE data sets type with corresponding category-groups (Algorithm A) and selected data (Algorithm B)

Category Group (X.M.N)	System Type		Associated groups	VLE data			
				Available		Selected	
				Sets	Points	Sets	Points
1.1.1	Saturated Fatty Acid	Saturated Fatty Acid	CH_2 COOH	23	226	4	58
1.1.2	Saturated Ester	Saturated Ester	CH_2 CCOO	26	246	9	80
	Saturated Ester	Saturated Hydrocarbon					
1.1.3	Glycerol	Methanol	GLY CH_3OH	20	196	9	118
1.1.4	Glycerol	Water	GLY H_2O	44	468	14	165
3.1.1	Saturated Fatty Acid	Saturated Ester	CH_2 COOH CCOO	1	8	1	8
3.2.1	Saturated Ester	Methanol	CH_2 CH_3OH CCOO	5	58	5	58
3.2.2	Saturated Ester	Ethanol	CH_2 OH CCOO	2	36	2	36
3.2.3	Saturated Monoglyceride	Saturated Ester	CH_2 OH_{acyl} CCOO	2	22	2	22
3.2.4	Glycerol	Saturated Alcohol	CH_2 OH GLY	34	390	11	146
3.2.5	Unsaturated Fatty Acid	Saturated Fatty Acid	CH_2 COOH CH=CH	3	35	1	14
	Unsaturated Fatty Acid	Saturated Hydrocarbon					
3.2.6	Unsaturated Ester	Saturated Ester	CH_2 CH=CH CCOO	3	31	2	22
	Unsaturated Triglyceride	Saturated Hydrocarbon					
6.1.1	Saturated Monoglyceride	Saturated Fatty Acid	CH_2 OH_{acyl} CCOO COOH	2	24	2	24
6.1.2	Unsaturated Ester	Methanol	CH_2 CH=CH CH_3OH CCOO	2	31	1	15
6.1.3	Unsaturated Ester	Ethanol	CH_2 CH=CH OH CCOO	2	26	2	26
6.1.4	Unsaturated Fatty Acid	Methanol	CH_2 COOH CH=CH CH_3OH	1	14	1	14
6.1.5	Saturated Fatty Acid	Saturated Alcohol	CH_2 CH=CH OH COOH	2	27	2	27
6.3.1	Unsaturated Triglyceride	Acetone	CH_2 CH=CH CH_2CO CCOO	1	13	1	13
6.3.2	Saturated Fatty Acid	Acetone	CH_2 CH=CH CH_2CO COOH	1	13	1	13
Total				174	1864	70	851

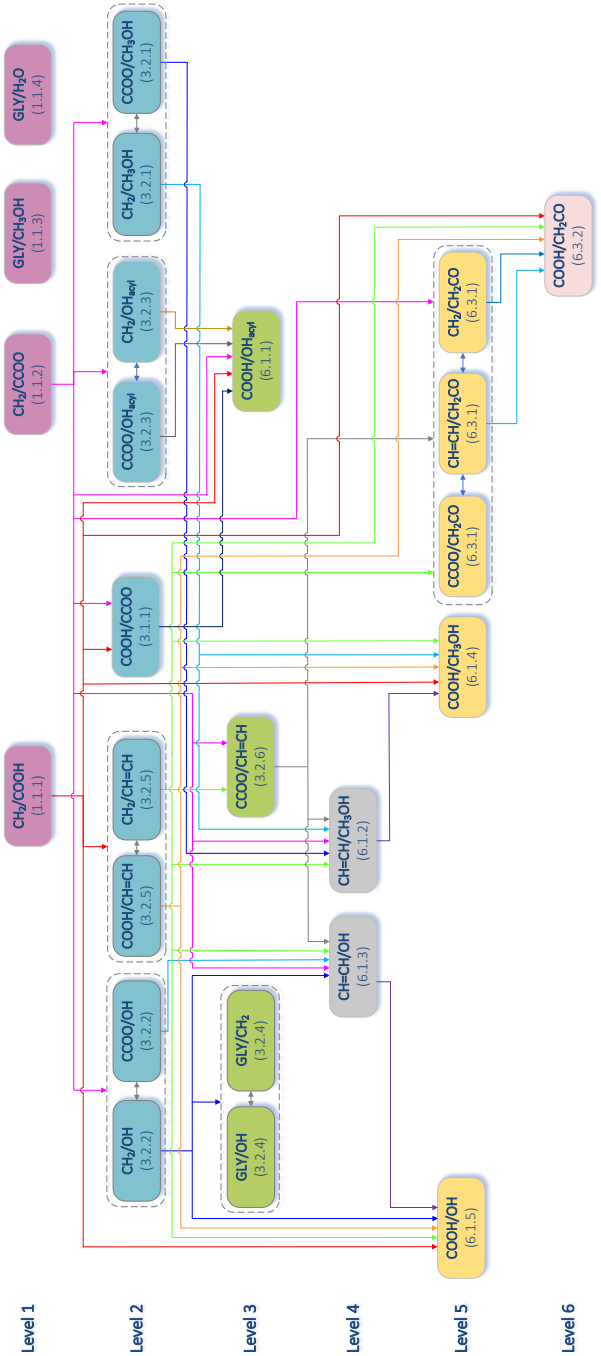


Figure 4.1 Parameter calculation sequence according to group-categories from Algorithm A and sensitivity analysis. The boxes contain information on parameter to be estimated and the category-group data sets that will be used for regression; dotted boxes are for the parameters that are estimated from the same category-group data sets. The regression of the parameters is performed from top to bottom and from left to right

4.3.2 Regression of model parameters

When available, the published parameters (Hansen et al., 1991) of Original UNIFAC model are used as initial estimates for the regression. For binary interactions involving OH_{acyl}, values corresponding to OH interactions are used as the initial estimates. For binary interactions involving GLY, zero is used as initial estimate. Vapour pressure models for all compounds are provided from the *Lipids database*.

Bubble point calculations are performed using gamma-phi approach, Eq. 4.1 The activity coefficients in Eq. 4.1 are supplied by the Original UNIFAC model, while, ideal gas model is assumed for the vapour phase. A similar approach is used for the binary group parameter interaction of different UNIFAC variants (e.g. Original UNIFAC (Fredenslund et al., 1977b), Lyngby Modified UNIFAC (Larsen et al., 1987), Dortmund Modified UNIFAC (Gmehling et al., 1993b)).

$$\varphi_i y_i P = \gamma_i x_i P_i^{sat} \tag{4.1}$$

where φ_i is assumed to be equal to 1 (ideal gas), y_i – vapour phase composition, P – total pressure, γ_i – activity coefficient, x_i – liquid phase composition, P_i^{sat} – saturation pressure, i – system compound (1 or 2)

The regression of the parameters is performed by minimizing the least squares (objective) function, Eq. 4.3. This objective function, Eq 4.2, takes into account also the regularization term (Balslev and Abildskov, 2002; Cunico et al., 2014) as given Eq.4.4.

$$F_{obj} = F_P + F_R \tag{4.2}$$

$$F_P = \sum_i \left(\frac{P^{\mathrm{exp}erimental} - P^{calculated}}{P^{\mathrm{exp}erimental}} \right)_i^2 \tag{4.3}$$

$$F_R = \frac{1}{\beta} \sum_m \sum_k \left(a_{mk} - a_{mk}^0 \right)^2 \tag{4.4}$$

where $P^{experimental}$ and $P^{calculated}$ are experimental and calculated pressure, β is an empirical term, set equal to 10^5, a_{mk} is estimated binary interaction parameter, and $a^0{}_{mk}$ is the initial value of the binary interaction parameter, in this case Original UNIFAC published parameters value or zero for the GLY interactions.

The regressed values of the binary group interaction parameters are given in Table 4.3, along with the temperature interval for which they were regressed.

The validation of the model (model application to systems similar to those used within regression) with the new parameters is presented in following two sections by considering the overall regression performance (Section 4.3.3), and by analysing individual systems belonging to different category groups (Section 4.3.4).

Table 4.3 Regressed binary group interaction parameters (Eq. 2.16) of the Original UNIFAC model for lipid systems

Group m	Group k	a_{mk}, K	a_{km}, K	T_{min} [a], K	T_{max} [a], K
CH_2	CH=CH	125.74	555.93	318.14	481.08
CH_2	OH	613.72	35.84	351.46	617.50
CH_2	CH_3OH	515.53	41.86	337.63	617.50
CH_2	CH_2CO	529.15	13.51	318.15	318.15
CH_2	CCOO	459.02	395.55	327.37	535.50
CH_2	COOH	320.95	1337.28	371.65	524.25
CH_2	GLY	137.56	45.83	232.15	561.18
CH_2	OH_{acyl}	50.30	499.23	461.24	493.38
CH=CH	OH	384.72	407.71	318.15	617.42
CH=CH	CH_3OH	1424.55	64.65	338.28	387.11
CH=CH	CH_2CO	528.31	-153.42	318.15	318.15
CH=CH	CCOO	54.61	135.28	318.14	514.61
CH=CH	COOH	998.50	1318.50	318.14	481.08
OH	CCOO	555.63	406.11	351.46	617.50
OH	COOH	294.83	37.73	318.15	318.15
OH	GLY	128.76	120.90	232.15	561.18
CH_3OH	CCOO	229.89	421.58	337.63	617.50
CH_3OH	COOH	-272.84	2981.07	318.15	318.15
CH_3OH	GLY	-7.25	159.54	318.15	561.18
H_2O	GLY	140.77	138.70	153.15	563.18
CH_2CO	CCOO	44.62	778.64	318.15	318.15
CH_2CO	COOH	247.02	39.48	303.13	318.15
CCOO	COOH	660.60	-256.39	386.15	427.15
CCOO	OH_{acyl}	253.23	124.02	461.24	493.38
COOH	OH_{acyl}	-129.89	222.89	462.67	498.35

[a] T_{min}, T_{max} – temperature range of the experimental data from which the parameters were regressed

4.3.3 Regression analysis

Regression analysis is performed using all available VLE data (all 174 data sets). The average relative deviation is shown for both the newly regressed parameters and the Original UNIFAC model with published parameters (Hansen et al., 1991) given in Table 4.4[4]. Only pressure deviation is reported since most of the data sets contain information only about liquid phase. For each category group the newly regressed parameters provide improved model performance. The lipid-based parameters lead to an overall improvement in ARD_2(%) of 7.8% which corresponds to 35% improvement compared to the Original UNIFAC model with published parameters. The improvements are given by the use of the new structural groups to

[4] For Original UNIFAC model, published parameters refers to the parameters from Hansen et al., 1991 which are the latest updated parameters for Original UNIFAC model from the model developers, and which are also known as VLE parameters.

describe the lipids (e.g. OH_{acyl} for mono- and diacylglycerols, and GLY for glycerol molecule) and by the new interaction parameter values.

Table 4.4 Performance (in terms of ARD(%) in kPa) of Original UNIFAC with published (Hansen et al., 1991) and lipid-based parameters (Perederic et al., 2018b) for binary VLE data sets available in *Lipids Database*

Category-group (X.M.N)	$ARD_1(\%)^a$	
	Published parameters (Pub.)[1]	Lipid-based parameters (Lip.)[2]
1.1.1	2.7	2.6
1.1.2	6.2	5.7
1.1.3	20.8	12.5
1.1.4	91.5	88.5
3.1.1	24.4	1.7
3.2.1	15.1	10.9
3.2.2	11.7	2.6
3.2.3	11.6	5.5
3.2.4	28.0	24.6
3.2.5	30.8	28.6
3.2.6	17.9	15.5
6.1.1	17.3	3.6
6.1.2	22.3	2.9
6.1.3	33.9	32.1
6.1.4	10.1	5.9
6.1.5	4.7	4.1
6.3.1	21.3	2.0
6.3.2	20.7	2.1
$ARD_2(\%)^b$	21.7	14.0

[1] (Hansen et al., 1991); [2] (Perederic et al., 2018b), *this work*

[a] $ARD_0 = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{P_i^{experimental} - P_i^{calculated}}{P_i^{experimental}}\right|$, N data points number, P – pressure, kPa.

$ARD_1(\%) = \frac{100}{M}\sum_{j=1}^{M} ARD_0$, M – data sets number within a category-group

[b] $ARD_2(\%) = \frac{100}{Tt}\sum_{k=1}^{T} ARD_1$, T – total data sets number

The parity plot of the Original UNIFAC model prediction using the two sets of parameters is showed in Figure 4.2. Significant improvements for the model with the lipid-based parameters can be noticed. The scattered points in the parity plot at the 101.33 kPa are related to glycerol based systems (e.g. Groups 1.1.3, 1.1.4 and 3.2.4), which presents a big deviation from experimental data, as it can be seen in Table 4.4. The prediction results are analysed also through the cumulative deviation plot, Figure 4.3. Differences between the model with the two

sets of parameters, published and lipid-based parameters, start to appear when more than 600 data points are used. This behaviour is given by the ideal behaviour of some systems, e.g. fatty acids, fatty esters systems (Groups 1.1.1, 1.1.2, 6.1.5), which perform similar with both parameters sets, also showed in Figure 4.4 for hexanoic acid (1) – octanoic acid (2) system and Figure 4.5 for methyl decanoate (1) - methyl octanoate system. It can be seen that for the fatty acids system, Figure 4.4, the model with the new binary group interaction parameters describes well the two phases even though chemical theory was not considered for the vapour phase to represent the acids dimerization phenomena. This can be explained by the ideal behaviour resemblance of such systems (Tsivintzelis et al., 2017). Likewise, the parameters do not differ much from the published parameters (Hansen et al., 1991), for which the chemical theory was considered for the vapour phase modelling. Experimental data about dimerization of carboxylic acids within vapour phase exist for compounds with up to six carbon atoms. Most of the studies had analysed carboxylic acid systems with up to four-five carbon atoms and it is stated that the interactions are much stronger in small chain compounds than it is the long chain compounds (Tsivintzelis et al., 2017). Special care should be taken for this type of systems, when the model is extrapolated to predict other properties such as enthalpy of mixing. Dedicated model for systems with carboxylic acid also fail to describe well the enthalpies of mixing when their parameters are fitted to VLE data (Tsivintzelis et al., 2017).

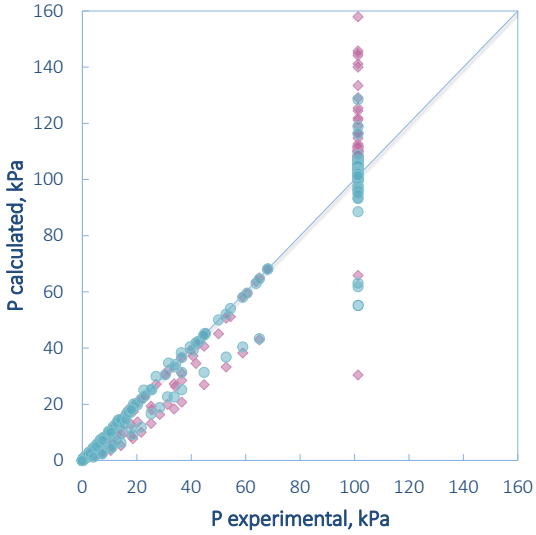


Figure 4.2 Parity plot of Original UNIFAC pressure prediction using published and lipid-based parameters vs. experimental pressure for binary VLE data sets: ♦ Original UNIFAC with published parameters, • Original UNIFAC with lipid-based parameters (All experimental data are reffered in Appendix B)

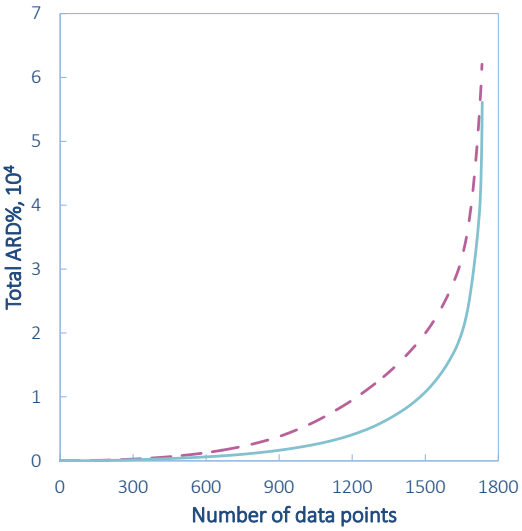


Figure 4.3 Cumulative ARD(%)[5] of all the VLE data points predicted using Original UNIFAC model with published and lipid-based: - - - Original UNIFAC with published parameters, — Original UNIFAC with lipid-based parameters. (All experimental data are reffered in Appendix B)

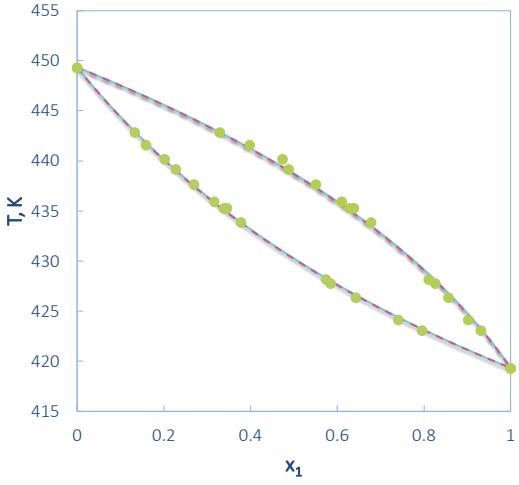


Figure 4.4 VLE prediction using Original UNIFAC model with published and lipid-based parameters for hexanoic acid (1) – octanoic acid (2) system (category group 1.1.1) at 13.33 kPa (Rose et al., 1958): ● experimental data, - - - Original UNIFAC with published parameters, — Original UNIFAC with lipid-based parameters

[5] $ARD(\%) = \sum_{i=1}^{N} \left| \frac{P_i^{experimental} - P_i^{calculated}}{P_i^{experimental}} \right|$, N – total VLE data points.

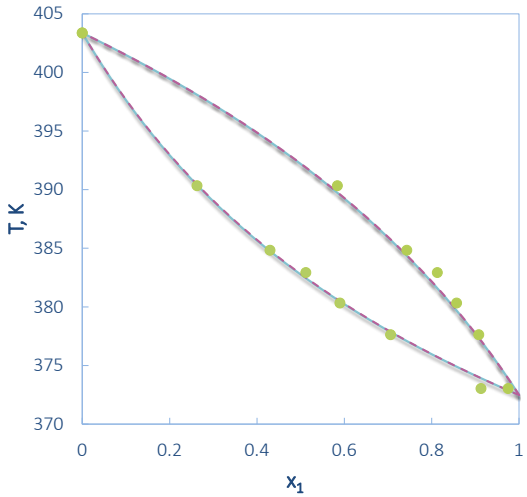


Figure 4.5 VLE prediction using Original UNIFAC model with published and lipid-based parameters for methyl decanoate (1) - methyl octanoate (2) system (category group 1.1.2) at 4 kPa (Rose and Supina, 1961): ● experimental data, - - - Original UNIFAC with published parameters, — Original UNIFAC with lipid-based parameters

4.3.4 Model performance

The model performance is analysed in more detail for some of the systems used within the validation step of the method.

As presented in the previous section, the model with published parameters (Hansen et al., 1991) and lipid-based parameters provides similar results, matching the experimental data for fatty acids systems and fatty esters systems (Categories 1.1.1 and 1.12). For the system alkane-methyl ester, Figure 4.6, as well as for the system fatty acid-fatty ester (Group 2.1.1), Figure 4.7, the model with the lipid-based parameters presents improvements in prediction compared to the model with published parameters. The Original UNIFAC with published parameters predicts a false liquid immiscibility for the system methyl oleate – methanol (Group 6.1.2), Figure 4.10. Through regression, model performance is improved both qualitatively and quantitatively for all the systems with small chain alcohols (e.g. methanol, ethanol) including both saturated and unsaturated lipid compounds, as presented in Figures 4.8-4.11.

Similarly, for the monocaprylin – methyl stearate system, Figure 4.12, a false immiscibility is predicted. For the system monocaprylin – stearic acid (Figure 4.13), the model with published parameters presents high deviations from experimental data. The addition of the OH_{acyl} group and the new values of the interaction parameters improved the VLE representation of systems with monoacylglycerol (e.g. better fitting, no false phase split). The OH_{acyl} is introduced because of a different behaviour of OH group compared to the one present in small chain alcohols. The effects of a secondary OH group, as well as, the influence of the rest of the

molecule (big molecule compared to short chain alcohols) give the different behaviour of the OH group in monoacylglycerol molecules.

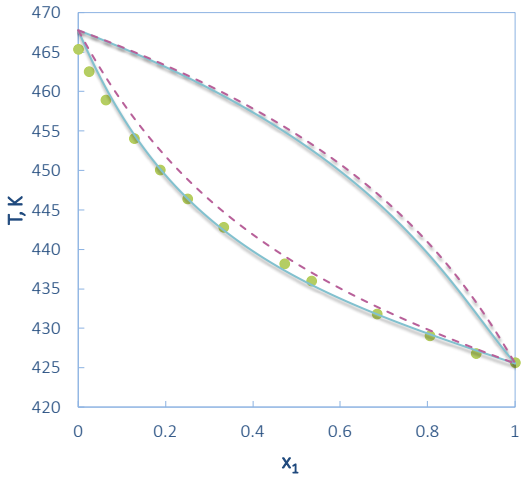


Figure 4.6 VLE prediction using Original UNIFAC model with published and lipid-based parameters for n-tetradecane (1) – methyl tetradecanoate (2) system (category group 1.1.2) at 0.50 kPa (Li et al., 2016): ● experimental data, - - - Original UNIFAC with published parameters, — Original UNIFAC with lipid-based parameters

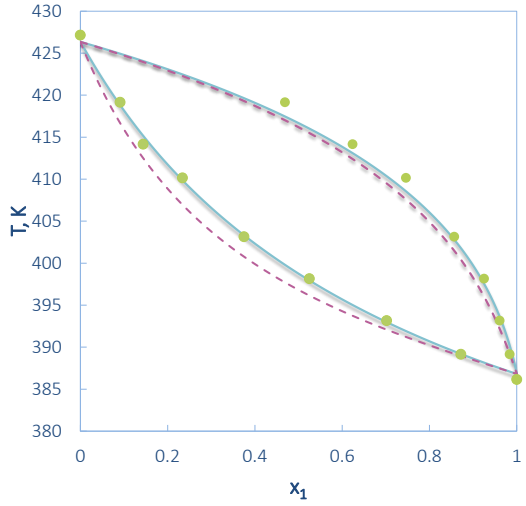


Figure 4.7 VLE prediction using Original UNIFAC model with published and lipid-based parameters for methyl-dodecanoate (1) – dodecanoic acid (2) system (category group 3.1.1) at 0.53 kPa (Monick et al., 1946): ● experimental data, - - - Original UNIFAC with published parameters, — Original UNIFAC with lipid-based parameters

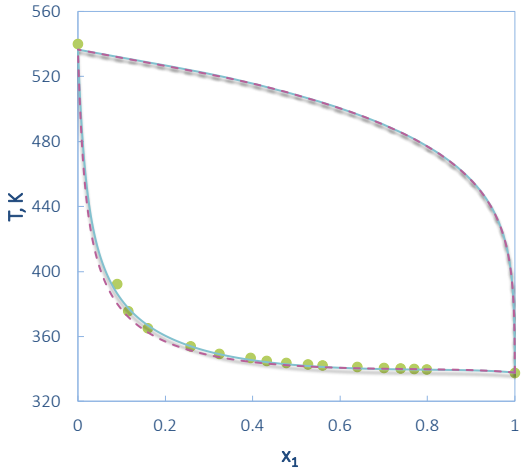


Figure 4.8 VLE prediction using Original UNIFAC model with published and lipid-based parameters for methyl-dodecanoate(1) – methanol (2) system (category group 3.2.1) at 101.33 kPa (Oliveira et al., 2010): ● experimental data, - - - Original UNIFAC with published parameters, — Original UNIFAC with lipid-based parameters

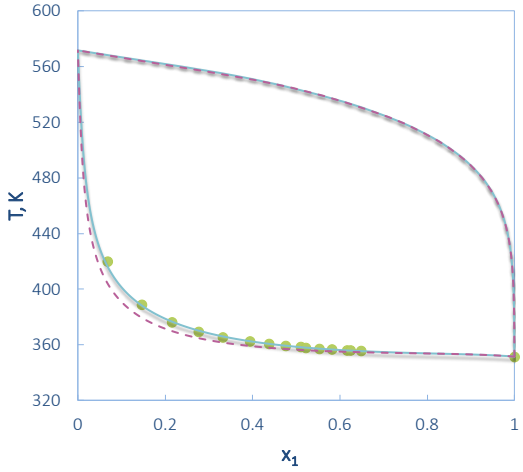


Figure 4.9 VLE prediction using Original UNIFAC model with published and lipid-based parameters for methyl-tetradecanoate(1) – ethanol (2) system (category group 3.2.2) at 101.33 kPa (Oliveira et al., 2010): ● experimental data, - - - Original UNIFAC with published parameters, — Original UNIFAC with lipid-based parameters

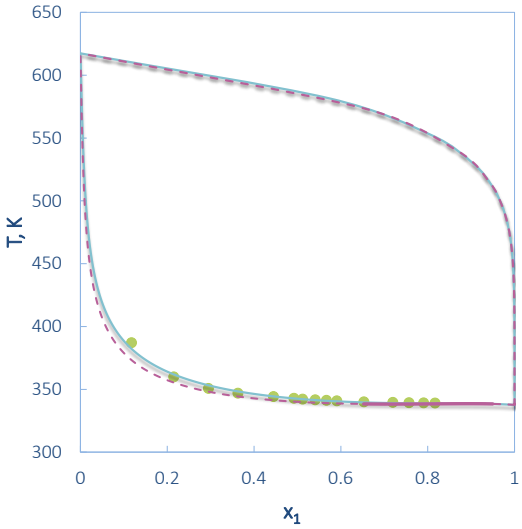


Figure 4.10 VLE prediction using Original UNIFAC model with published and lipid-based parameters for methyl oleate (1) – methanol (2) system (category group 6.1.2) at 101.33 kPa (Oliveira et al., 2009): ● experimental data, - - - Original UNIFAC with published parameters, — Original UNIFAC with lipid-based parameters

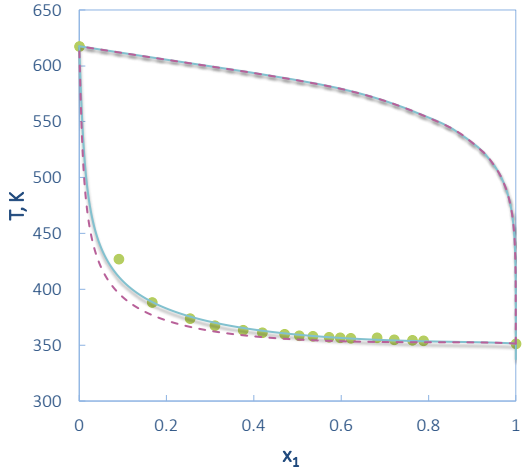


Figure 4.11 VLE prediction using Original UNIFAC model with published and lipid-based parameters for methyl oleate (1) – ethanol (2) system (category group 6.1.3) at 101.33 kPa (Oliveira et al., 2009): ● experimental data, - - - Original UNIFAC with published parameters, — Original UNIFAC with lipid-based parameters

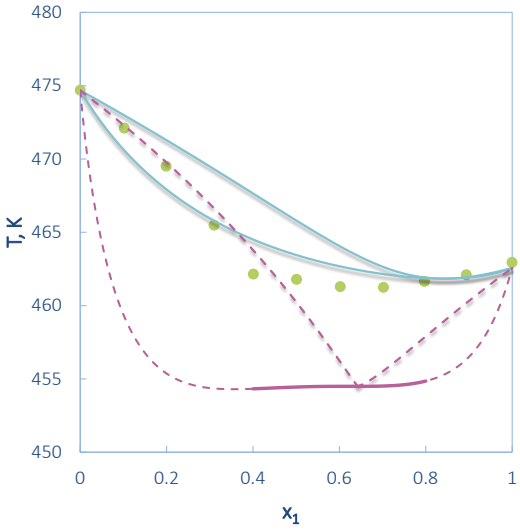


Figure 4.12 VLE prediction using Original UNIFAC model with published and lipid-based parameters for monocaprylin (1) – methyl stearate (2) system (category number 3.2.3) at 1.20 kPa (Cunico et al., 2015): ● experimental data, - - - Original UNIFAC with published parameters, — Original UNIFAC with lipid-based parameters — two phase split

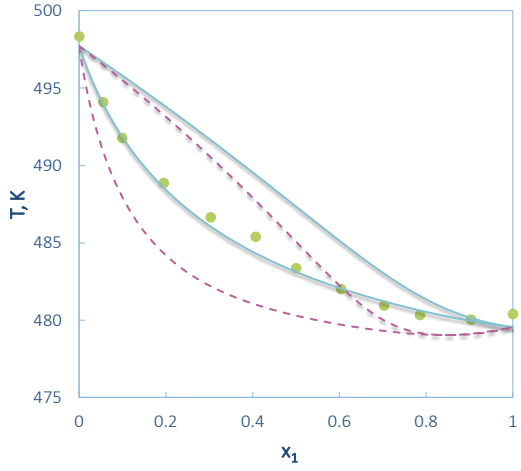


Figure 4.13 VLE prediction using Original UNIFAC model with published and lipid-based parameters for monocaprylin (1) – palmitic acid (2) system (category number 6.1.1) at 1.20 kPa (Cunico et al., 2015): ● experimental data, - - - Original UNIFAC with published parameters, — Original UNIFAC with lipid-based parameters

A similar problem can be present for systems with glycerol, where the three OH groups are connected to adjacent carbon atoms and lead to strong intra- and intermolecular interactions (Bessa et al., 2016; Kang et al., 2015). For this reason a group to describe the whole glycerol molecule, GLY, is introduced. The same approach is used in the NIST-modified UNIFAC model (Kang et al., 2015), and in the latest extension of Dortmund UNIFAC (Constantinescu and Gmehling, 2016; Gmehling, 2015). The use of the GLY group improves the prediction in systems with glycerol: glycerol-alcohol, Figures 4.14-4.16, and glycerol-water, Figure 4.17. Unfortunately, considerable deviations still occur, especially for the glycerol-water systems (Category-group 1.1.4).

An extra validation of the Original UNIFAC model with the lipid-based parameters is perfomed with some newly identified systems, which were not included within the database at the time this work was performed. The systems are ethyl esters (e.g. ethyl hexanoate, ethyl decanoate, ethy tetradecanoate) with n-tetradecane within temperature interval 373.15-453.15 K (Benziane et al., 2013). As defined earlier, validation considers similar systems (e.g. ester-alkanes), while different systems are included within the extrapolation capabilities (see Chapter 5). It should be mentioned that within regression methyl esters-alkanes systems were used, while the new systems include ethyl esters-alkanes. The system ethy-decanoate – n-tetradecane, Figure 4.19, presents a non-ideal behaviour, for which the model with the lipid-based parameters exhibits superior performance compared to the model with published parameters. For the other systems, as presented in Figure 4.18 and 4.20, similar or better perfromance is obtained for the model with published parameters.

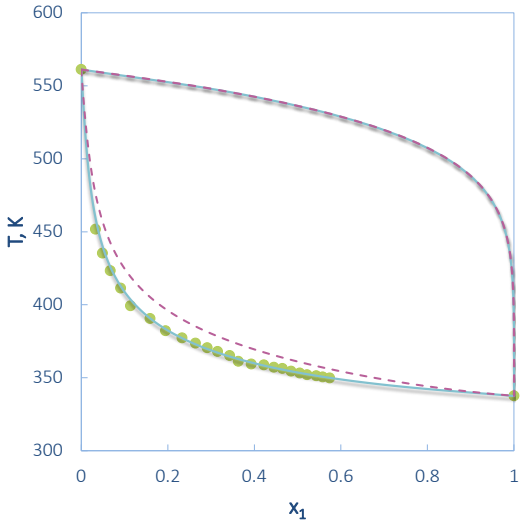


Figure 4.14 VLE prediction using Original UNIFAC model with published and lipid-based parameters for glycerol (1) – methanol (2) system at 101.33 kPa (Oliveira et al., 2009): ● experimental data, - - - Original UNIFAC with published parameters, — Original UNIFAC with lipid-based parameters

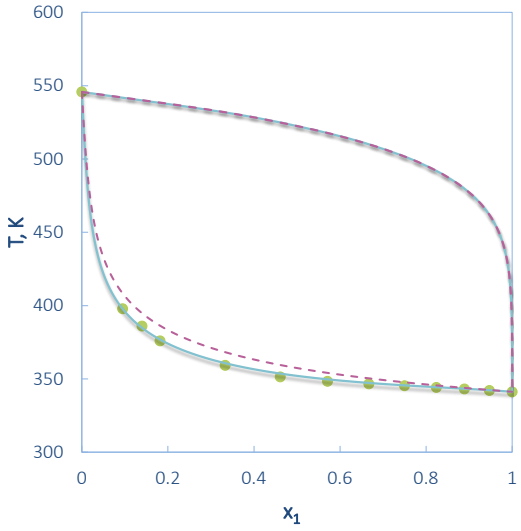


Figure 4.15 VLE prediction using Original UNIFAC model with published and lipid-based parameters for glycerol (1) – ethanol (2) system at 66.70 kPa (Veneral et al., 2013): ● experimental data, - - - Original UNIFAC with published parameters, — Original UNIFAC with lipid-based parameters

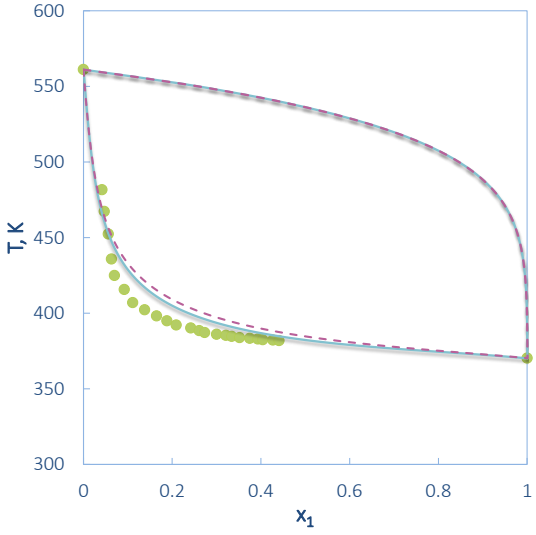


Figure 4.16 VLE prediction using Original UNIFAC model with published and lipid-based parameters for glycerol (1) – 1-propanol (2) system at 101.33 kPa (Oliveira et al., 2009): ● experimental data, - - - Original UNIFAC with published parameters, — Original UNIFAC with lipid-based parameters

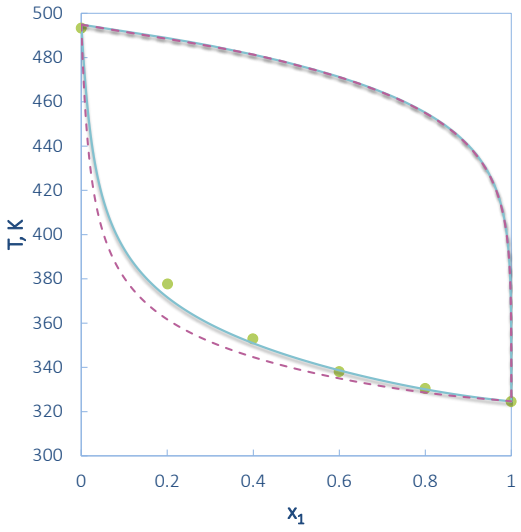


Figure 4.17 VLE prediction using Original UNIFAC model with published and lipid-based parameters for glycerol (1) – water (2) system at 66.70 kPa (Oliveira et al., 2009): ● experimental data, - - - Original UNIFAC with published parameters, — Original UNIFAC with lipid-based parameters

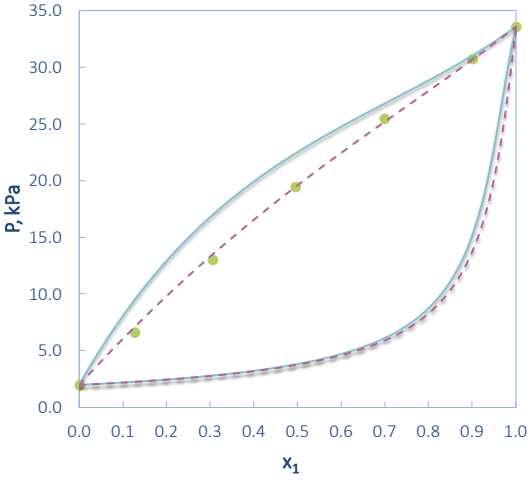


Figure 4.18 VLE prediction using Original UNIFAC model with published and lipid-based parameters for ethyl hexanoate (1) – n-tetradecane (2) system at 403.15 K (Benziane et al., 2013): ● experimental data, - - - Original UNIFAC with published parameters, — Original UNIFAC with lipid-based parameters

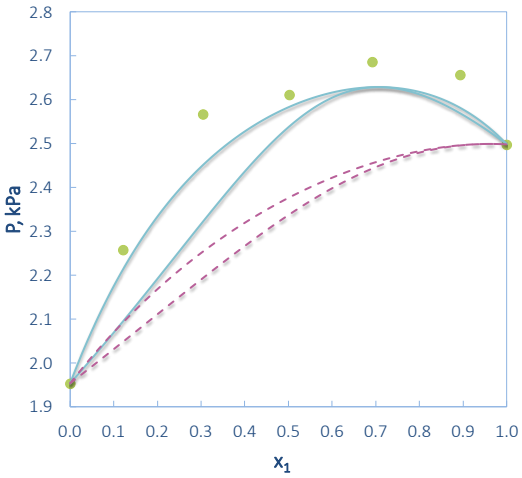


Figure 4.19 VLE prediction using Original UNIFAC model with published and lipid-based parameters for ethyl decanoate (1) – n-tetradecane (2) system at 403.15 K (Benziane et al., 2013): ● experimental data, - - - Original UNIFAC with published parameters, — Original UNIFAC with lipid-based parameters

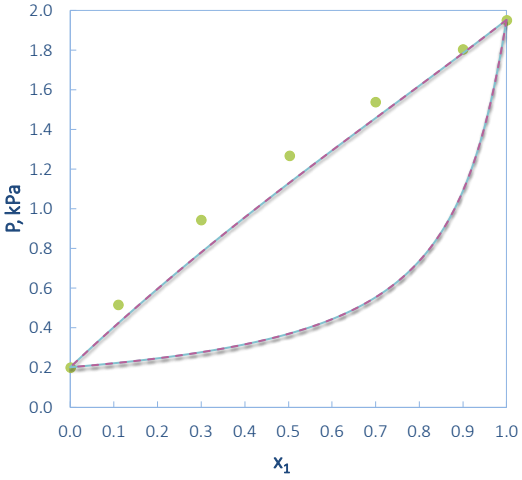


Figure 4.20 VLE prediction using Original UNIFAC model with published and lipid-based parameters for ethyl tetradecanoate (1) – n-tetradecane (2) system at 403.15 K (Benziane et al., 2013): ● experimental data, - - - Original UNIFAC with published parameters, — Original UNIFAC with lipid-based parameters

The validation of the OH_{acyl} group and some of its binary group interaction parameters is performed on a new dataset recently published: dodecanoic acid – monocaprylin (Damaceno and Ceriani, 2018b). The dataset corresponds to category group 6.1.1 and it was not included within the method application (this systems is not included in the results presented in Table 4.4). The Original UNIFAC model with lipid-based parameters (ARD_1(%)=1.10%) have a significant improvement for the system representation compared to the model with published parameters (ARD_1(%)=5.95%).

Overall, the Original UNIFAC model with the lipid-based parameters gives a better representation for VLE of lipid related systems. The Original UNIFAC model with lipid-based parameters perform similar to the model with published parameters for nearly ideal systems (e.g. Groups 1.1.1, 1.1.2, 3.2.5, 3.2.6,). Considerable improvements are made for non-ideal systems (e.g. Groups 3.2.3, 6.1.1) and systems with acetone (e.g. Groups 6.3.1, 6.3.2), as well as for some systems of lipids with short chain alcohols (e.g. 3.2.1, 3.2.2, 6.1.2, 6.1.4). Less significant improvements are achieved for unsaturated lipids with alcohols (e.g. Group 6.1.3). The glycerol related systems presents a significant improvement in their representation using the lipid-based parameters, as well as the new GLY group, compared to the model with published parameters. However, compared to the other categories groups, deviations of glycerol related systems are considerably higher. This can be a result of model capabilities of representing highly polar systems on one hand, and on the other hand it can be due to the quantity and quality of the available data (e.g. many systems are available for glycerol-alcohols/water from different sources).

4.4 Other UNIFAC models

The systematic identification method was applied to other UNIFAC variants. The most important results and some additional ones are presented here. Results for all UNIFAC variants and parameters are given in Table 4.5.

Table 4.5 Performance (in terms of ARD(%) in kPa) of different UNIFAC models using published and lipid-based parameters

Model	Original UNIFAC*		Linear UNIFAC			Lyngby Modified UNIFAC		Dortmund Modified UNIFAC	
Param. X.M.N	Pub. [1]	Lip. [2]	Pub. [3]	NIST [4]	Lip. [5]	Pub. [6]	Lip. [5]	Pub. [7]	Lip. [5]
	$ARD_1(\%)$[a]								
1.1.1	2.7	2.6	2.2	2.2	2.2	2.3	2.2	2.3	2.2
1.1.2	6.2	5.7	5.2	5.2	5.1	5.0	4.9	5.1	4.8
1.1.3	20.8	12.5	19.1	24.6	9.3	17.1	11.1	19.4	10.3
1.1.4	91.5	88.5	68.8	95.6	48.7	78.9	51.0	198.0	56.8
3.1.1	24.4	1.7	8.3	2.5	1.6	9.8	1.5	10.1	4.3
3.2.1	15.1	10.9	9.4	13.8	5.1	17.6	14.7	9.0	8.3
3.2.2	11.7	2.6	2.6	3.5	2.2	9.6	4.3	6.6	5.3
3.2.3	11.6	5.5	24.1	25.9	3.8	9.2	4.4	3.9	3.8
3.2.4	28.0	24.6	22.8	26.0	21.9	21.9	20.6	17.3	15.9
3.2.5	30.8	28.6	23.2	42.7	21.8	20.6	19.6	18.4	14.5
3.2.6	17.9	15.5	9.3	14.7	9.2	4.6	4.5	7.6	7.5
6.1.1	17.3	3.6	3.9	6.4	1.4	17.1	1.9	22.2	5.9
6.1.2	22.3	2.9	4.3	5.6	4.0	24.7	15.4	9.5	4.9
6.1.3	33.9	32.1	13.5	14.1	6.9	23.8	12.1	10.7	10.6
6.1.4	10.1	5.9	18.2	21.4	8.1	33.9	8.7	8.6	6.3
6.1.5	4.7	4.1	11.4	5.0	6.7	13.2	6.6	7.8	5.3
6.3.1	21.3	2.0	21.5	22.0	1.2	16.8	11.2	8.7	8.5
6.3.2	20.7	2.1	18.7	1.8	1.0	4.6	4.0	7.8	2.4
$ARD_2(\%)$[b]	21.7	14.0	15.9	18.5	8.9	18.4	11.0	20.7	9.9

[1] (Hansen et al., 1991); [2] (Perederic et al., 2018b), *this work;* [3] (Hansen et al., 1992); [4] (Kang et al., 2011), *calculations made in this work;* [5] (Damaceno et al., 2018b); [6] (Larsen et al., 1987), [7] (Weidlich and Gmehling, 1987); * *results repeated from Table 4.4 to make the comparison easier to follow, Pub. – Published paramters, Lip. – Lipid-based parameters.*

[a] $ARD_0 = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{P_i^{experimental} - P_i^{calculated}}{P_i^{experimental}}\right|$, N data points number, P – pressure, kPa.

$ARD_1(\%) = \frac{100}{M}\sum_{j=1}^{M} ARD_0$, M – data sets number within a category-group

[b] $ARD_2(\%) = \frac{100}{T}\sum_{k=1}^{T} ARD_1$, T – total data sets number

For UNIFAC models considering only the published parameters, the best performance is achieved by Linear UNIFAC (15.9%) followed by Lyngby Modified UNIFAC (18.4%), Linear UNIFAC with NIST parameters (18.5%), Dortmund Modified UNIFAC (20.7%) and Original UNIFAC (21.7%). All the models with lipid-based parameters give better predictions for VLE compared to the published parameters. The best results for the lipid-based parameters are in the following order: Linear UNIFAC (8.9%), Dortmund Modified UNIFAC (9.87%), Lyngby Modified UNIFAC (11.0%) and Original UNIFAC (14.0%). The overall model performance improvement from published to lipid-based parameters varies from 36% for Original UNIFAC model up to 52% for Dortmund Modified UNIFAC and Linear UNIFAC (considering the NIST parameters). The general trend is similar for all the models, as it was previously presented. For saturated fatty acids (Group 1.1.1) and saturated fatty esters systems (Group 1.1.2) only modest performance differences across all models and parameters sets are achived. The smallest improvement for the lipids-based parameters is for unsaturated fatty acids and ester systems (Groups 3.2.5 and 3.2.6), with the best results corresponding to Lyngby Modified and Dortmund Modified UNIFAC models. Significant improvements are achieved for representation of systems which contain acetone (Group 6.3.1 and 6.3.2) when using lipid-based parameters especially for Original UNIFAC and Linear UNIFAC models. Similar results are obtained for the Dortmund UNIFAC model with published and lipid-based parameters. All the UNIFAC variants with the lipid-based parameters give a better representation for the alcohol containing systems (e.g. Groups 3.2.1, 3.2.2, 6.1.4, 6.1.5) compared to models with the published parameters. An exception is the fatty acid – alcohol systems (e.g. Group 6.1.2 and 6.1.3), where only minor improvements in the systems representation are achieved. The improvement, both quantitative and qualitative, in systems representation discussed in this paragraph are related only to new parameters values.

The OH_{acyl} group with the new interactions, as well as new values for other parameters, lead to better representation of the monoacylglycerol based systems (e.g. Groups 3.2.3 and 6.1.1), presented in Figure 4.21. The performance for some of the models with published parameters is presented in Figure 2.3. Glycerol based systems, using the GLY molecular group, are significantly better represented when using lipid-based parameters compared to the published parameters. To note that for the models with published parameters, glycerol is represented by CH_2, CH and OH groups. An exception is Dortmund UNIFAC, where OH secondary, OH_s, and primary, OH_p, are used for describing OH groups. The deviations are still high, and this represents a limitation of the model in the representation of highly polar systems.

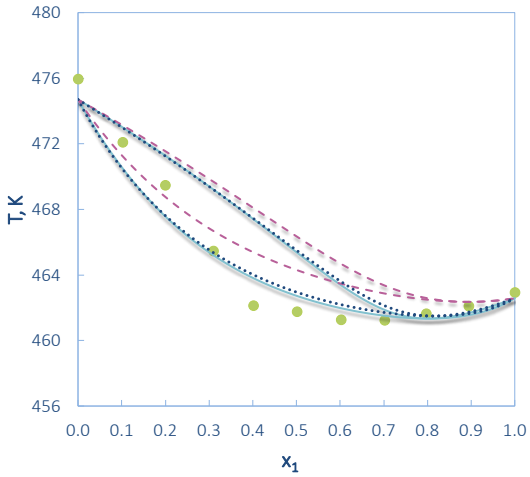


Figure 4.21 VLE prediction using Linear, Lyngby Modified and Dortmund Modified UNIFAC models with lipid-based parameters for monocaprylin (1) – methyl hexadecanoate (2) system at 1.2 kPa (Cunico et al., 2015): ● experimental data, — Linear UNIFAC, - - - Lyngby Modified UNIFAC, • •• Dortmund Modified UNIFAC with lipid-based parameters

Summary

The systematic identification method presented in Chapter 3 has been successfully applied to Original UNIFAC, as well as Linear, Lyngby Modified and Dortmund Modified UNIFAC. All the models use the same collection of VLE datasets taken from the *Lipids Database*, and same calculation sequence as presented in Section 4.3 of the chapter. The Original UNIFAC model, as well as the other UNIFAC models, presents qualitative and quantitative improvements within VLE representation of lipid systems resulting from addition of new groups to represent lipids related compounds (e.g. OH_{acy}, GLY) and from the systematic approach applied for the regression of the parameters. OH_{acyl} related binary group interactions help to eliminate the false phase split prediction for monoacylglycerol systems. The GLY group and the related binary group interaction parameters give lower deviations in VLE predictions for glycerol systems compared to the original published parameters, but significant deviations still occur. An overall better fit of experimentally measured data are given by the new matrix of binary group interaction parameters even though for certain parameters there is insufficient experimental data. The Original UNIFAC model with lipid-based parameters is validated for four new systems, not included in the method application: ethyl hexanoate, decanoate and dodecanoate with n-tetradecane and dodecanoic acid – monocaprylin. Improved results are obtained for non-ideal systems. The model(s) with the lipid-based parameters should be used with confidence only for lipids systems. Mixing the lipid-based parameters with parameters from other models should be performed with care. Further fine-tuning of parameters resulted from category-groups with few data sets (e.g. 3.1.1, 3.2.1, 3.2.2, 3.2.3, 6.1.1, 6.1.3, 6.3.1, 6.1.4, 6.3.1, 6.3.2) should be considered when new data become available.

5

SYSTEMATIC IDENTIFICATION METHOD: PREDICTIVE ABILITIES

The systematic identification method for data analysis and phase equilibria modelling presented in Chapter 3 was successfully applied for different UNIFAC variants. In this chapter, the models with the lipid-based parameters are extrapolated to new VLE systems and SLE prediction. Method extrapolation for design of experiments is presented as well.

Chapter structure and contents:

5.1 VLE prediction: the UNIFAC models with lipid-based parameters are tested for representation of new VLE data.

5.2 SLE prediction: results presentation for UNIFAC models with the lipid-based parameters extrapolation for SLE representation.

5.3 Need for new data: method application for experimental data planning.

The work form the basis of following publications (1) *Perederic, O.A., Cunico, L.P., Kalakul, S., Sarup, B., Woodley, J.M., Kontogeorgis, G.M., Gani, R., 2018. Systematic identification method for data analysis and phase equilibria modelling for lipids systems. Journal of Chemical Thermodynamics 121, 153–169;* (2) *Perederic, O.A., Cunico, L.P., Sarup, B., Woodley, J.M., Gani, R, 2017. A Systematic Identification Method for Thermodynamic Property Modelling. Antonio Espuña, Moisès Graells, Luis Puigjaner (Editors), Proceedings of the 27th European Symposium on Computer Aided Process Engineering – ESCAPE 27, Computer Aided Chemical Engineering, Elsevier, 40, 205-210,* (3) *Damaceno, D.S., Perederic, O.A., Ceriani, R., Kontogeorgis, G.M., Gani, R., 2018. Improvement of predictive tools for vapor-liquid equilibrium based on group contribution methods applied to lipid technology. Fluid Phase Equilibria 470, 249–258.*

In the previous chapter, the performance of UNIFAC model(s) with the published and new lipid-based parameters was compared for the binary VLE description. The UNIFAC model(s) with lipid-based parameters gives better results (lower ARD) than the model with the published parameters, passing the validation test. In this chapter, the extrapolation capabilities of the UNIFAC variants with the lipid-based parameters are analysed and discussed for VLE and SLE prediction. The results for LLE prediction using all the UNIFAC variants with lipid-based, published and other parameters are presented in Appendix D. The method capabilities to identify data needed for model improvements, presented in Section 5.3, has materialised in experimental work trials which are presented in Appendix E.

5.1 VLE PREDICTION

Newly published VLE data was used to test the extrapolation capabilities of the Original UNIFAC model with lipid-based parameters. The new systems with the associated structure groups and the prediction results for Original UNIFAC model with published, NIST and lipid-based parameters are given in Table 5.1. The first three systems from Table 5.1 correspond to category-group 6.1.1 based on their associated structure groups. For these systems, better results are obtained for the VLE prediction using lipid-based parameters compared to publish and NIST parameters for Original UNIFAC model. The last systems from the table do not have any correspondence within the category group list identified with the method (see Table 4.2). The OH-related binary interaction parameters used for the fatty alcohols systems are regressed only from systems containing ethanol. The OH group and related interaction from short chain alcohols can have a different behaviour compared to the ones in long chain alcohols. The interaction between OH and OH_{acyl} is considered zero for systems involving the two groups. The extrapolation of OH-related parameters from small chain alcohols to longer chain alcohols (fatty alcohols) results in higher ARD(%) for the associated systems (Systems number 4 and 5 from Table 5.1) compared to the performance of the Original UNIFAC model with published and NIST parameters. The VLE prediction with NIST parameters have similar performance as the Original UNIFAC model with published parameters, with two exceptions: tributyrin – mononanoin, for which better results are achieved, and hexadecanol - mononanoin, for which the prediction is not as good as the model with the published parameters.

Besides the new binary VLE datasets recently available in the literature, multicomponent VLE data was screened as well. Unfortunately, only nine data sets are available for multicomponent mixtures. From these systems, six are at high pressures (over 1200 kPa) and cannot be considered to be represented with UNIFAC based models, which are dedicated only to low pressure systems. One system is represented by sunflower biodiesel, glycerol and ethanol, and could not be used to test the parameters since several interaction parameters for glycerol (GLY interaction) are missing (e.g. GLY-CH_2COOH, GLY-OH_{acyl}). Two systems are composed of fatty acid (pentanoic and octanoic acid), methanol and water. The Original UNIFAC model with the lipid-based parameters is used for the prediction of octanoic acid – methanol – water system, measured at 101.33 kPa. The values from the missing parameters from the lipid parameter matrix (CH_3OH-H_2O, $COOH$-H_2O) are taken from the first-order KT UNIFAC (Kang et al., 2002). The calculation for this system was done with PRO II using the *Lipids Database* with the Original UNIFAC lipid-based parameters (Table 4.3 and (Perederic et al., 2018b)) and first-order KT UNIFAC (Kang et al., 2002) parameters covering for the missing parameters. The first order KT UNIFAC model parameters (Kang et al., 2002) are selected over the published parameters for Original UNIFAC (Hansen et al., 1991), since it is proven that the Original UNIFAC with published parameter and also other UNIFAC variants public available up to 2002, are not able to give a good representation for systems involving cyclic compounds (Kang et al., 2002) like sterols, tocopherols, tocotrienols. These types of compounds are found in vegetable oils (Rao, 2001), and they are vital in oil deodorisation and other lipid-related processes. The ARD(%) obtained for the octanoic acid – methanol – water (Hollo and Lengyel, 1960) is 0.9, which is accepted as a good result. In order to draw more conclusions on their performance, it would be useful to test the extrapolation of the lipid-based parameters both alone and coupled with the first-order KT UNIFAC parameters for other systems as well.

Table 5.1 Original UNIFAC MODEL performance using different sets of parameters for new binary VLE datasets

System	Associated groups	ARD(%)[a]		
		Pub. [3]	NIST [4]	Lip. [5]
Mononononanoin – Monolaurin [1]	CH_2 CH_2COO OH_{acyl}	4.5	4.5	1.8
Tributyrin – Mononononanoin [2]	CH_2 CH_2COO OH_{acyl}	5.1	1.9	3.8
Dinonanoin – Octacosane [2]	CH2 CH_2COO OH_{acyl}	13.9	14.3	12.6
Hexadecanol – Mononononanoin [1]	CH_2 OH CH_2COO OH_{acyl}	2.9	8.9	3.5
Octadecanol – Monolaurin [1]	CH_2 OH CH_2COO OH_{acyl}	1.9	1.9	8.4
Methyl Myristate – Hexadecanol [2]	CH_2 CH_2COO OH	7.0	6.8	10.7
Hexadecanol – Octadecanol [2]	CH_2 OH	2.7	2.7	1.4

[1] (Damaceno and Ceriani, 2017a); [2] (Damaceno and Ceriani, 2018b); [3] (Hansen et al., 1991); [4] (Kang et al., 2011); [5] (Perederic et al., 2018b), *Pub. – Published parameters, Lip. – Lipid-based parameters.*

[a] $ARD = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{P_i^{experimental} - P_i^{calculated}}{P_i^{experimental}}\right|$, N data points number, P – pressure, kPa.

5.2 SLE PREDICTION

The parameters obtained with the method are extrapolated to SLE prediction for lipid systems. The SLE data extracted from *Lipids Database*, and presented in Appendix C, is organized in category groups by applying the data organization algorithm (Algorithm A) as was previously done for the VLE data. For consistency, the same name of category-groups from VLE is used to describe the SLE data sets involving similar associated structure groups. A new category group is defined in the case of SLE, named "Others". This category-group contains unsaturated triacylglycerols – saturated fatty acids and saturated triacylglycerols – unsaturated fatty acids type of systems. The SLE data sets type used for testing the extrapolation capabilities of the UNIFAC variants with the lipid-based parameters is given in Table 5.2.

All the SLE calculations are performed with ICAS-MoT (Sales-Cruz and Gani, 2003). SLE is calculated using Eq. 5.1. The melting temperature (T_m) is taken from literature when it is available; otherwise values from *Lipids Database* are used. The values used in the calculations for heat of fusion (H_f) are taken from *Lipids Database*.

$$\ln\left(\gamma_i x_i\right) = \frac{\Delta H_f}{R}\left(\frac{1}{T_{m,i}} - \frac{1}{T}\right) \tag{5.1}$$

where γ_i is the activity coefficient of compound i, x_i is the mole fraction of the compound with higher melting point, ΔH_f is the fusion enthalpy of compound i, R is the ideal gas constant, $T_{m,i}$ is the melting point of compound i, and T is the mixture melting temperature.

The extrapolation results for Original, Linear, Lyngby Modified and Dortmund Modified UNIFAC model using both published and lipid-based parameters are listed in Table 5.3. It has to be taken into account that the parameters are not only extrapolated to another type of phase equilibria, but also to another range of temperatures (see Table 4.3 and Table 5.3). The performance of Original UNIFAC model with published and lipid-based parameters is analysed also through parity plot, Figure 5.1, and cumulative deviation plot, Figure 5.2.

A slight overall improvement in SLE prediction is noticed for Original UNIFAC model using lipid-based parameters compared to the published parameters, as presented in Table 5.2, Figures 5.1 and Figure 5.2. The biggest improvement is achieved for 6.3.2 and "Other" category groups. The Linear UNIFAC model has better overall performance for published parameters. At the group category level, the model with the lipid-based parameters performs better for 6.3.2 and "Other" group categories. Lyngby Modified UNIFAC model with lipid-based parameters gives a slightly better overall improvement. Similar to the other two models presented, Linear UNIFAC with lipid-based parameters shows a higher degree of improvement for 6.3.2 and "Other" categories. Dortmund Modified UNIFAC model with published parameters gives better prediction, both for overall and category group level, compared to the model with lipid-based parameters. This larger deviation for Dortmund Modified UNIFAC with lipid-based parameters could be due to the R_k and Q_k parameters, which are not regressed for lipid systems in this work. It has to be taken into account that the

extrapolation of the parameters is performed outside the range of temperatures (see Table 5.2 and Table 4.3) besides the phase equilibria type, and this could affect the prediction of the models using the lipid-based parameters.

Table 5.2 Database used for the SLE predictions with Original UNIFAC model organized according Algorithm A (Chapter 3)

Category Group	System type		Constitutive groups	Data sets
1.1.1	Saturated Fatty Acid	Saturated Fatty Acid	CH_2 COOH	12
1.1.2	Saturated Ester	Saturated Ester	CH_2 CCOO	9
3.2.5	Unsaturated Fatty Acid	Saturated Fatty Acid	CH_2 COOH CH=CH	5
3.2.6	Unsaturated Ester	Saturated Ester	CH_2 CH=CH CCOO	8
	Saturated Triacylglycerol	Unsaturated Triacylglycerol		
6.3.2	Saturated Fatty Acid	Acetone	CH_2 CH=CH CH_2CO COOH	1
Other*	Unsaturated Triacylglycerol	Saturated Fatty Acid	CH_2 CH=CH CH_2COO COOH	9
	Saturated Triacylglycerol	Unsaturated Fatty Acid		
Total				44

* Other category-group contains constitutive groups that were not in any of the VLE identified category-groups.

Table 5.3 Performance (in terms of ARD(%) in K) of UNIFAC variants with published and lipid-based parameters for binary SLE data sets available in *Lipids Database*

Model	Original UNIFAC		Linear UNIFAC		Lyngby Modified UNIFAC		Dortmund Modified UNIFAC		Temperature range, K	
Param. X.M.N	Pub.[1]	Lip.[2]	Pub.[3]	Lip.[4]	Pub.[5]	Lip.[4]	Pub.[6]	Lip.[4]	T_{min}	T_{max}
	$ARD_1(\%)$[a]									
1.1.1	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	278	344
1.1.2	1.2	1.1	1.3	1.3	1.2	1.3	1.2	1.2	272	314
3.2.5	0.5	0.5	0.4	1.7	0.4	0.4	0.4	0.6	265	342
3.2.6	2.3	2.2	2.3	2.4	2.4	2.3	2.3	2.3	221	339
6.3.2	0.4	0.1	0.4	0.2	2.2	2.2	1.4	1.4	334	330
Other	2	1.6	2.9	2.2	4.8	3.5	1.8	3.8	259	342
$ARD_2(\%)$[b]	1.2	1.1	1.4	1.5	2.0	1.8	1.3	1.7		

[1] (Hansen et al., 1991); [2] (Perederic et al., 2018b), *this work*; [3] (Hansen et al., 1992); [4] (Damaceno et al., 2018b); [5] (Larsen et al., 1987), [6] (Weidlich and Gmehling, 1987); *Pub. – published parameters Lip. – lipid-based parameters.*

[a] $ARD_0(\%) = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{T_i^{experimental} - T_i^{calculated}}{T_i^{experimental}}\right|$, N data points number, T – temperature, K

$ARD_1(\%) = \frac{100}{M}\sum_{j=1}^{M} ARD_0$, M – data sets number within a category-group

[b] $ARD_2(\%) = \frac{100}{Tt}\sum_{k=1}^{T} ARD_1$, T – total data sets number

Analysing the performance for all UNIFAC variants with published and lipid-based parameters, Table 5.3, shows that Original UNIFAC model with lipid-based parameters gives the best predictions for SLE, and it is followed by the Original UNIFAC model with published parameters, Dortmund Modified UNIFAC with published parameters and Linear UNIFAC with published and lipid-based parameters. From all the UNIFAC variants, Dortmund Modified UNIFAC model is the only model that does not presents any improvement for SLE prediction when the lipid-based parameters are used. The extrapolation results show that the UNIFAC variants with lipid-based parameters can be used for SLE prediction. This should be done with care, as different temperature ranges and behaviours are encountered for this type of systems and phase equilibria. Original UNIFAC is the recommended model using both lipid-based and published parameters.

A few examples of SLE prediction of the Original UNIFAC model with the published and lipid-based parameters are presented in Figures 5.3-5.5 for the following systems: stearic acid – trilinoleine, tripalmitin –linoleic acid, and linoleic acid – oleic acid. The last system presented in Figure 5.5 has a eutectic point at 265 K and x_1 = 0.7973 (*1*= linoleic acid). The temperature is under estimated by 1.5 K and 1.0 K respectively when using the model with the published and lipid-based parameters. The models using published and lipid-based parameters predicted the eutectic composition as 0.80 and 0.81. An example using lipid-based parameters for all the UNIFAC variants is presented in Figure 5.6 for the system ethyl linoleate - ethyl stearate.

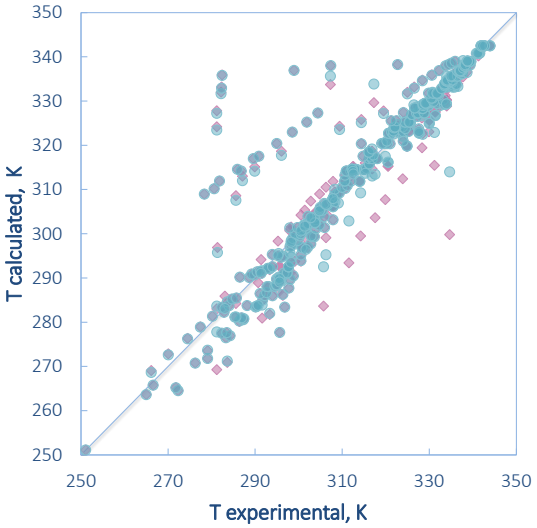


Figure 5.1 Parity plot of Original UNIFAC temperature prediction using published and lipid-based parameters vs. experimental temperature for binary SLE data sets: ♦ Original UNIFAC with published parameters, • Original UNIFAC with lipid-based parameters (All experimental data are reffered in Appendix C)

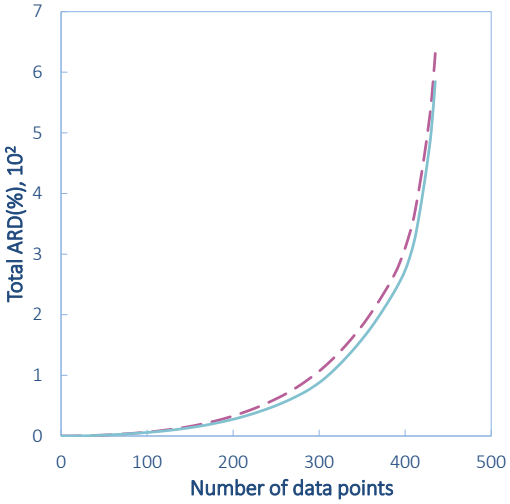


Figure 5.2 Cumulative ARD(%)[6] of all the SLE data points predicted using using Original UNIFAC model with published and lipid-parameters: - - - Original UNIFAC with published parameters, — Original UNIFAC with lipid-based parameters (All experimental data are reffered in Appendix C)

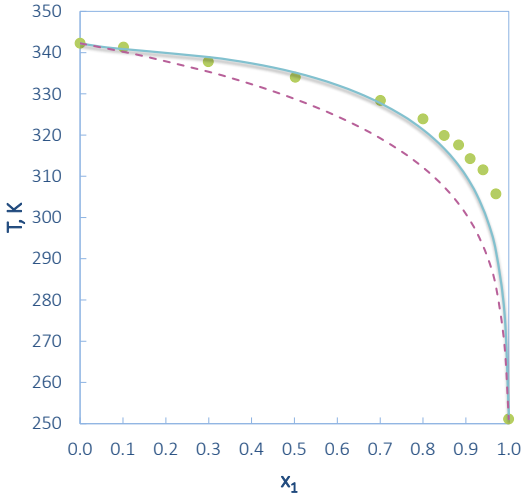


Figure 5.3 SLE prediction using Original UNIFAC model with published and lipid-based parameters for stearic acid (1) – trilinoleine (2) (Nishimura et al., 2011): ● experimental data - - - Original UNIFAC with published parameters, — Original UNIFAC with lipid-based parameters

[6] $ARD(\%) = \sum_{i=1}^{N} \left| \frac{T_i^{experimental} - T_i^{calculated}}{P_i^{experimental}} \right|$, N – total SLE data points.

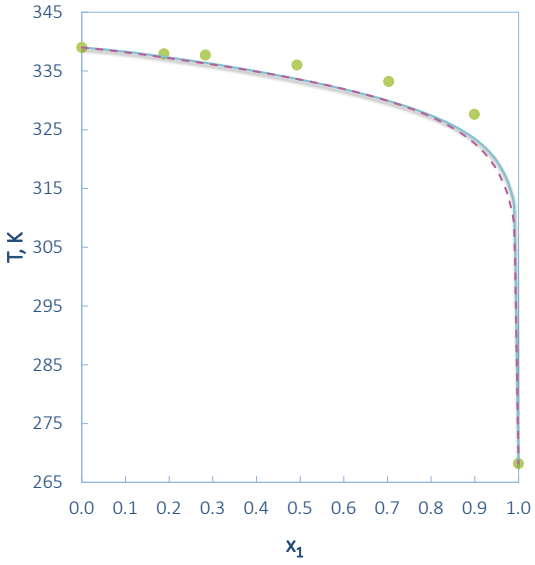


Figure 5.4 SLE prediction using Original UNIFAC model with published and lipid-based parameters for tripalmitin (1) – linoleic acid (1) (Costa et al., 2010): ● experimental data - - - Original UNIFAC with published parameters, — Original UNIFAC with lipid-based parameters

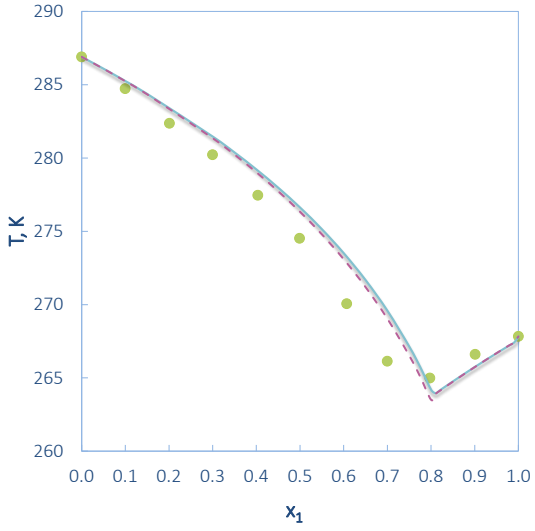


Figure 5.5 SLE prediction using Original UNIFAC model with published and lipid-based parameters for linoleic acid (1) – oleic acid (2) (Rolemberg, 2002): ● experimental data - - - Original UNIFAC with published parameters, — Original UNIFAC with lipid-based parameters

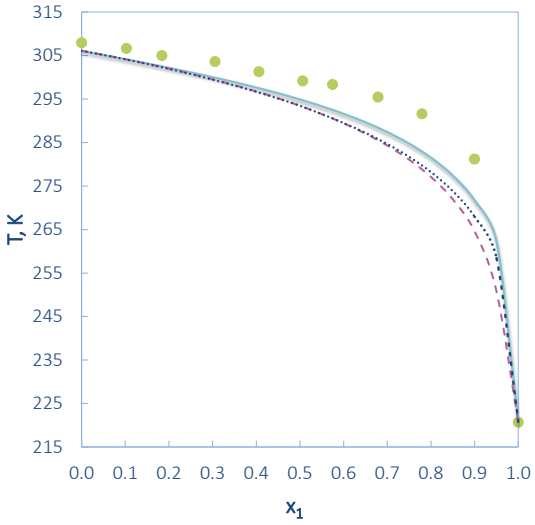


Figure 5.6 SLE prediction using Linear, Lyngby Modified and Dortmund Modified UNIFAC[7] models with lipid-based parameters for ethyl linoleate (1) - ethyl stearate (2) (Boros et al., 2009): ● experimental data, — Original UNIFAC, - - - Linear UNIFAC, ••• Lyngby Modified UNIFAC

[7] The performance of Dortmund Modified UNIFAC and Lyngby Modified UNIFAC are similar for this SLE system and for this reason only Lyngby Modified UNIFAC is represented in the plot.

5.3 Need for new data

Insufficient experimental data or low quality data represent the main drawback in developing and extending the predicting capabilities of any property model. For the case of different UNIFAC variants dedicated to lipid systems, an example of insufficient and low quality data is given by the unsaturated lipid compound systems which present the CH=CH structural group. The data available for these systems are very limited, and the quality is considerably low (see also the discussion from Chapter 2, Section 2.2.2.3), leading to gaps in the interaction matrix and to parameters with high uncertainty.

Even though in the selection algorithm the quality of the data is considered for data sets selection, overall low quality data sets involving the same interaction parameters will lead to uncertainties for these parameters. In addition, the limited amount of data, do not allow for the VLE validation for certain groups interactions parameters, as is the case for the ones from following group categories: 3.1.1, 3.2.1, 3.2.2, 3.2.3, 6.1.1, 6.1.3, 6.3.1, 6.1.4, 6.3.1, 6.3.2. However, some of the parameters from the mentioned category groups are checked when they are extrapolated for SLE prediction. The methodology, and especially the resulting calculation sequence, can be used for identifying and planning necessary phase equilibria data in order to cover the gaps within the binary interaction matrix, to improve the parameters prediction and to have a regression in a step-by-step approach for all the binary pairs involved. Examples of systems that would require VLE measurements are presented in Table 5.4. The examples are classified into four categories: (I) data sets for step-by-step regression, (II) data sets to fill in the gaps within the interaction matrix, (III) data sets to improve the performance of the available binary group interaction parameters, and (IV) other systems involved in lipid-related processes. When some or all types of data mentioned in Table 5.4 become available, a re-estimation of (certain) parameters should be performed by using the proposed method. For the case of data included in the third category (III), it is sufficient to identify the parameters within the available calculation sequence (see Figure 4.1) and to re-estimate the identified parameters and the ones that are dependent on them.

Based on the list of identified systems to fill in the gaps within the interaction matrix, given in Table 5.4, an attempt to extend the parameter matrix by measuring new phase equilibria data was made. Four binary group interaction parameters of high importance for modelling and design of lipid systems are identified: GLY-CH_2COO, GLY-COOH, GLY-CH=CH, GLY-OH_{acyl}. Using Table 5.4 and properties of lipid compounds of interest, three systems that provide these parameters were identified and selected to be measured experimentally. The focus of this project was on the phase equilibria modelling, hoewer with the limited time for the experiments this resulted in the need of more efforts for data collection. Details regarding this work are presented in Appendix E.

Table 5.4 Examples of systems that would require VLE measurements to fill in the gaps within the lipids based parameter matrix

	System Type		Constitutive groups	Observation
I VLE systems for step-by-step regression				
1	MAG/DAG	Saturated Fatty Ester	CH_2 CH_2COO OH_{acyl}	This alternative will allow the independent regression of binary pairs involved in 3.2.3 category group.
2	Glycerol	Hydrocarbon (long chain with even number of carbons preferably)	CH_2 GLY	This alternative will allow independent regression of the binary pairs from category-group 3.2.4
3a	Unsaturated Fatty Acid	Unsaturated Fatty Acid	CH_2 CH=CH COOH	These two alternatives, Alternative 3 (a and/or b) and 4 (a and/or b), will allow the estimation of the two pairs in 3.2.5 category-group to be regressed independently from different data sets. The regression will be done in a step by step approach.
3b	Unsaturated Fatty Acid	Saturated Fatty acid		
4a	Unsaturated Fatty Ester	Unsaturated Fatty Ester	CH_2 CH=CH CH_2COO	
4b	Unsaturated Fatty Ester	Saturated Fatty Ester	CH_2 CH=CH CH_2COO	
5	Acetone	Saturated Fatty Acid	CH_2 CH_3CO COOH	These alternatives (Alternative 5-6) will allow independent regression of the binary group interaction parameters from category-group 6.1.1
6	Acetone	Saturated Fatty Ester	CH_2 CH_3CO CH_2COO	
II VLE systems for filling the gaps within the interaction matrix				
1	Saturated Fatty Acid	Water	CH_2 COOH H_2O	These alternatives (Alternative 1-10) will allow filling the gaps within the binary group interaction parameter matrix.
2	Saturated Fatty Ester	Water	CH_2 CH_2COO H_2O	
3	Unsaturated Fatty Acid	Water	CH_2 CH=CH COOH H_2O	
4	Unsaturated Fatty Ester	Water	CH_2 CH=CH CH_2COO H_2O	
6	MAG/DAG	Methanol	CH_2 CH_2COO OH_{acyl} CH_3OH	
7	MAG/DAG	Alcohol	CH_2 CH_2COO OH_{acyl} OH	
8	MAG/DAG	Glycerol	CH_2 CH_2COO OH_{acyl} GLY	

Table 5.4 Examples of systems that would require VLE measurements to fill in the gaps within the lipids based parameter matrix (Continued)

	System Type		Constitutive groups	Observation
9	MAG/DAG	Unsaturated Fatty Acid	CH_2 CH=CH CH_2COO COOH OH_{acyl}	
10	MAG/DAG	Unsaturated Fatty Ester	CH_2 CH=CH CH_2COO OH_{acyl}	
III More data sets to improve the parameters performances and to extend the parameters validation				
1	Saturated Fatty Acid	Saturated Ester	CH_2 CH_2COO COOH	These alternatives (Alternative 1-9) will allow the validation of the available parameters.
2	Unsaturated Fatty Acid	Saturated/Unsaturated Fatty Acid	CH_2 CH=CH COOH	
3	MAG/DAG	Saturated Fatty Ester	CH_2 CH_2COO OH_{acyl}	
4	Unsaturated Ester	Methanol	CH_2 CH=CH CH_2COO CH_3OH	
5	Unsaturated Ester	Alcohol	CH_2 CH=CH CH_2COO OH	
6	Unsaturated Fatty Acid	Methanol	CH_2 CH=CH COOH CH_3OH	
7	Unsaturated Fatty Acid	Alcohol	CH_2 CH=CH COOH OH	
8	TAG/Saturated Fatty Ester	Acetone	CH_2 CH_2COO CH_3CO	
9	Saturated Fatty Acid	Acetone	CH_2 COOH CH_3CO	
IV Other systems involved in lipids related processes				
1	Saturated/Unsaturated Fatty Acid/Ester	Sterol	CH_2 CH=CH CH_2COO COOH $CH_{2,cyclyc}$	These alternatives (Alternative 1-2) will extend the interaction matrix of parameters, and will allow a better description of lipids related processes (e.g.: deodorisation)
2	Saturated/Unsaturated Fatty Acid/Ester	Tocopherol	CH_2 CH=CH CH_2COO COOH aCH[a], aCH-OH[b], $CH_{2,cyclyc}$, -O-$_{cyclyc}$, aCH-CH_2[b]	

[a]aCH stands for aromatic CH or C

[b] aCH in front of a group means that the group is connected to an aromatic ring

MAG – monoacylglycerol, DAG – diacylglycerol, TAG - triacylglycerol

Summary

The lipid-based parameters for the Original UNIFAC are extrapolated to other binary VLE systems than those covered within the method application and validation, giving satisfactory results. The Original UNIFAC model with the lipid-based parameters combined with first order KT UNIFAC parameters are tested for a ternary systems (octanoic acid – methanol – water) giving satisfactory results. More multicomponent data are needed in order to get conclusive results for the lipid-based parameters extrapolation capabilities, as well as the prediction capabilities of the combined parameters (lipid-based parameters and first order KT UNIFAC parameters) for the Original UNIFAC model. All the UNIFAC variants: Original, Linear, Lyngby Modified and Dortmund Modified UNIFAC are extrapolated for binary SLE data. The lipid-based parameters give almost identical results as the published parameters, with most of the improvements being noticed for 6.3.2 and "Other" group categories. It can be concluded that the Original UNIFAC model gives the best prediction for binary SLE with both lipid-based and published parameters. It is showed that the method can be used to plan the experiments in order to expand and to fill in the gaps within the binary group interaction parameter matrix, to have a step-by-step regression, and to improve the performance of available parameters.

6

LIPID THERMODYNAMIC MODELS APPLIED TO LIPID PROCESSING: SOLVENT FRACTIONATION

In the previous chapters, the phase equilibria of lipids were presented from a data availability-quality and modelling point of view and a systematic identification method was proposed and applied in order to improve the phase equilibria prediction for lipid system using group contribution methods. The aim is to use and apply these models to develop and improve lipids related processes, as it is presented in this chapter. The lipid parameters discussed in Chapter 4 were used in the modeling design, and analysis of Shea Oil Fractionation.

Chapter structure and contents:

6.1 Process importance and description: the market and economic background of fractionation process are described along with the fractionation process principles, and available technologies.

6.2 Process modelling, simulation and analysis: the workflow, the process flowsheet diagram, raw materials and products are defined; the process base case model and simulation are described; the process performances and sustainability are analyzed and discussed.

6.3 Process improvements: three process alternatives are proposed and compared with the base case.

In the previous chapters, the phase equilibria of lipids was presented from a data availability-quality and modelling point a view, and a systematic identification method was proposed and applied in order to improve the phase equilibria prediction for lipid system using group contribution methods. The aim is to use and apply these models to develop and improve lipid related processes, as it is presented in this chapter. The lipid-based parameters for Original UNIFAC model resulted from the method and presented in Chapter 4 are used in the modelling, design and analysis of Shea Oil Solvent Fractionation.

The chapter is structured in three sections presenting the process importance, the method used to develop the model and perform design, analysis and identify hot spots for improvement.

The work forms the basis of the following publication: *Perederic, O.A.,* Appel, A., Sarup, B., Woodley, J.M., Kontogeorgis, G.M., Gani, R., 2018. Design and Analysis of Edible Oil Processes Containing Lipids. Friedl, A., Klemeš, J.J., Radl, S., Varbanov, P.S., Wallek, T. (Editors), *Proceedings of the 28th European Symposium on Computer Aided Process Engineering – ESCAPE 28, Computer Aided Chemical Engineering, Elsevier, 43, 737-742.*

6.1 Process importance and description

Specialty fats and oils markets have expanded continuously over the last years. In 2017 the fats market reached a value of 2.13 billion USD, while the oil market accounted for 14.67 billion USD. The market forecast announced a 1.53 billion USD growth for specialty fats and a 6.52 billion USD growth for specialty oils by 2023 (Report Buyer, 2018). The specialty fats and oil industry expansion is determined and influenced by different factors such as: population growth and urbanization, changes in consumer eating habits (increased consumption of confectionary and processed foods), preferences and awareness (healthy fats, products with lower caloric fats, products obtained through green/bio processes), policy changes[8], product innovation (products containing healthy fats, better shelf life products, products with improved organoleptic properties, etc.), increased usage in personal care products (e.g. lotions, creams and balms) and pharmaceutical products (e.g. supplements). The industry expansion is determined by other economic reasons, such as: food service sector expansion, rise of disposable income of the population, presence of domestic and international companies specialized in fats and oils industry, etc(Report Buyer, 2018). The most important sources of specialty fats and oils are: palm, palm kernel, cotton seed, soybean, illipe, kokum, sal nut and shea oils.

The main fats and oils modification processes are hydrogenation, interesterification and fractionation.

The fats hydrogenation process is performed by heterogonous catalysis. It consists of saturating the fatty acids available in the triacylglycerols (TAGs), which results in solidification of liquid oils and fats. In the past, the process allowed the margarine and shortening industries to expand by using liquid fat sources such as soybean oil. In addition, marine fats

[8] European Union Directive 2000/36/EC allows cocoa butter equivalents (CBEs) to be used in chocolate products; CBEs need to come from 6 specific sources banning the use of chemical modified fats.

(e.g. whale and fish oils) which are highly unstable without hydrogenation, are now used in food applications (Dijkstra, 2007). Currently, the fat hydrogenation process is losing importance as a result of increasing awareness of adverse health effects of trans fatty acids (Mouratidou et al., 2014) and environmental impact of the catalyst disposed from the process, even though the process was changed to use new catalysts and to produce low-trans fats (Wang, 2011). Increased agricultural production of frying oils, with low linoleic acid content, plays a significant role in hydrogenation decline as well.

The interesterification process can be used to produce oils similar to those resulting from hydrogenation using an alkali methoxide catalyst (Dijkstra, 2007). Generally, interesterification refers to fatty acid esters reacting with acids, esters or alcohols. Within the lipid processing industry, the interesterification is a rearrangement of the fatty acyl groups within the same or different triglycerides (Kellens and Calliauw, 2013). The disadvantage is that all possible TAGs isomers can result from the reaction, including the TAGs with saturated fatty acid in the sn-2 position (Dijkstra, 2007) which proved to have negative metabolic effects in humans (Karupaiah and Sundram, 2007). An alternative to the classic catalytic process is to use a 1,3 specific lipase enzymes to perform the interesterification (Verstringe et al., 2012). Some enzymes need up to 1% water content for activation, and this can result in production of diacylglycerols (DAGs) and monoacylglycerols (MAGs), leading to the need for further purification steps which increases the processing cost (Dijkstra, 2007). The enzymatic pathway is preferred over the chemical one only when the enzyme cost does not exceed the oil loss from the chemical process. However, from an industrial point of view, the chemical process is preferred due to its robustness (Kellens and Calliauw, 2013).

Fractionation can be defined as a reversible thermo-mechanical separation in which a multicomponent mixture is separated in several fractions with specific characteristics (Kellens et al., 2007) based on driving forces of different properties between coexistent phases (e.g. melting point, solubility, volatility) (Bek-Pedersen and Gani, 2004). In the lipid processing industry, fractionation refers to the crystallization based separation which can be performed in one or more steps and it is used to tailor the chemical composition of resulting fractions used in specific applications under controlled temperature conditions (Kellens et al., 2007). A particular case of fractionation is winterization, used to separate high melting triglycerides from vegetable oil in order to have a product with improved cold tolerance (Gibon, 2006). Other types of fractionation developed and applied for the separation of oils and fats include molecular distillation and supercritical carbon dioxide separation. These processes have particular advantages regarding the separation efficiencies, and are usually applied for separation of minor components such as tocotrienols (Liu et al., 2008), tocopherols (Mendes et al., 2005; Moraes et al., 2006), and other nutraceutical compounds. The application of these methods is limited to specific applications as a result of their economics (high investments, extensive energy consumption, etc.).

The main technologies used for fractionation at the industrial scale are: dry fractionation, solvent fractionation and detergent fractionation. Their application depends on the feedstock composition of the lipid system and the required product specification.

Dry fractionation, also known as simple crystallisation or crystallisation from the melt, is the crystallization from the liquid oil/fat by cooling down without adding any other compounds to facilitate the process. At the heart of the process is the cooling strategy, which affects the crystals structure and composition. Two cooling strategies are used within the industry: the oil temperature driven when the cooling agent flowrate is controlled by the oil temperature (e.g. applied by Fractionnement Tirtiaux, Belgium), or a programmed cooling temperature, (e.g. applied by DeSmet Ballestra, Belgium) which keeps a constant temperature difference between oil and cooling agent (Hamm, 1986). Dry fractionation is applied when the melting temperature difference of the compounds to be separated is high enough. The process is used in animal fat and vegetable oils separation, fatty acids separation, butter manufacture, and others.

Detergent fractionation (known also as Lipofrac) is similar to dry fractionation in the crystallization part of the process, but for the phase separation, a detergent is added to the mixture to allow easier separation of the crystals during the filtration or centrifugation step (Kellens et al., 2007). This method is mainly used in animal fat processing (Shahidi, 2005).

The solvent fractionation consists of performing the crystallization in the presence of a solvent, and it is used when the separation of the desired fractions cannot be achieved through dry fractionation. The main solvents used are acetone and hexane, but other solvents, such as ethanol, isopropanol, low molecular ketones, azeotropic mixtures (acetone/n-hexane, ethanol/cyclohexane) are reported in the literature as well (Dijkstra, 2007). The advantages of solvent fractionation are: faster crystallization time due to lower viscosity of the mixture, higher selectivity as a result of dilution (lower oil quantity entrapped in the crystal), more material that can be crystallized (also as a result of lowered viscosity) in one step (e.g. in dry fractionation this can be done in several steps), higher separation efficiency of the crystals from mother liquor by washing with fresh solvent. Along with the advantages, a series of disadvantages are present: working with flammable solvents which need safety precautions, process energy requirements in terms of both cooling (lower temperatures for higher material quantities) and heating requirements (solvent recovery through distillation), and solvent loss (Dijkstra, 2007).

Solvent fractionation is carried out in three steps: (1) crystallization, (2) separation of the solid phase from the liquid matrix, and (3) solvent recovery.

In the crystallization step, the high melting point compounds, mainly TAGs, are separated in the solid phase when the liquid reaches or passes the saturation temperature. The crystallization process can be classified in two types: spontaneous and induced, and depends on the concentration, Figure 6.1. Spontaneous crystallization takes place in the unstable zone, which is placed above the saturation curve at very high concentration of compounds that solidify. Induced crystallization needs seeding crystal(s) and /or stirring, and it occurs when the composition is in the metastable zone (above and very close to the saturation curve). Induced crystallization is the most common for lipid systems. The boundary between the metastable zone and unstable zone depends on the cooling rate. Higher solid fat concentration and lower temperatures are achieved for higher cooling rates (Timms, 2005).

The crystallization process consists of two stages: nucleation then growth. Nucleation refers to the formation of the smallest crystal, nucleus crystal, which can exist in a solution at given temperature conditions. The growth stage starts when molecules from the adjacent liquid layer diffuse and assimilate to the nucleus crystal. If small pieces of the growing crystal are removed and if these are large enough to not redissolve, they act as a secondary nuclei leading to secondary nucleation. Another process is crystal dissolution, which is a result of increasing temperature around the crystal, an effect of crystallization process (exothermic process). Secondary nucleation and crystal dissolution lead to imperfect crystals with variable size distribution which impact the final product characteristics (Timms, 2005). All these phenomena and subsequent events dictate the most important parameters within crystallization: liquid temperature and heat transfer, which are dependent on: the stirring and cooling conditions (flowrate and temperature). If the cooling takes place too fast, solid solutions are formed. A solid solution occurs when some of the molecules from the liquid phase are incorporated in the solid phase, even though these molecules are not at the solidification temperature.

When the crystallization is performed in the presence of a solvent, the nucleation and growth are faster, allowing higher cooling rates and shorter crystallization time. The solvent dilutes the liquid phase allowing for faster heat transfer rates and lower quantities of entrained oil within the solid phase. Solvent fractionation influences the crystal form by promoting the β crystallization. The β crystallization form is the most stable and it is more selective towards symmetric monounsaturated triacylglycerols (SMUT or SUS).

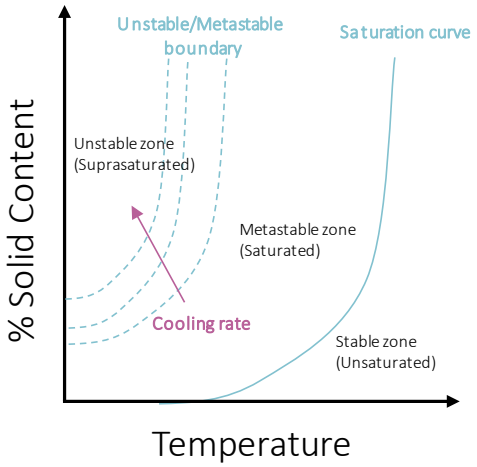


Figure 6.1. Crystallization diagram showing the saturation curve and the bounry between metastable and unstable zones at different cooling rates (Adapted from (Timms, 2005))

In the separation step, the crystals need to be separated from the liquid phase. The bulk liquid removal can be done by centrifugation, filtration and pressing. Independent of the separation technique, some liquid will always remain entrained in the solid phase. Reduced

viscosity of the liquid due to solvent usage and solvent washing of the solid leads to a better separation of the crystals form the mother liquor. The efficiency of this separation affects the final product composition and quality.

Solvent fractionation is applied when the separation of the products needs to be very sharp, and it is not possible to be achieved using dry fractionation. Solvent fractionation is used in the following applications: SMUT enrichment products from palm stearin midfraction (Kang et al., 2013), steric rich butters used cocoa butter alternative formulations from high stearic high oleic sunflower oil (Salas et al., 2011), cocoa butter stearin production from low quality cocoa butter (Buscato et al., 2017), mango kernel stearin production (Jin et al., 2017), rice bran spread production (Bakota et al., 2013), increased palm mid fraction production (Parra, 2000), sal fat stearin production (Reddy and Prabhakar, 1989), shea butter fractionation, high melting point stearin production by acetone and hexane fractionation (Bootello et al., 2015) and other specialty fats products.

The increase of cocoa butter prices over the last years as a result of chocolate market expansion resulted in a high interest to produce cheaper and more readily available alternatives for cocoa butter (Salas et al., 2011). Cocoa butter alternatives are classified into three categories depending on the amount they mix with cocoa butter to produce a homogenous product: (1) cocoa butter substitutes (CBS – maximum 5%), (2) cocoa butter replacements (CBR – mix up to 20%), and (3) cocoa butter equivalents (CBE – mix well in any proportion) which can be used as cocoa butter improvers (CBI – enhance chocolate properties) or only as cocoa butter extenders (CBEX – they provide properties as cocoa butter, and increase economic feasibility) (Verstringe et al., 2012). The only accepted fats sources in chocolate alongside cocoa butter and milk fat, as stated by the EU Directive 2000/36/EC , are: illipe, kokum, mango, sal, and shea. Coconut oil is accepted only for ice cream chocolate coatings (Timms, 2012).

Shea butter is used in cosmetic (lotions, creams, and soaps) and pharmaceutical products (cholesterol lowering pills and arthritis remedies), but its main application is in the chocolate industry as a cocoa butter equivalent. By solvent fractionation of Shea butter, two products are obtained: shea stearin and shea olein. In Table 6.1 a typical composition of shea oil, shea stearin and shea olein are given. The special properties of shea butter and its products are given by the high amounts of SUS triglycerides like stearic-oleic-stearic triglyceride. Shea stearin fraction is used as cocoa butter improver (CBI) in chocolate products to enhance the fat profile and stability, to reduce fat blooming and migration, to provide softness of the final product as well as gloss and snap properties, all of these characteristics contribute to an extended shelf life with improved properties of the final product (Smith, 2012).

Table 6.1. Detailed composition of Shea oil, shea olein and shea stearin resulted from hexane fractionation (Zhang et al., 2017)

Triacylglycerols profile				Fatty acids profile			
TAG	Shea Oil	Shea Olein	Shea Stearin	Fatty acid	Shea Oil	Shea Olein	Shea Stearin
C30	.	-	-	C8:0	-	-	-
C32	1.02 ± 0.02	2.67 ± 0.37	1.78 ± 0.13	C10:0	-	-	-
C34	-	-	-	C12:0	0.09 ± 0.03	0.13 ± 0.01	0.03 ± 0.01
C36	-	-	-	C14:0	0.02 ± 0.01	0.09 ± 0.01	0.02 ± 0.01
C38	0.45 ± 0.01	1.01 ± 0.01	2.31 ± 0.02	C16:0	3.56 ± 0.27	4.24 ± 0.15	2.47 ± 0.01
C40	5.22 ± 0.65	10.74 ± 0.98	2.91 ± 0.02	C18:0	43.50 ± 2.11	35.59 ± 1.35	58.24 ± 2.09
C42	-	-	-	C18:1	44.47 ± 1.83	50.15 ± 2.10	34.18 ± 1.38
C44	-	-	-	C18:2	6.11 ± 0.19	6.95 ± 0.03	2.89 ± 0.79
MPP	1.54 ± 0.12	2.56 ± 0.03	0.08 ± 0.01	C18:3	0.15 ± 0.02	0.08 ± 0.01	0.05 ± 0.01
PPP	-	-	-	C20:0	1.44 ± 0.39	1.46 ± 0.07	1.65 ± 0.02
MOP	1.72 ± 0.01	3.32 ± 0.01	0.37 ± 0.01	C20:1	0.27 ± 0.04	0.39 ± 0.07	0.08 ± 0.01
MLiP	0.61 ± 0.01	1.20 ± 0.01	0.10 ± 0.01	C22:0	0.16 ± 0.04	0.17 ± 0.01	0.17 ± 0.04
PPS	0.04 ± 0.01	0.06 ± 0.01	0.17 ± 0.01	SFA	48.77 ± 2.85	41.68 ± 1.60	62.55 ± 2.15
POP	0.39 ± 0.01	-	0.40 ± 0.01	MUFA	44.74 ± 1.87	50.54 ± 2.17	34.26 ± 1.39
MOO	0.03 ± 0.01	-	-	PUFA	6.32 ± 0.21	7.12 ± 0.04	2.96 ± 0.80
PLiP	0.12 ± 0.01	0.19 ± 0.01	0.10 ± 0.01				
MLiO	-	-	-				
PSS	0.31 ± 0.01	0.09 ± 0.01	0.56 ± 0.09	Notation			
POS	5.50 ± 0.03	5.25 ± 0.02	5.25 ± 0.17	*SFA*	*Saturated Fatty Acid*		
POO	2.27 ± 0.17	3.80 ± 0.30	0.44 ± 0.16	*MUFA*	*Mono- unsaturated Fatty Acids*		
PLiS	1.52 ± 0.02	2.13 ± 0.02	0.45 ± 0.01	*SFA*	*Saturated Fatty Acid*		
PLiO	0.85 ± 0.01	1.18 ± 0.01	0.15 ± 0.01	*MUFA*	*Mono- unsaturated Fatty Acids*		
PLiLi	0.13 ± 0.01	0.33 ± 0.01	0.20 ± 0.01	*PUFA*	*Poly-unsaturated Fatty Acids*		
SSS	1.25 ± 0.05	0.86 ± 0.21	1.71 ± 0.82	*TAG*	*Triacylglycerol*		
SOS	40.84 ± 1.21	7.03 ± 0.75	74.11 ± 2.10	*C30-44*	*Tag with 30-44 carbon atoms*		
SOO	23.49 ± 0.88	37.04 ± 1.15	4.57 ± 0.95	*M*	*Myristic*		
OOO	4.12 ± 0.19	7.37 ± 0.53	0.67 ± 0.25	*O*	*Oleic*		
SLiO	4.21 ± 0.62	7.37 ± 0.73	0.71 ± 0.21	*P*	*Palmitic*		
OLiO	1.11 ± 0.33	1.34 ± 0.17	0.38 ± 0.07	*S*	*Stearic*		
OLiLi	0.79 ± 0.08	2.14 ± 0.13	0.13 ± 0.02	*Li*	*Linoleic*		
SOA	2.13 ± 0.11	1.05 ± 0.04	3.66 ± 0.32	*A*	*Arachidic*		
AOO	1.12 ± 0.10	1.65 ± 0.07	0.23 ± 0.01				

6.2 Process modelling, simulation and analysis

The shea butter fractionation process consists of three parts: crystallization and solids separation from liquid phase, solvent recovery, and solvent cooling, as presented in the simplified PFD, given in Figure 6.2. The process is modelled and analysed with a method consisting of four steps (Perederic et al., 2018a): (1) problem definition and process data collection, (2) process modelling, design and simulation, (3) process performance analysis (e.g. energy, economic and environmental analysis),and (4) process hot-spots identification and retrofit solutions (Cameron and Gani, 2011). These steps cover the stage two, the design stage, within the three stage approach for synthesis and design (Bertran et al., 2017). The aim is to improve the process performance, such as, energy consumption, and environmental impact and to maintain the product quality through a systematic approach, as well as to apply the Original UNIFAC model using the newly developed parameters for lipid systems.

In the problem definition and process data collection step the aim of the process is defined and all the process specifications, data and thermodynamic information are collected from literature and industry (Alfa Laval). The *Lipids database* is used to provide all the pure compound and mixture thermodynamic information. The process modelling, design and simulation step provides details regarding the models used for simulation performed in PRO/II (Schneider Electric Software, 2016) and design of equipment (Biegler et al., 1997). Process performance analysis (3) is performed with ECON (Saengwirun, 2011) for economic analysis and WAR algorithm (Cabezas et al., 1997) implemented in ICAS (Gani et al., 1997) for the environmental impact assessment. In the last step, process hot-spots identification and retrofit solutions (4), the process hot spots are identified based on the results from step 3 and they are tackled for improvement through process integration and other retrofit solutions. After all the improvement solutions are implemented, the economic analysis and environmental impact assessment are performed for the new alternative(s), and the process performances are compared with the ones from the base case (Step 2-3).

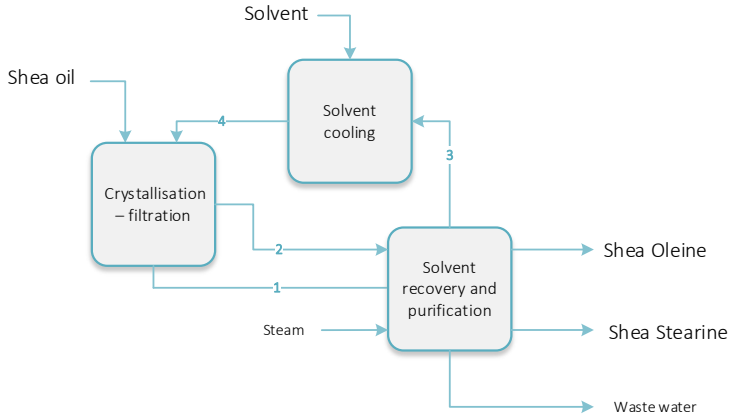


Figure 6.2. Shea butter fractionation simplified PFD

6.2.1 Problem definition and process data collection

The process flowsheet diagram is based on Alfa Laval information and literature data. The PFD for the base case scenario in presented in Figure 6.3. The Shea oil and the main product specifications are given in Table 6.2. Detailed stream information is presented in Appendix F. It is assumed that the oil is dried before entering the process. Shea oil is heated up to 50 °C to erase the thermal history of the sample, and then is mixed with the solvent (acetone) cooled to - 5 °C in the crystallizer. High solvent purity is required, since water or other impurities can affect the crystallization process. The crystallization process takes place at - 5 °C. The two products: shea stearin, solid, and shea olein, liquid, are separated and washed with acetone. Further a series of flash units working at different temperatures aim to maximize the solvent recovery from the products. A steam stripping column is used for each product finishing by removing remaining acetone traces. Solvent from the vapour products of S01, S02 (strippers), C04 and C07 (flashes) is recovered in an acetone-water distillation column (T1) and recycled back to the process. All the other flash vapour products are recycled straight to the solvent recycle. The water resulted from the distillation column is considered as waste and its treatment is not taken into account within this analysis. The solvent stream that is recycled contains small amounts of water. Most of this water is separated in the first flash of the olein and stearin streams (C01, C05). The vapours separated from C05 flash are split: one stream is recycled back in the solvent recycle (S-05VAPRECY), while the other one (S-05VAPCOL) is recycled to the acetone-water distillation column feed (S-08B) in order to avoid water accumulation in the system. The choice of splitting the vapour product from C05 flash (S-05VAP), instead of vapour product of C01 flash (S-01VAP), is the higher concentration of water in S-05VAP stream, leading to a smaller stream to be recycled in the distillation column (a bigger stream recycle to column feed would lead to higher energy consumption in the column). The cooling of the solvent, depicted in the PFD as one heat exchanger unit (E15), is performed in a refrigeration cycle with ammonia, which is considered in the costing stage. Shea stearin is considered the main product, while shea olein is a by-product, and both are considered for revenues in the economic analysis. The process parameters such as solvent-to-oil ratio, separation factors, and process conditions are given in Table 6.3, while the process utilities specifications are presented in Table 6.4. The aim of the process is to obtain the two products with the given specification and minimum solvent (<1 mg/kg) and water (<0.5%) content, to recover and recycle the solvent, and to have minimum energy consumption, and material loses.

Table 6.2. Feed and product composition

Compound class	Shea Butter, wt. %	Shea Stearin, wt. %
TAGs	88.49	95.49
DAGs	1.00	1.00
MAGs	0.08	0.08
FAs	10.00	3.00
TOCOs	0.12	0.12
Sterols	0.25	0.25
Ester Sterols	0.05	0.05
Squalene	2.50E-03	2.50E-03

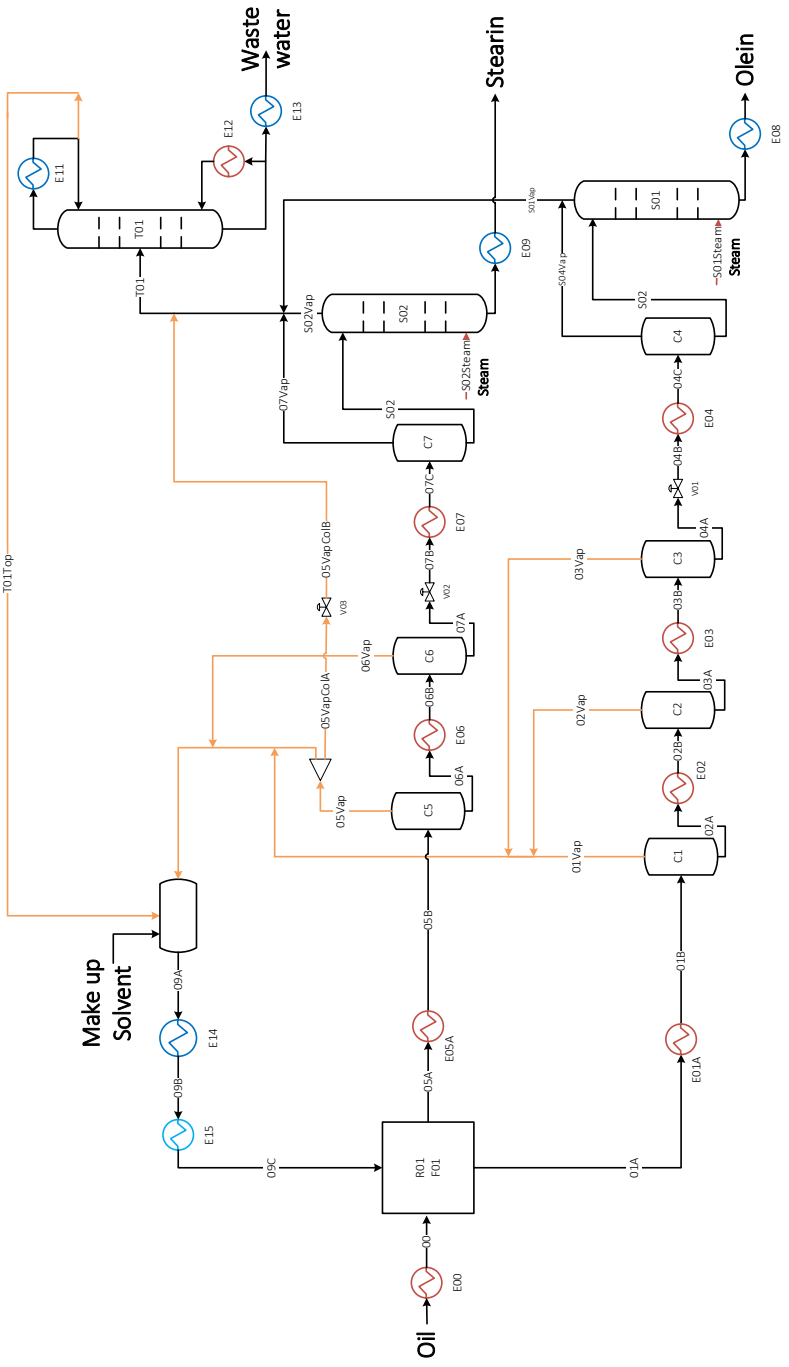


Figure 6.3. Shea butter fractionation PFD for base case scenario

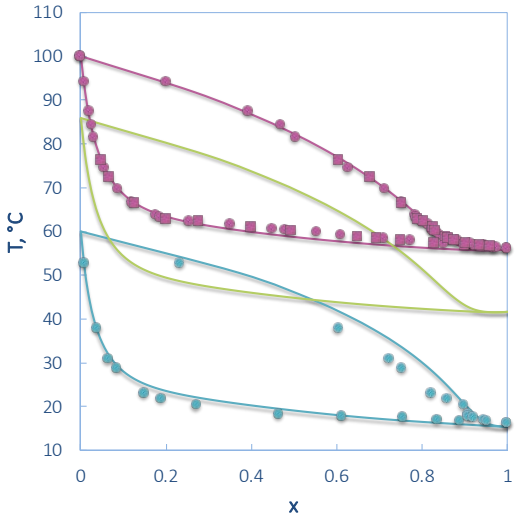


Figure 6.4. Water-acetone vapour liquid equilibria at diferent pressures: UNIFAC prediction — 101.33 kPa, — 60 kPa, — 20 kPa; experimental data • 101.33 kPa (Huang et al., 1984), ■ 101.33 kPa (Verhoeye and Deschepper, 1973), • 20 kPa (Verhoeye and Deschepper, 1973)

Table 6.3. Process specifications

Parameter	Unit	Value
Feed flow	kg/h	2000
Feed:Solvent	wt. ratio	1:4
Crystallization temperature (SC1)	°C	-5
Stearin yield (S-05A)	wt. %	47
Olein yield (S-01A)	wt. %	53
Solvent:Stearin ratio (SC1: S-05A)	wt. ratio	1:1
Flash (C01-C03, C05-C06): Pressure	bar	1.0
Flash (C04, C07): Pressure	bar	0.2
Flash (C01): Acetone separation	wt.fr.	0.5000
Flash (C02): Acetone separation	wt.fr.	0.9000
Flash (C03): Acetone separation	wt.fr.	0.9000
Flash (C04): Acetone separation	wt.fr.	0.7000
Flash (C05): Acetone separation	wt.fr.	0.9000
Flash (C06): Acetone separation	wt.fr.	0.7500
Flash (C07): Acetone separation	wt.fr.	0.9000
Splitter (SP1): recycle to column fraction (S-01VAP)	wt.fr.	0.1500
Strippers (S01, S02): acetone recovery in top product (S-04-STRIP-VP, S-07-STRIP-VP)	mg/kg	0.9999
Distillation column (T1): acetone recovery	wt. fr.	0.9950
Distillation column (T1): water recovery	wt. fr.	0.9950
Distillation column (T1): working pressure	bar	0.2000

Table 6.4. Utilities specifications

Hot Utilities	Pressure, bar	Cold Utilities	Temperature, °C	
			Supply	Target
LP steam	4	Cold water	20	30
Process steam	1	Ammonia	-15	-15

The *Lipids Database* (Perederic et al., 2018) is used for providing all the necessary thermo-physical property data (e.g. vapour pressures, melting points, phase equilibria behaviour) for all the compounds involved. Lipid-based binary interaction parameters for Original UNIFAC model are provided with the database (Perederic et al., 2018).

6.2.2 Process modelling, design and simulation

The process model is developed in PRO/II 10.0. The *Lipids Database* is linked to PRO/II, which provides easy access to all the thermo-physical data as mentioned earlier.

A simple mass balance using a stream calculator (SC1) was used to represent the crystallization, filtration and washing operations, since there was not enough data available to perform rigorous modelling for these operations, and the interest was focused on solvent recovery. The temperature selection in the flash units was determined based on the amount of acetone to be separated from the mixture and the oil degradation temperature limit. The oil, due to the presence of unsaturated compounds, can degrade at temperature higher than 110 °C. Selected flash temperature conditions are listed in Table 6.3.

The pressure in the distillation column is 0.2 bar. This selection is based on the amount of water to be removed from the process and on the acetone-water VLE behaviour at different pressures, Figure 6.4. The system presents a low boiling point azeotrope at pressures higher than atmospheric (See Figure 6.4 for data at 689 kPa). With decreasing pressure, the azeotropic point translates into a pinch area. The pinch area covers the 0.9 to 1 acetone mole fraction region for atmospheric pressure. The pinch area gets smaller with decreasing the pressure, and disappears completely at pressures lower than 10 kPa. Water-acetone VLE, Figure 6.4, is predicted using the UNIFAC model with lipid-based and KT parameters. The quality factor of the experimental data presented in Figure 6.4 is: Q=1, Q=0.95 for data at P=101.33 kPa (Huang et al., 1984; Verhoeye and Deschepper, 1973) and Q=0.23 for data at P=0.2 (Al-Shhaf, 1993). The quality factor calculation was performed with TDE and includes the results of several consistency test as presented in Chapter 2.

All the remaining unit operations (e.g: flash, heat exchanger, column, pump, valve) were modelled using rigorous models available in PRO/II. The mass balance of the process on the category of compounds is presented in Table 6.5. Detailed information regarding the mass balance is given in Appendix F. The equipment design was performed following the principles presented by Biegler (Biegler et al., 1997).

Table 6.5. Mass balance for Shea butter acetone fractionation process for base case scenario

	FEED OIL	MAKE_UP SOLVENT	S01 STEAM	S02 STEAM	STEARIN	OLEIN	WASTE WATER
Phase	Liquid	Liquid	Vapour	Vapour	Liquid	Liquid	Liquid
Temperature, °C	25	20	120	120	50	30	30
Pressure, bar	1	1	2	2	1	1	1
TAGs, kg/h	1769.8	0.00	0.0	0.0	897.6	872.2	0.0
DAGs, kg/h	20.0	0.00	0.0	0.0	9.4	10.6	0.0
MAGs, kg/h	1.6	0.00	0.0	0.0	0.8	0.8	0.0
FAs, kg/h	200.1	0.00	0.0	0.0	28.2	171.9	0.0
Minors, kg/h	8.5	0.00	0.0	0.0	4.0	4.5	0.0
Acetone, kg/h	0.0	0.03	0.0	0.0	0.0	0.0	0.0
Water, kg/h	0.0	0.00	16.8	13.2	2.6	3.3	24.2

6.2.3 Process performance analysis

The process performance was carried out in terms of energy requirements, economic indicators (CAPEX, OPEX) and environmental impact. The energy balance for all heat exchangers and crystallizer are given in Table 6.6. The heat of crystallization process was estimated by considering individual crystallization of each component, and by using the heat of fusion of pure components from the *Lipids Database* (Perederic et al., 2018b). The total cold utility consumption is 1.81 MW, and the total hot utility consumption is 1.97 MW.

Table 6.6 Energy balance for the base case scenario (1)

Unit Name	Duty, kW	Utility type
E00	32.77	LP
E01	807.83	LP
E02	461.81	LP
E03	45.59	LP
E04	16.55	LP
E05	160.21	LP
E06	50.68	LP
E07	14.02	LP
E08	28.44	CW
E09	16.83	CW
E11	154.65	Ammonia
E12	88.59	LP
E13	1.21	CW
E14	1236.63	CW
E15	210.39	Ammonia
Crystallizer	43.45	LP
Total Cold Utility	1648.15	CW, Ammonia
Total Hot Utility	1721.50	LP

Based on the equipment detailed design, the economic performances were analysed with ECON. The pumps necessary for the process were considered within the analysis, but they are not represented in the process PFD. The process rate of return (ROR) is 22%, with a brake-even point of the process of 1.8 years, as showed in Figure 6.4. Total capital investment is 4.74 M€, total product cost is 21.18 M€/year, and the manufacturing cost is 19.26 M€/year. The utilities represent 30% of the manufacturing cost. More details on the economic analysis results are presented in Table 6.8 and Appendix F.

Table 6.8. Base case scenario CAPEX and OPEX

CAPEX, M€		OPEX, M€/year	
Total Capital Investment (TCI)	4.74	Total Product Cost	21.18
Total Direct Cost	3.37	Variable Cost	19.11
Total indirect cost	1.15	Fixed Charges	0.14
Fixed-capital Investment (FCI)	4.72	Manufacturing Cost	19.26
Working Capital Investments (WC)	0.02	General Expense	1.75

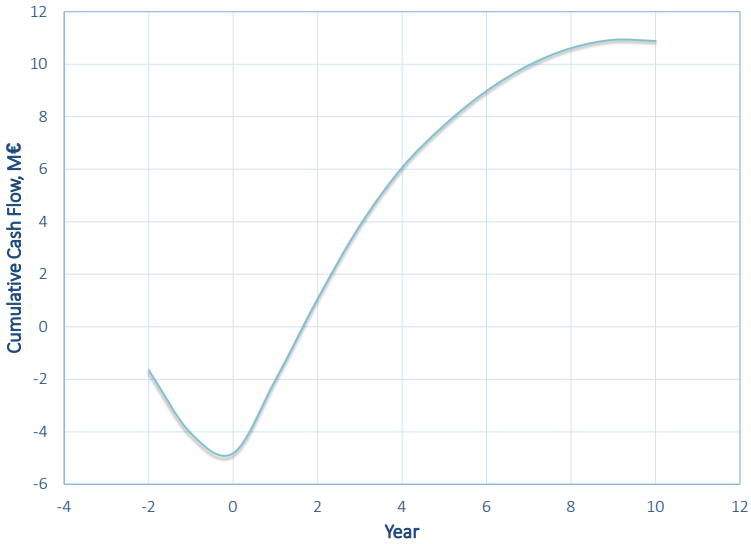


Figure 6.5. Cumulative cash flow for the base case scenario

Environmental impact was performed with ICAS, and it was analyzed for the waste water stream. Most of the impact was generated by acetone: over 90% of HTPI and TTP values, and PCOP, and over 80% for HTPE and ATP. As it can be noticed, the waste stream has no effect on global warming potential, ozone depletion and acidification potential.

Table 6.7. Environmental impact results for base case scenario

Indicator[a]	Unit	Value
HTPI	$1/LD_{50}$	0
HTPE	1/TWA	5.57E-06
ATP	$1/LC_{50}$	6.18E-06
TTP	$1/LD_{50}$	1.74E-03
PCOP	C_2H_2 eq	1.05E-02
GWP	CO_2 eq	0
ODP	CFC-11 eq	0
AP	H^+ eq	0

[a] HTPI – human toxicity potential by ingestion, HTPE – human toxicity by exposure, ATP – aquatic toxicity potential, GWP – global warming potential, PCOP – photochemical oxidation potential, AP – acidification potential, HTC – human toxicity carcinogenic.

6.2.4 Process hot-spots identification and retrofit solutions

Process analysis results show that improvements can be made with respect to utility consumption, where it:

- Reduces the utility consumption in heat exchangers E01, E02 (LP steam) and E14 (CW) through heat integration
- Reduces the utility consumption for flash units (LP steam) by changing flash units operating parameters (T and P) to allow the heat integration of vapour products with flash feed streams.
- Retrofit of the by-product (shea olein) separation sequence to reduce water (steam) feed in the system and to decreases investment costs through intensified separation solution.

Based on the identified improvement opportunities, three process alternatives (1-3) are presented in the next section of the chapter.

6.3 Process improvements

Each of the proposed process alternatives are presented individually and the most important modifications compared to the base case are highlighted. The economic and environmental impact results for the three proposed alternatives are compared at the end of this section.

6.3.1 Process alternative 1

Process alternative 1 is based on the heat integration performed for the base case scenario. All the cold and hot streams from the process were considered except the streams related to the reboiler and condenser of the acetone-water distillation column. An initial selection for minimum temperature difference of 10 °C was proposed, but this option led to higher costs compared to lower values of minimum temperature difference. The final selected minimum temperature difference is 5.69 °C, and it was done based on capital and operating costs. The maximum allowed process-to-process heat recovery for selected temperature difference is 983.39 kW, as presented in the shifted composite curve diagram, Figure 6.6. The minimum hot utility requirement is 673.23 kW and the minimum cold utility requirement is 367.20 kW. The pinch point is located at 57.19 °C (T*, shifted temperature) (actual process temperatures pinch: 54.34 and 60.04 °C). The balance grand composite curve, Figure 6.7, gives the utility (LP, CW and Ammonia) placement and satisfies the minimum heat and cold utility requirements.

The proposed heat exchanger network is presented in Figure 6.7, and results in the addition of three new heat exchangers. Table 6.8 lists all the new and/or modified heat exchangers duties. The recovered heat for the proposed network is 370.96 kW, which represent 37% of the total allowed heat recovery. The utility consumption drops with 24.5% for cold utility and 22.1% for hot utility compared to the base case requirements.

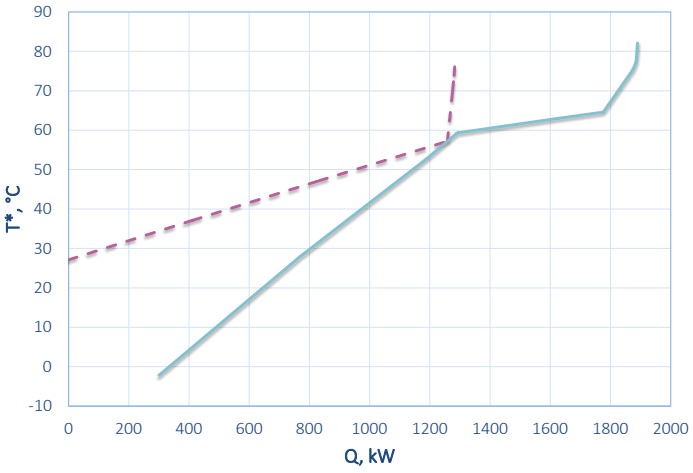


Figure. 6.6 Shifted composite curves for the base case scenario heat integration problem: — cold composite curve, - - - hot composite curve

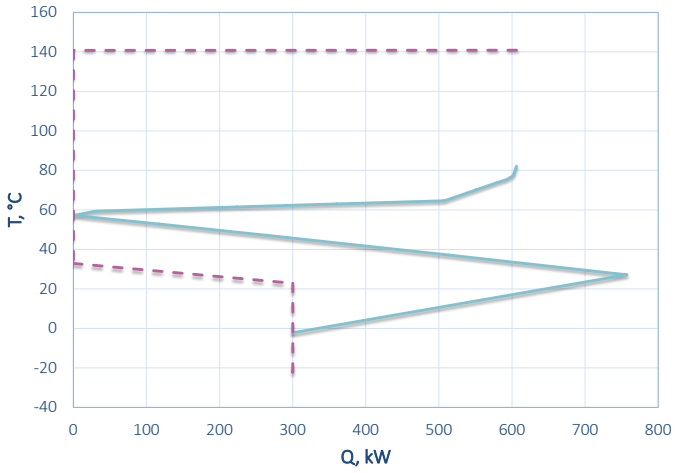


Figure. 6.7 Process grand composite curves for the base case scenario heat integration problem: — process grand curve, - - - utility grand composite curve

Table 6.8. Duty modification in the process alternative 1 compared to the base case

Unit Name	Duty, kW	Utility type
E00	32.77	-
E01A	272.44	-
E01B	535.38	LP
E05A	65.75	-
E05B	94.45	LP
E14	865.67	CW

6.3.2 Process alternative 2

In process alternative 2, the operating temperature and pressure of the flash units were modified in order to allow the heat recovery of the vapours by heating the feed streams of the units. The following assumptions were made: no changes in the last flash pressure of each product is made (C04 and C07), the strippers feed composition is kept the same in order to have the same amount of water (steam) entering the process and the same specifications for the final products were maintained, the temperature of the first flash feed (C01 and C05) was considered at 50 °C (based on the heat integration results from process alternative 1). A difference in flash units pressure was considered in order to allow the heat integration. All the new flash parameters are given in Table 6.9. The split factor in SP1 splitter was modified in order to keep the same amount of water recycled to the distillation column. The new split factor was calculated to be 0.9784. The heat exchanger network developed for the Process Alternative 1 remains the same. The PFD for process alternative 2 is presented in Figure 6.8. In Table 6.10 the duty and utilities assignment of each heat exchanger is also given.

The process alternative 2 presents a decrease of 47% for the cold utilities requirements compared to the base case and a 61% decrease for the hot utility requirements. The total recovered heat is 854.8 kW.

Table 6.9. New flash units parameters

Unit	Pressure, bar	Temperature, °C
C01	1.00	56.25
C02	2.00	78.55
C03	2.30	107.6
C04	0.20	79.32
C05	1.00	58.85
C06	2.00	99.08
C07	0.20	75.77

Table 6.10 Energy balance for the process alternative 2

Unit Name	Duty, kW	Utility type
E00	32.77	-
E01A	272.44	-
E01B	22.11	-
E02	394.44	-
E03	423.54	LP
E04	8.95	CW
E05A	65.75	-
E05B	67.27	-
E06	100.73	LP
E07	15.92	CW
E08	28.45	CW
E09	16.83	CW
E11	74.82	Ammonia
E12	102.43	LP
E13	1.21	CW
E14	522.03	CW
E15	210.39	Ammonia
Crystallizer	43.45	LP
Total Cold Utility	878.59	CW, Ammonia
Total Hot Utility	670.15	LP

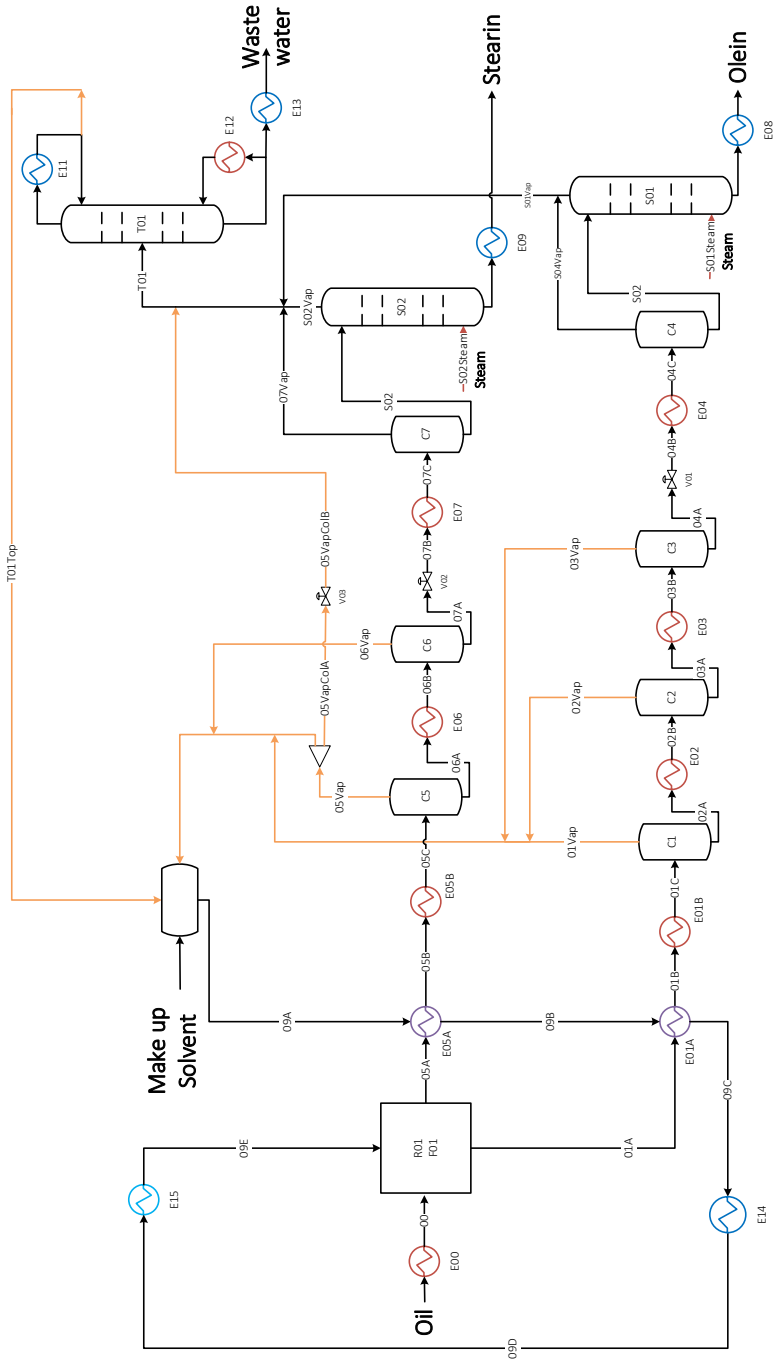


Figure 6.7. Shea butter fractionation PFD for process alternative 1

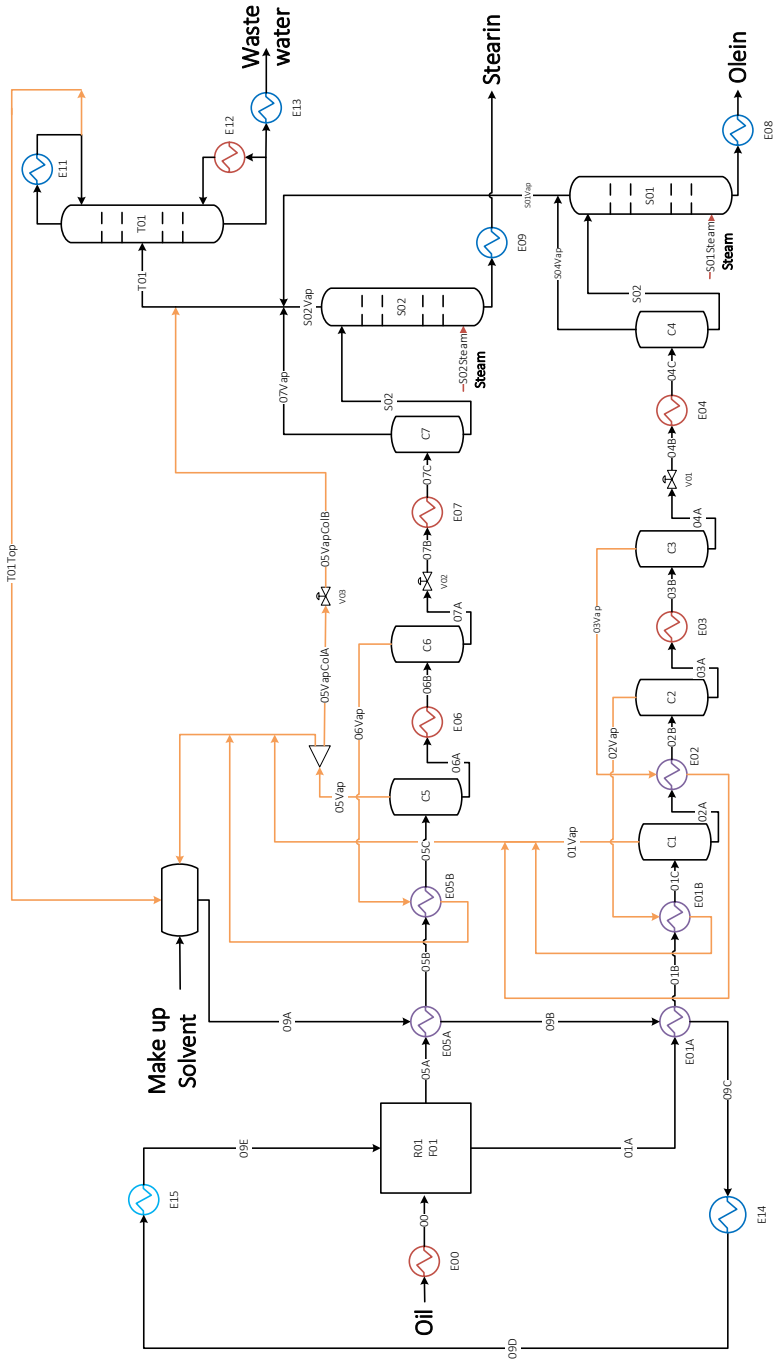


Figure 6.8 Figure 6.8. Shea butter fractionation PFD for process alternative 2

6.3.3 Process alternative 3

Process alternative 3 considers a side draw distillation column for the by-product (shea olein) and solvent purification. The side draw column, Figure 6.9, replaces the flash C04, steam stripper S1, and distillation column T1. The design of the side stream column was performed based on the driving force method of Bek-Pedersen et al. (Bek-Pedersen and Gani, 2004). The column is design with 15 trays (without counting the reboiler and condenser), the feed is placed on tray number 8, and the side draw is placed on tray number 11. The mass balance on category of compounds is presented in Table 6.11. The column reboiler duty is almost double compared to the base case, while the acetone in the waste stream is ten times higher.

Table 6.11. Mass balance for side draw column

	FEED OIL	MAKE_UP SOLVENT	S-07 STEAM	STEARIN	OLEIN	WASTE WATER
Phase	Liquid	Liquid	Vapor	Liquid	Liquid	Liquid
Temperature, °C	25	20	120	50	30	30
Pressure, bar	1	1	2	1	1	1
TAGs, kg/h	1769.8	0.00	0.0	897.6	872.2	0.0
DAGs, kg/h	20.0	0.00	0.0	9.4	10.6	0.0
MAGs, kg/h	1.6	0.00	0.0	0.8	0.8	0.0
FAs, kg/h	200.1	0.00	0.0	28.2	171.9	0.0
Minors, kg/h	8.5	0.00	0.0	4.0	4.5	0.0
Acetone, kg/h	0.0	9.33	0.0	0.0	0.1	9.3
Water, kg/h	0.0	0.00	13.2	2.6	1.7	9.2

6.3.4 Process performance analysis

The economic and environmental impact analysis was performed for all three process alternatives. The differences are presented compared to the base case. The main CAPEX and OPEX modifications for process alternatives are given in Annex F, Table F.5. The cumulative cash flow for the base case and process alternatives are presented in Figure 6.10. Process alternative 3 presents the best economic performances, and it has the same environmental performances as the base case and process alternative 1. It is to be mentioned, that if duty is considered for the war algorithm, then the lowest environmental impact will be for process alternative 2. The environmental impact for the waste water stream for process alternative 3 is given in Table 6.12.

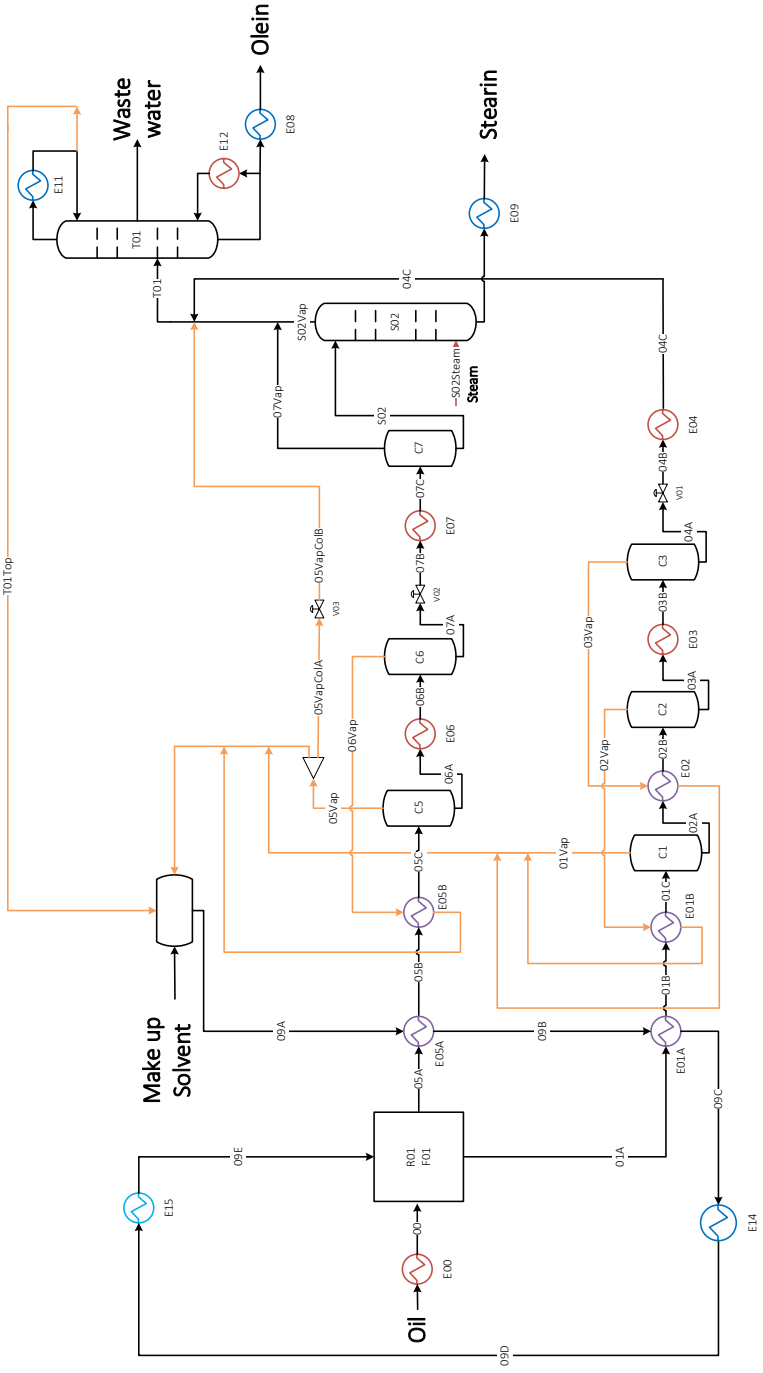


Figure 6.9. Shea butter fractionation PFD process alternative 3

Table 6.12. Environmental impact results for process alternative 3

Indicator	Unit	Process Alternative 2	Process Alternative 3
HTPI	$1/LD_{50}$	1.96E-03	5.62E-01
HTPE	1/TWA	6.21E-06	1.60E-03
ATP	$1/LC_{50}$	6.81E-06	1.60E-03
TTP	$1/LD_{50}$	1.96E-03	5.62E-01
PCOP	C_2H_2 eq.	1.19E-02	3.39E+00
GWP	CO_2 eq	0.00E+00	0.00E+00
ODP	CFC-11 eq	0.00E+00	0.00E+00
AP	H^+ eq	0.00E+00	0.00E+00

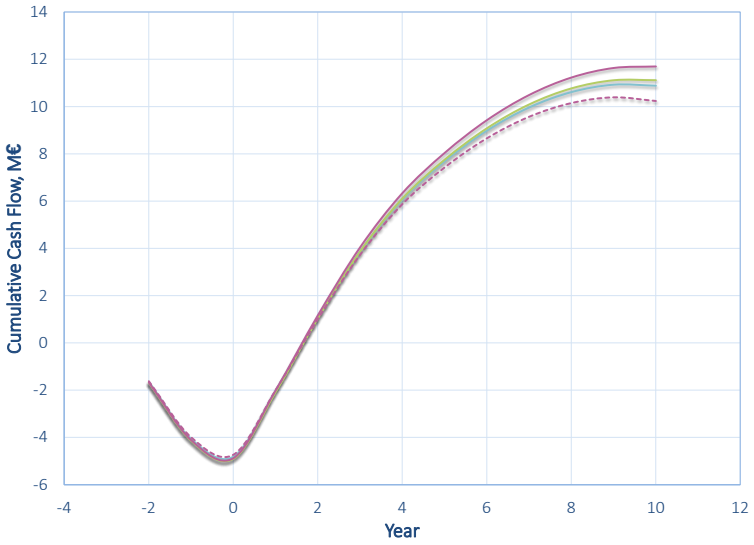


Figure 6.10.Cumulative cash flow diagram for the base case (—) and process alternatives 1 (—), 2 (—) and 3 (- - -)

Summary

This chapter presents an overview of the lipid modification process. The lipid fractionation technological alternatives are described and the most important process parameters are highlighted.

Shea oil acetone fractionation process is presented and analysed through a method consisting in four steps. Improvements to the base case scenario are made and analysed through three process alternatives. Process alternative 2, where flash units parameters are retrofit to allow heat integration, proves to have the best economic and environmental performances.

Final Remarks

In this last part of the thesis the conclusions and achievements are presented. Suggestions for the future work, along with perspectives within the filed are presented as well.

Contents

Conclusions

Future work

CONCLUSIONS

At the beginning of this thesis it was showed the crucial role that thermodynamic models play within the description of chemical systems, and their use in developing and improving new processes. All of these models are based on available experimental data and its quality is critical in order to get models capable of describing and predicting accurately the properties and phase behaviour of different chemical compounds and their mixtures. For lipid systems, the challenges come from the vast amount of compounds involved, for which it is difficult to have complete sets of experimental data. Even though classic thermodynamic models like NRTL, UNIQUAC or more advanced ones like CPA, SAFT proved to perform very well in describing such systems, they need extensive experimental data in order to be able to describe broader systems/mixtures. It was shown that the best option for lipid-based system are the group contribution models like UNIFAC (in many of its variants), in order to describe the lipid systems using a minimum amount of data to adapt the model to provide a good description for these types of systems.

Through a systematic approach, a method for selecting experimental data and for estimating the parameters of group contribution models was proposed and applied for different UNIFAC variants for identifying new parameters dedicated to lipid systems. The parameters were validated and tested for extrapolation capabilities. All the UNIFAC variants with the new parameters showed improvements for the description of binary VLE lipid systems. The temperature dependence term proved useful wich resulted in lower deviation of the predictive values reported to the experimental data. The models with the lipids-based parameters were extrapolated to VLE of different systems than the ones within the regression, and satisfactory results were achieved. The extrapolation was performed on other types of phase equilibria as well. The SLE prediction indicated the Original UNIFAC model with the lipid based parameters as the model with the best performances. The proposed method was used to identify the gaps of the lipid-based UNIFAC models, and to propose new experimental data to be measured in order to expand the model application and to improve its performances.

Further, using the available methods and tools, the Original UNIFAC model with the lipid-based parameters and the *Lipids Database* were used for the modelling, design and analysis of Shea oil solvent fractionation. The process was improved through retrofit by applying heat integration. An intensified solution was analysed with the further need of improvement.

A summary of the achievements of this thesis are as follows:

- A systematic identification method for data analysis and phase equilibria modelling was developed. The method was applied successfully to different UNIFAC model variants.
- Different UNIFAC variants with the lipid-based parameters were validated using binary VLE data. The models extrapolation capabilities were tested for different VLE systems, and other phase equilibria.
- Method capabilities to identify the gaps are showed within design of experiments. Original UNIFAC model with the lipid-based parameters and the *Lipids Database* were used to design, model, analyse and improve a process characteristic to lipid industry.

FUTURE WORK

The subject of this thesis could be further developed in different research directions related to thermodynamics, process and tools development. More specifically, ideas for each of the suggested directions are presented below.

Thermodynamics

- As it was earlier suggested in the thesis, more experimental data to improve the parameters performances and to fill in the gaps of the parameter matrix could be performed. The detail list of systems that would help to improve the UNIFAC models for lipids was presented in Table 5.4 in Chapter 5.
- Uncertainty analysis for the model parameters would provide useful insight about the model performances.
- The estimation of the parameters could be performed using different objective functions and solvers. An example could be using the maximum likelihood objective function along with the experimental data uncertainty, which is available for the data published in the last years.
- A systematic approach for SLE kinetics would be very useful for developing processes and products for lipid industry. A group-contribution model would represent a useful tool and would allow further developments for lipid-related processes and products.

Process

- Solvent design for lipid fractionation for identifying new solvents more suitable for edible application, and with less environmental impact. This could be done if detailed SLE kinetic models are available.
- Expansion of available knowledge within lipid processing, in order develop superstructure-based like systems for lipid refinery development where new optimum processing paths can be identified using and adapting the framework developed by Bertram et al for biorefinery networks (Bertran et al., 2017). This would include databases development for the Super-O tool used in superstructure optimisation for this type of problems.

Tools

- Besides the Original UNIFAC model, the other UNIFAC variants could be included in the automated procedure of creating the database for PRO II.
- A tool based on the proposed methodology could be developed, and could be used to regress the parameters automatically after all the experimental data has been added. The data could be added automatically by connecting the tool to TDE (Diky et al., 2012) or other database, or could be added by the user. All the other steps from the method: consistency check, data selection, data organising, identification of the calculation sequence and regression could be done automatically. At each of these steps the user should have access, allowing a better flexibility of the tool.

APPENDIX A
LIPIDS DATABASE STRUCTURE

The lipid compounds are classified in 18 categories presented in Table A.1, which cover 334 compounds, out of which 8 compound are non-lipid compounds (water, methanol, ethanol, n-hexane, acetone, 1-propanol, 2-propanol, 1-butanol) covered in *Others* category.

The overview of the mixture data is given in Chapter 2. The Lipids Database includes the LLE multicomponent data provided by Bessa and collaborators, and which was used in the paper *A new UNIFAC parameterization for the prediction of liquid-liquid equilibrium of biodiesel systems* (Bessa et al., 2016). The overview of the binary VLE, SLE and LLE used for the calculations is given in Appendix B, C and D. The database contains all the parameter tables for all the UNIFAC variants mentioned in this work.

The database can use following models for the multicomponent phase equilibria calculation: NRTL (Renon and Prausnitz, 1968), UNIQUAC (Denis S. Abrams and Prausnitz, 1975), Original UNIFAC (Fredenslund et al., 1975), UNIFAC-CI (Mustaffa et al., 2011), PC-SAFT(Gross and Sadowski, 2002).

Table A.1 Lipid compounds classification used in *Lipids Database*

Category Number	Category Name	Number of compounds
1	Carotenoids	8
2	Diglycerides	41
3	Ethyl esters	28
4	Ethylhexyl esters	9
5	Fatty acids	29
6	Isopropyl esters	3
7	Methyl esters	28
8	Monoglycerides	15
9	Pesticides	14
10	Triterpenealcohols	8
11	Others	16
12	Ubiquinones	5
13	Phospholipids	14
14	Sterol-esters	7
15	Sterols	5
16	Triglycerides	85
17	Vitamin E	9
18	Fatty alcohol	10

The properties for which experimental data and models are available in the database are presented in Tables A.2 and A.3

Table A.2 Experimental data* available in the *Lipids Database*

Primary Properties	Functional Properties
Melting Temperature	Vapor Pressure
Boiling Temperature	Liquid Density
Critic Temperature	Liquid Viscosity
Critic Pressure	Surface Tension
Critic Volume	Liquid Thermal Conductivity
Formation Enthalpy	Liquid Heat Capacity
Formation Gibbs Enthalpy	Vapor Pressure

* The experimental data are not covering all the compound and properties.

Table A.3 Pure compound property models available in the *Lipids Database*

Primary properties	Secondary Properties	Functional properties
Melting Temperature	Compressibility factor	Vapour Pressure
Boiling Temperature	Acentric factor	Liquid Density
Critical Temperature	Specific gravity at 289 K	Liquid Viscosity
Critical Pressure	Molar volume at 298 K	Surface Tension
Critical Volume	Solubility parameter at 298 K	Liquid Thermal Conductivity
Formation Enthalpy		Liquid Enthalpy
Formation Gibbs Enthalpy		Ideal Enthalpy
Molecular weight		Vaporization Enthalpy
Compressibility factor		Vapour Viscosity
Fusion Enthalpy		Vapour Thermal Conductivity
Specific gravity 289 K		
Acentric Factor		
Liquid volume at 298 K		
Dipole moment		

Table A.4 Pure compound property correlations* used in the *Lipids Database*

Property	Correlation
Vapour Pressure, liquid viscosity	$\ln(\text{Prop}) = C_1 + \frac{C_2}{T} + C_3 \ln T + C_4 T^{C_5} + C_6 T^3 + C_7 T^6 + \frac{C_8}{T^2} + \frac{C_9}{T^4} + C_{10} T^2$
Liquid Enthalpy, Liquid Density, Liquid Thermal Conductivity, Surface Tension, Ideal Enthalpy, Vapour viscosity	$\text{Prop} = \sum_{i=1}^{n} C_i T^{i-1}$
Vaporisation enthalpy	$\text{Prop} = C_1 (1 - T_r)^X$; $X = C_2 + C_3 T_r + C_4 T_r^2 + C_5 T_r^3$; $T_r = T/T_c$
Vapour Thermal Conductivity	$\text{Prop} = C_1 T^{C_2} / (1 + C_3 / T + C_4 / T^2)$

*All the correlations are DIPPR correlations wildly available in process-product simulators and other computer-aided tools.

APPENDIX B
VLE DATASETS

The binary VLE data systems identified with the method which was presented in Chapter 3, are listed in Table B.1 highlighting the results from the two algorithms of the method (Algorithm A and Algorithm B). The detailed list of the VLE data is given in Table B.2. The table includes the results from the consistency test applied using TDE (Diky et al., 2012) as follows: T1 – Herington test (Wisniak, 1994), T2 - Van Ness test (Van Ness et al., 1973),T3 – Point test (Kojima et al., 1990; Kurihara et al., 2004), T4 - Infinite dilution test (Kojima et al., 1990; Kurihara et al., 2004), T5 – End point test (Kang et al., 2010). The EOS test was not included since it was not applicable for majority of data sets with the exception of systems number 115-117 from Table B.2. These systems were not considered for the regression since they are at very high temperatures, close to methanol critical temperature point. The systems used for further validation of the parameters (Chapter 4) are listed in Table B.3. The systems used for parameters extrapolation (Chapter 5) are listed in Table B.4

Table B.1 Overview of the systems used for each category group as resulted from Algorithm A (Data Organisation) and Algorithm B (Data selection) application

Category Group X.M.N	Category Systems (Algorithm A) (No. from Table B.2 Column 1)	Selected systems selected for regression (Algorithm B) (No. from Table B.2 Column 1)
1.1.1	1 - 23	1 - 4
1.1.2	24 - 49	24 - 33
1.1.3	50 - 69	50 - 59
1.1.4	70 - 113	70 - 84
3.1.1	114	114
3.2.1	115-119	118-119
3.2.2	120-121	120-121
3.2.3	122-123	122-123
3.2.4	124-157	124-134
3.2.5	158-160	158
3.2.6	161-163	161-162
6.1.1	164-165	164-165
6.1.2	166-167	166-167
6.1.3	168-169	168
6.1.4	170	170
6.1.5	171-172	171-172
6.3.1	173	173
6.3.2	174	174

The new data used for validation presented in Chapter 4, but which was not included in the method application is listed in Table B.3.

Table B.2 Binary VLE data sets used for the systematic identification method application

No.	System compounds 1	2	Data Type	Data points no	iso T, K	isoP, kPa	Q_{VLE} (TDE)
1	Octanoic acid	Hexanoic acid	PTXY	15	-	13.33	0.65
2	Octanoic acid	Hexanoic acid	PTXY	12	-	2.67	0.56
3	Octanoic acid	Hexanoic acid	PTXY	17	-	6.67	0.49
4	Dodecanoic acid	Tetradecanoic acid	PTXY	11	-	0.53	0.24
5	Tetradecanoic acid	Hexadecanoic acid	PTXY	11	-	6.60	0.17
6	Dodecanoic acid	Tetradecanoic acid	PTXY	9	-	0.53	0.15
7	Tetradecanoic acid	Hexadecanoic acid	PTXY	12	-	6.70	0.12
8	Dodecanoic acid	Tetradecanoic acid	PTXY	13	-	6.70	0.11
9	Dodecanoic acid	Tetradecanoic acid	PTXY	13	-	1.30	0.11
10	Tetradecanoic acid	Hexadecanoic acid	PTXY	12	-	0.40	0.11
11	Octanoic acid	Decanoic acid	PTXY	9	-	13.30	0.1
12	Octanoic acid	Decanoic acid	PTXY	9	-	2.70	0.1
13	Hexadecanoic acid	Octadecanoc acid	PTXY	8	-	0.53	0.1
14	Tetradecanoic acid	Hexadecanoic acid	PTXY	12	-	1.30	0.086
15	Dodecanoic acid	Tetradecanoic acid	PTXY	6	-	0.50	0.022
16	Tetradecanoic acid	Hexadecanoic acid	PTXY	8	-	0.50	0.014
17	Octanoic acid	Hexanoic acid	PTXY	13	-	1.30	0.01
18	Dodecanoic acid	Tetradecanoic acid	PTXY	13	-	0.37	0.003
19	Octanoic acid	Hexanoic acid	PTXY	11	-	13.30	0
20	Hexanoic acid	Octanoic acid	PTXY	13	-	1.30	0
21	Octanoic acid	Hexanoic acid	PTXY	11	-	4.00	0
22	Decanoic	Dodecanoic acid	PTXY	14	-	0.47	0
23	Decanoic	Dodecanoic acid	PTXY	14	-	13.30	0
24	Methyl decanoate	Methyl octanoate	PTX	6	-	5.30	0.76
25	Methyl tetradecanoate	n-Tetradecane	PTX	11	-	5.00	0.71
26	Methyl tetradecanoate	n-Pentadecane	PTX	9	-	5.00	0.62
27	Methyl decanoate	Methyl octanoate	PTX	6	-	4.00	0.56
28	Methyl Dodecanoate	Methyl tetradecanoate	PTXY	4	-	5.30	0.52
29	Methyl tetradecanoate	n-Hexadecane	PTX	10	-	5.00	0.4
30	Methyl decanoate	Methyl octanoate	PTX	6	-	13.33	0.38
31	Methyl decanoate	Methyl octanoate	PTX	7	-	6.60	0.33
32	Methyl dodecanoate	Methyl tetradecanoate	PTXY	5	-	6.60	0.32

Individual consistency test results (TDE)					Reference
Q_1	Q_2	Q_3	Q_4	Q_5	
Passed	Failed	N/A	Failed	0.93	Rose, A.; Acciarri, J. A.; Williams, E. T. Chem. Eng. Data Ser., 1958, 3, 210-2
Failed	Failed	N/A	Failed	0.93	Rose, A.; Acciarri, J. A.; Williams, E. T. Chem. Eng. Data Ser., 1958, 3, 210-3
Passed	Failed	N/A	Failed	0.76	Rose, A.; Acciarri, J. A.; Williams, E. T. Chem. Eng. Data Ser., 1958, 3, 210-4
Passed	Failed	N/A	Failed	0.42	Rao, M. V.; Rao, V. K.; Husain, A.; Chari, K. S. Indian J. Technol., 1963, 1, 441
Failed	Failed	N/A	Failed	0.46	Matricarde Falleiro, R. M.; Meirelles, A. J. A.; Krahenbuhl, M. A.; J. Chem. Thermodyn., 2010, 42, 70-77.
Failed	Failed	N/A	Failed	0.51	Monick, J. A.; Allen, H. D.; Marlies, C. J. Oil and Soap (Chicago), 1946, 23, 177
Failed	Failed	N/A	Failed	0.42	Muller and Stage, 1965
Failed	Failed	N/A	Failed	1	Muller and Stage, 1962
Failed	Failed	N/A	Failed	0.32	Muller and Stage, 1963
Failed	Failed	N/A	Failed	0.23	Muller and Stage, 1967
N/A	Failed	N/A	N/A	0.1	Muller and Stage, 1961
N/A	Failed	N/A	N/A	0.1	Muller and Stage, 1961
N/A	Failed	N/A	N/A	0.1	Williams, F. C.; Osburn, J. O. J. Am. Oil Chem. Soc., 1949, 26, 663
Failed	Failed	N/A	Failed	0.26	Muller and Stage, 1966
Failed	Failed	N/A	Failed	0.13	Williams, F. C.; Osburn, J. O. J. Am. Oil Chem. Soc., 1949, 26, 663
Failed	Failed	N/A	Failed	0.1	Williams, F. C.; Osburn, J. O. J. Am. Oil Chem. Soc., 1949, 26, 663
N/A	Failed	N/A	N/A	0.1	Muller and Stage, 1963
Failed	Failed	N/A	Failed	0.03	Muller and Stage, 1964
N/A	N/A	N/A	N/A	0	Muller and Stage, 1961
N/A	N/A	N/A	N/A	0	Muller and Stage, 1961
N/A	N/A	N/A	N/A	0	Muller and Stage, 1962
N/A	N/A	N/A	N/A	0	Muller and Stage, 1961
N/A	N/A	N/A	N/A	0	Muller and Stage, 1961
Passed	Passed	N/A	Failed	1	Rose, A.; Supina, W. R.; J. Chem. Eng. Data, 1961, 6, 173
Passed	Passed	N/A	Failed	0.97	Li, H., Luo, H., Xia, S., Ma, P., Fluid Phase Equilib., 2016, 408, 47–51.
Passed	Passed	N/A	Failed	0.85	Li, H., Luo, H., Xia, S., Ma, P., Fluid Phase Equilib., 2016, 408, 47–51.
Failed	Passed	N/A	Failed	1	Rose, A.; Supina, W. R.; J. Chem. Eng. Data, 1961, 6, 173
Passed	Failed	N/A	Failed	0.8	Rose, A.; Supina, W. R.; J. Chem. Eng. Data, 1961, 6, 176
Passed	Passed	N/A	Failed	0.8	Li, H., Luo, H., Xia, S., Ma, P., Fluid Phase Equilib., 2016, 408, 47–51.
Failed	Failed	N/A	Failed	0.83	Rose, A.; Supina, W. R.; J. Chem. Eng. Data, 1961, 6, 173
Failed	Failed	N/A	Failed	0.77	Rose, A.; Supina, W. R.; J. Chem. Eng. Data, 1961, 6, 174
Passed	Failed	N/A	Failed	0.54	Rose, A.; Supina, W. R.; J. Chem. Eng. Data, 1961, 6, 175

Table B.2 Binary VLE data sets used for the systematic identification method application (Continued)

No.	System compounds 1	2	Data Type	Data points no	iso T, K	isoP, kPa	Q_{VLE} (TDE)
33	Methyl dodecanoate	Methyl tetradecanoate	PTXY	5	-	4.00	0.25
34	Methyl hexanoate	Methyl octanoate	PTX	3	-	2.60	0.25
35	Methyl hexanoate	Methyl octanoate	PTX	3	-	4.00	0.25
36	Methyl hexanoate	Methyl octanoate	PTX	4	-	5.30	0.25
37	Methyl hexanoate	Methyl octanoate	PTX	43	-	6.60	0.25
38	Ethyl tetradecanoate	Ethyl hexanoate	PTXY	12	-	1.57	0.24
39	Methyl hexadecanoate	Methyl octadecanoate	PTXY	10	-	10.00	0.24
40	Methyl hexadecanoate	Methyl octadecanoate	PTXY	9	-	5.00	0.14
41	Ethyl hexadecanoate	Ethyl octadecanoate	PTX	9	-	5.33	0.074
42	Methyl hexadecanoate	Methyl octadecanoate	PTXY	9	-	1.00	0.069
43	Ethyl tetradecanoate	Ethyl hexanoate	PTXY	13	-	1.00	0.051
44	Ethy tetradecanoate	Ethyl hexanoate	PTXY	14	-	0.50	0.033
45	Methyl hexadecanoate	Methyl octadecanoate	PTXY	9	-	0.10	0.021
46	Methyl tetradecanoate	Methyl hexadecanoate	PTXY	10	-	1.40	0.001
47	Methyl tetradecanoate	Methyl hexadecanoate	PTXY	11	-	1.00	0.001
48	Methyl Dodecanoate	Methyl tetradecanoate	PTXY	7	-	13.30	0.001
49	Methyl tetradecanoate	Methyl hexadecanoate	PTXY	11	-	0.50	0.001
50	Glycerol	Methanol	PTX	5	334.97	-	0.5
51	Glycerol	Methanol	PTX	11		45.30	0.38
52	Glycerol	Methanol	PTX	11	-	66.70	0.33
53	Glycerol	Methanol	PTX	11	-	53.30	0.33
54	Glycerol	Methanol	PTX	11	-	46.70	0.33
55	Glycerol	Methanol	PTX	11	-	60.00	0.33
56	Glycerol	Methanol	PTX	11	-	32.02	0.33
57	Glycerol	Methanol	PTX	23	-	101.33	0.25

Individual consistency test results (TDE)					Reference
Q_1	Q_2	Q_3	Q_4	Q_5	
N/A	N/A	N/A	N/A	0.49	Rose, A.; Supina, W. R.; J. Chem. Eng. Data, 1961, 6, 176
N/A	N/A	N/A	N/A	0.49	Rose, A.; Supina, W. R.; J. Chem. Eng. Data, 1961, 6, 177
N/A	N/A	N/A	N/A	0.49	Rose, A.; Supina, W. R.; J. Chem. Eng. Data, 1961, 6, 178
N/A	N/A	N/A	N/A	0.49	Rose, A.; Supina, W. R.; J. Chem. Eng. Data, 1961, 6, 179
Failed	Failed	N/A	Failed	0.74	Rose, A.; Supina, W. R.; J. Chem. Eng. Data, 1961, 6, 180
Failed	Passed	N/A	Failed	0.52	Tang, Z., Du, Z., Min, E., Gao, L., Jiang, T., Han, B., Fluid Phase Equilib., 2006, 239, 8–11.
Passed	Failed	N/A	Failed	0.37	Hou, J., Xu, S., Ding, H., Sun, T., J. Chem. Eng. Data, 2012, 57, 2632–2639.
Passed	Failed	N/A	Failed	0.18	Hou, J., Xu, S., Ding, H., Sun, T., J. Chem. Eng. Data, 2012, 57, 2632–2639.
Failed	Failed	N/A	Failed	0.3	Akisawa Silva, L.Y., Matricarde Falleiro, R.M., Meirelles, A.J. A., Krähenbühl, M. A., Thermochim. Acta, 2011, 512, 178–182.
Failed	Failed	N/A	Failed	0.27	Hou, J., Xu, S., Ding, H., Sun, T., J. Chem. Eng. Data, 2012, 57, 2632–2639.
Failed	Failed	N/A	Failed	0.24	Tang, Z., Du, Z., Min, E., Gao, L., Jiang, T., Han, B., Fluid Phase Equilib., 2006, 239, 8–11.
Failed	Failed	N/A	Failed	0.15	Tang, Z., Du, Z., Min, E., Gao, L., Jiang, T., Han, B., Fluid Phase Equilib., 2006, 239, 8–11.
Failed	Failed	N/A	Failed	0.08	Hou, J., Xu, S., Ding, H., Sun, T., J. Chem. Eng. Data, 2012, 57, 2632–2639.
Failed	Failed	N/A	Failed	0.01	Chen, R., Ding, H., Liu, M., Zhou, H., Chen, N., Fluid Phase Equilib., 2014, 382, 133–138.
Failed	Failed	N/A	Failed	0.01	Chen, R., Ding, H., Liu, M., Zhou, H., Chen, N., Fluid Phase Equilib., 2014, 382, 133–138.
Failed	Failed	N/A	Failed	0.01	Rose and Supina, 1961 J. CHEM. ENG. DATA, 6, 173-179
Failed	Failed	N/A	Failed	0.01	Chen, R., Ding, H., Liu, M., Zhou, H., Chen, N., Fluid Phase Equilib., 2014, 382, 133–138.
N/A	N/A	N/A	N/A	1	Dulitskaya, K. A. Zh. Obshch. Khim., 1945, 15, 9-21
N/A	N/A	N/A	N/A	0.75	Soujanya, J.; satyavathi, B.; Vittal Prasad, T. E. J. Chem. Thermodyn., 2010, 42, 621 (-624)
N/A	N/A	N/A	N/A	0.67	Veneral, J.G., Junior, D.L.R., Mazutti, M. a., Voll, F. a P., Cardozo-Filho, L., Corazza, M.L., Oliveira, J.V., J. Chem. Thermodyn., 2013, 60, 46–51.
N/A	N/A	N/A	N/A	0.67	Veneral, J.G., Junior, D.L.R., Mazutti, M. a., Voll, F. a P., Cardozo-Filho, L., Corazza, M.L., Oliveira, J.V., J. Chem. Thermodyn., 2013, 60, 46–51.
N/A	N/A	N/A	N/A	0.67	Veneral, J.G., Junior, D.L.R., Mazutti, M. a., Voll, F. a P., Cardozo-Filho, L., Corazza, M.L., Oliveira, J.V., J. Chem. Thermodyn., 2013, 60, 46–51.
N/A	N/A	N/A	N/A	0.66	Veneral, J.G., Junior, D.L.R., Mazutti, M. a., Voll, F. a P., Cardozo-Filho, L., Corazza, M.L., Oliveira, J.V., J. Chem. Thermodyn., 2013, 60, 46–51.
N/A	N/A	N/A	N/A	0.65	Soujanya, J.; satyavathi, B.; Vittal Prasad, T. E. J. Chem. Thermodyn., 2010, 42, 621 (-624)
N/A	N/A	N/A	N/A	0.5	Oliveira, M.B., Teles, A.R.R., Queimada, A.J., Coutinho, J.A.P., Fluid Phase Equilib., 2009, 280, 22–29.

Table B.2 Binary VLE data sets used for the systematic identification method application (Continued)

No.	System compounds 1	2	Data Type	Data points no	iso T, K	isoP, kPa	Q_{VLE} (TDE)
58	Glycerol	Methanol	PTX	11	-	20.00	0.25
59	Glycerol	Methanol	PTX	6	493.00	-	0.25
60	Glycerol	Methanol	PTX	5	523.00	-	0.25
61	Glycerol	Methanol	PTX	4	543.00	-	0.25
62	Glycerol	Methanol	PTX	11	-	13.30	0.2
63	Glycerol	Methanol	PTX	11	-	26.70	0.19
64	Glycerol	Methanol	PTX	5	322.98	-	0.18
65	Glycerol	Methanol	PTX	11	-	33.30	0.15
66	Glycerol	Methanol	PTX	9	313.13	-	0.13
67	Glycerol	Methanol	PTX	11	-	6.70	0.087
68	Glycerol	Methanol	PTX	5	297.99	-	0.075
69	Glycerol	Methanol	PTX	11	-	40.00	0.063
70	Glycerol	Water	PTX	7	343.12	-	0.5
71	Glycerol	Water	PTX	8	322.97	-	0.5
72	Glycerol	Water	PTX	7	347.97	-	0.5
73	Glycerol	Water	PTX	10		95.30	0.5
74	Glycerol	Water	PTX	9		63.84	0.44
75	Glycerol	Water	PTX	10		54.72	0.42
76	Glycerol	Water	PTX	10		41.54	0.38
77	Glycerol	Water	PTX	7	347.97	-	0.37
78	Glycerol	Water	PTX	8	322.98	-	0.37
79	Glycerol	Water	PTX	6	-	101.33	0.33
80	Glycerol	Water	PTX	5	-	66.70	0.33
81	Glycerol	Water	PTX	19	298.14	-	0.33

Individual consistency test results (TDE)					Reference
Q_1	Q_2	Q_3	Q_4	Q_5	
N/A	N/A	N/A	N/A	0.5	Veneral, J.G., Junior, D.L.R., Mazutti, M. a., Voll, F. a P., Cardozo-Filho, L., Corazza, M.L., Oliveira, J.V., J. Chem. Thermodyn., 2013, 60, 46–51.
N/A	N/A	N/A	N/A	0.49	Shimoyama, Y.; Abeta, T.; Zhao, L.; Iwai, Y. Fluid Phase Equilib., 2009, 284, 64-69
N/A	N/A	N/A	N/A	0.49	Shimoyama, Y.; Abeta, T.; Zhao, L.; Iwai, Y. Fluid Phase Equilib., 2009, 284, 64-69
N/A	N/A	N/A	N/A	0.49	Shimoyama, Y.; Abeta, T.; Zhao, L.; Iwai, Y. Fluid Phase Equilib., 2009, 284, 64-69
N/A	N/A	N/A	N/A	0.4	Veneral, J.G., Junior, D.L.R., Mazutti, M. a., Voll, F. a P., Cardozo-Filho, L., Corazza, M.L., Oliveira, J.V., J. Chem. Thermodyn., 2013, 60, 46–51.
N/A	N/A	N/A	N/A	0.38	Veneral, J.G., Junior, D.L.R., Mazutti, M. a., Voll, F. a P., Cardozo-Filho, L., Corazza, M.L., Oliveira, J.V., J. Chem. Thermodyn., 2013, 60, 46–51.
N/A	N/A	N/A	N/A	0.17	Dulitskaya, K. A. Zh. Obshch. Khim., 1945, 15, 9-21
N/A	N/A	N/A	N/A	0.31	Veneral, J.G., Junior, D.L.R., Mazutti, M. a., Voll, F. a P., Cardozo-Filho, L., Corazza, M.L., Oliveira, J.V., J. Chem. Thermodyn., 2013, 60, 46–51.
N/A	N/A	N/A	N/A	0.25	Campbell, F. H.,. Trans. Faraday Soc., 1915, 11, 91
N/A	N/A	N/A	N/A	0.17	Veneral, J.G., Junior, D.L.R., Mazutti, M. a., Voll, F. a P., Cardozo-Filho, L., Corazza, M.L., Oliveira, J.V., J. Chem. Thermodyn., 2013, 60, 46–51.
N/A	N/A	N/A	N/A	0.15	Dulitskaya, K. A. Zh. Obshch. Khim., 1945, 15, 9-21
N/A	N/A	N/A	N/A	0.13	Veneral, J.G., Junior, D.L.R., Mazutti, M. a., Voll, F. a P., Cardozo-Filho, L., Corazza, M.L., Oliveira, J.V., J. Chem. Thermodyn., 2013, 60, 46–51.
N/A	N/A	N/A	N/A	1	Campbell Trans. Faraday Soc., 1915, 11, 91
N/A	N/A	N/A	N/A	1	Dulitskaya, K. A. Zh. Obshch. Khim., 1945, 15, 9-21
N/A	N/A	N/A	N/A	1	Dulitskaya, K. A. Zh. Obshch. Khim., 1945, 15, 9-21
N/A	N/A	N/A	N/A	1	Soujanya, J.; Satyavathi, B.; Vittal Prasad, T. E. J. Chem. Thermodyn., 2010, 42, 621-624
N/A	N/A	N/A	N/A	0.89	Soujanya, J.; Satyavathi, B.; Vittal Prasad, T. E. J. Chem. Thermodyn., 2010, 42, 621-625
N/A	N/A	N/A	N/A	0.84	Soujanya, J.; Satyavathi, B.; Vittal Prasad, T. E. J. Chem. Thermodyn., 2010, 42, 621-626
N/A	N/A	N/A	N/A	0.75	Soujanya, J.; Satyavathi, B.; Vittal Prasad, T. E. J. Chem. Thermodyn., 2010, 42, 621-627
N/A	N/A	N/A	N/A	0.75	Dulitskaya, K. A. Zh. Obshch. Khim., 1945, 15, 9-21
N/A	N/A	N/A	N/A	0.75	Dulitskaya, K. A. Zh. Obshch. Khim., 1945, 15, 9-21
N/A	N/A	N/A	N/A	0.67	Lewis J., Soc. Chem. Ind. (London), 1922, 41, 97
N/A	N/A	N/A	N/A	0.67	Veneral, J.G., Junior, D.L.R., Mazutti, M. a., Voll, F. a P., Cardozo-Filho, L., Corazza, M.L., Oliveira, J.V., J. Chem. Thermodyn., 2013, 60, 46–51.
N/A	N/A	N/A	N/A	0.67	Kirgintsev, A. N.; Lukyanov, A. V. Izv. Akad. Nauk SSSR, Ser. Khim., 1962, No. 8, 1479-81

Table B.2 Binary VLE data sets used for the systematic identification method application (Continued)

No.	System compounds 1	2	Data Type	Data points no	iso T, K	isoP, kPa	Q_{VLE} (TDE)
82	Glycerol	Water	PTX	9		29.38	0.31
83	Glycerol	Water	PTX	10		14.19	0.26
84	Glycerol	Water	PTX	7	279.99	-	0.25
85	Glycerol	Water	PTX	6	-	101.33	0.25
86	Glycerol	Water	PTX	5	-	13.30	0.21
87	Glycerol	Water	PTX	5	-	6.70	0.17
88	Glycerol	Water	PTX	8	363.15	-	0.17
89	Glycerol	Water	PTX	8	353.15	-	0.15
90	Glycerol	Water	PTX	25	298.00	-	0.15
91	Glycerol	Water	PTX	11	-	3.33	0.12
92	Glycerol	Water	PTX	11	-	13.33	0.098
93	Glycerol	Water	PTX	12	-	6.67	0.088
94	Glycerol	Water	PTX	11	-	1.33	0.088
95	Glycerol	Water	PTX	16		101.33	0.079
96	Glycerol	Water	PTX	8	343.15	-	0.055
97	Glycerol	Water	PTX	8	283.15	-	0.034
98	Glycerol	Water	PTX	10		101.33	0.032
99	Glycerol	Water	PTX	11		61.32	0.025
100	Glycerol	Water	PTX	11		74.66	0.024
101	Glycerol	Water	PTX	10		87.99	0.023
102	Glycerol	Water	PTX	16		66.70	0.023
103	Glycerol	Water	PTX	14		21.33	0.022
104	Glycerol	Water	PTX	12		47.99	0.021
105	Glycerol	Water	PTX	8	293.15	-	0.014
106	Glycerol	Water	PTX	8	303.15	-	0.013
107	Glycerol	Water	PTX	26		33.30	0.013
108	Glycerol	Water	PTX	8	333.15	-	0.011

Individual consistency test results (TDE)					Reference
Q_1	Q_2	Q_3	Q_4	Q_5	
N/A	N/A	N/A	N/A	0.62	Soujanya, J.; Satyavathi, B.; Vittal Prasad, T. E. J. Chem. Thermodyn., 2010, 42, 621-625
N/A	N/A	N/A	N/A	0.51	Soujanya, J.; Satyavathi, B.; Vittal Prasad, T. E. J. Chem. Thermodyn., 2010, 42, 621-625
N/A	N/A	N/A	N/A	0.49	Dulitskaya, K. A. Zh. Obshch. Khim., 1945, 15, 9-21
N/A	N/A	N/A	N/A	0.49	Gruen, A.; Wirth, T. Angew. Chem., 1919, 32, 59-62
N/A	N/A	N/A	N/A	0.41	Veneral, J.G., Junior, D.L.R., Mazutti, M. a., Voll, F. a P., Cardozo-Filho, L., Corazza, M.L., Oliveira, J.V., J. Chem. Thermodyn., 2013, 60, 46–51.
N/A	N/A	N/A	N/A	0.35	Veneral, J.G., Junior, D.L.R., Mazutti, M. a., Voll, F. a P., Cardozo-Filho, L., Corazza, M.L., Oliveira, J.V., J. Chem. Thermodyn., 2013, 60, 46–51.
N/A	N/A	N/A	N/A	0.34	Zaoui-Djelloul-Daouadji, M., Negadi, A., Mokbel, I., Negadi, L., J. Chem. Thermodyn., 2014, 69, 165–171.
N/A	N/A	N/A	N/A	0.3	Zaoui-Djelloul-Daouadji, M., Negadi, A., Mokbel, I., Negadi, L., J. Chem. Thermodyn., 2014, 69, 165–171.
N/A	N/A	N/A	N/A	0.31	To, E. C. H.; Davies, J. V.; Tucker, M.; Westh, P.; Trandum, C.; Suh, K. S.; Koga, Y., J. Solution Chem., 1999, 28(10), 1137-1157
N/A	Failed	N/A	N/A	0.03	Sokolov, N. M.; Tsygankova, L. N.; Zhavoronkov, N. M.Khim. Prom-st., 1972, 48, 96-7
N/A	Failed	N/A	N/A	0.31	Sokolov, N. M.; Tsygankova, L. N.; Zhavoronkov, N. M.Khim. Prom-st., 1972, 48, 96-8
N/A	Failed	N/A	N/A	0.3	Sokolov, N. M.; Tsygankova, L. N.; Zhavoronkov, N. M.Khim. Prom-st., 1972, 48, 96-9
N/A	Failed	N/A	N/A	0.3	Sokolov, N. M.; Tsygankova, L. N.; Zhavoronkov, N. M.Khim. Prom-st., 1972, 48, 96-10
Passed	Failed	N/A	Faield	0.18	Chen, D. H. T.; Thompson, A. R. J. Chem. Eng. Data, 1970, 15, 471
N/A	N/A	N/A	N/A	0.11	Zaoui-Djelloul-Daouadji, M., Negadi, A., Mokbel, I., Negadi, L., J. Chem. Thermodyn., 2014, 69, 165–171.
N/A	N/A	N/A	N/A	0.07	Zaoui-Djelloul-Daouadji, M., Negadi, A., Mokbel, I., Negadi, L., J. Chem. Thermodyn., 2014, 69, 165–171.
N/A	Failed	N/A	Failed	0.18	Stewart, G. W. Phys. Rev., 1928, 32, 153
Failed	Failed	N/A	Failed	0.16	Stewart, G. W. Phys. Rev., 1928, 32, 153
Failed	Failed	N/A	Failed	0.17	Stewart, G. W. Phys. Rev., 1928, 32, 153
Failed	Failed	N/A	Failed	0.17	Stewart, G. W. Phys. Rev., 1928, 32, 153
Failed	Failed	N/A	Faield	0.18	Rho and Kang, 1997 (DECHEMA)
Failed	Failed	N/A	Failed	0.14	Stewart, G. W. Phys. Rev., 1928, 32, 153
Failed	Failed	N/A	Failed	0.16	Stewart, G. W. Phys. Rev., 1928, 32, 153
N/A	N/A	N/A	N/A	0.03	Zaoui-Djelloul-Daouadji, M., Negadi, A., Mokbel, I., Negadi, L., J. Chem. Thermodyn., 2014, 69, 165–171.
N/A	N/A	N/A	N/A	0.03	Zaoui-Djelloul-Daouadji, M., Negadi, A., Mokbel, I., Negadi, L., J. Chem. Thermodyn., 2014, 69, 165–171.
Failed	Failed	N/A	Faield	0.1	Rho and Kang, 1997 (DECHEMA)
N/A	N/A	N/A	N/A	0.02	Zaoui-Djelloul-Daouadji, M., Negadi, A., Mokbel, I., Negadi, L., J. Chem. Thermodyn., 2014, 69, 165–171.

Table B.2 Binary VLE data sets used for the systematic identification method application (Continued)

No.	System compounds 1	2	Data Type	Data points no	iso T, K	isoP, kPa	Q_{VLE} (TDE)
109	Glycerol	Water	PTX	8	313.15	-	0.011
110	Glycerol	Water	PTX	8	323.15	-	0.01
111	Glycerol	Water	PTX	19		13.30	0.01
112	Glycerol	Water	PTX	11	373.12	-	0.005
113	Glycerol	Water	PTX	9	273.15	-	0.034
114	Methyl dodecanoate	Dodecanoic acid	PTXY	9	-	0.53	0.027
115	Methyl dodecanoate	Methanol	PTXY	7	493.00	-	0.5
116	Methyl dodecanoate	Methanol	PTXY	6	523.00	-	0.5
117	Methyl dodecanoate	Methanol	PTXY	7	543.00	-	0.5
118	Methyl dodecanoate	Methanol	PTX	15	-	101.33	0.25
119	Methyl tetradecanoate	Methanol	PTX	15	-	101.33	0.25
120	Methyl dodecanoate	Ethanol	PTX	17	-	101.33	0.25
121	Methyl tetradecanoate	Ethanol	PTX	15	-	101.33	0.25
122	Glyceryl monooctanoate	Methyl hexadecanoate	PTX	11	-	1.20	0.009
123	Glyceryl monooctanoate	Methyl hexadecanoate	PTX	11	-	2.50	0.009
124	Glycerol	Ethanol	PTX	9	333.15	-	0.46
125	Glycerol	2-Propanol	PTX	9	343.15	-	0.45
126	Glycerol	Ethanol	PTX	11	-	66.70	0.33
127	Glycerol	Ethanol	PTX	11	-	60.00	0.33
128	Glycerol	Ethanol	PTX	11	-	53.30	0.33
129	Glycerol	Ethanol	PTX	11	-	46.70	0.33
130	Glycerol	Ethanol	PTX	11	-	40.00	0.33

Individual consistency test results (TDE)					Reference
Q_1	Q_2	Q_3	Q_4	Q_5	
N/A	N/A	N/A	N/A	0.02	Zaoui-Djelloul-Daouadji, M., Negadi, A., Mokbel, I., Negadi, L., J. Chem. Thermodyn., 2014, 69, 165–171.
N/A	N/A	N/A	N/A	0.02	Zaoui-Djelloul-Daouadji, M., Negadi, A., Mokbel, I., Negadi, L., J. Chem. Thermodyn., 2014, 69, 165–171.
Failed	Failed	N/A	Faield	0.1	Rho and Kang, 1997 (DECHEMA)
N/A	N/A	N/A	N/A	0.01	Drucker, K.; Moles, E. Z. Phys. Chem., Stoechiom. Verwandschaftsl., 1911, 75, 405
N/A	N/A	N/A	N/A	0.07	Zaoui-Djelloul-Daouadji, M., Negadi, A., Mokbel, I., Negadi, L., J. Chem. Thermodyn., 2014, 69, 165–171.
Failed	Failed	N/A	Failed	0.11	Monick, J. A.; Allen, H. D.; Marlies, C. J.; Oil and Soap (Chicago), 1946, 23, 177
N/A	N/A	N/A	N/A	0.5	Shimoyama, Y.; Iwai, Y.; Jin, B. S.; Hirayama, T.; Arai, Y.; Fluid Phase Equilib., 2007, 257, 217-222
N/A	N/A	N/A	N/A	0.5	Shimoyama, Y.; Iwai, Y.; Jin, B. S.; Hirayama, T.; Arai, Y.; Fluid Phase Equilib., 2007, 257, 217-223
N/A	N/A	N/A	N/A	0.5	Shimoyama, Y.; Iwai, Y.; Jin, B. S.; Hirayama, T.; Arai, Y.; Fluid Phase Equilib., 2007, 257, 217-224
N/A	N/A	N/A	N/A	0.5	Oliveira, M.B., Miguel, S.I., Queimada, A.J., Coutinho, J.A.P., Ind. Eng. Chem. Res., 2010, 49, 3452–3458.
N/A	N/A	N/A	N/A	0.5	Oliveira, M.B., Miguel, S.I., Queimada, A.J., Coutinho, J.A.P., Ind. Eng. Chem. Res., 2010, 49, 3452–3458.
N/A	N/A	N/A	N/A	0.5	Oliveira, M.B., Miguel, S.I., Queimada, A.J., Coutinho, J.A.P., Ind. Eng. Chem. Res., 2010, 49, 3452–3458.
N/A	N/A	N/A	N/A	0.5	Oliveira, M.B., Miguel, S.I., Queimada, A.J., Coutinho, J.A.P., Ind. Eng. Chem. Res., 2010, 49, 3452–3458.
N/A	N/A	N/A	N/A	0.02	Cunico, L.P., Damaceno, D.S., Matricarde Falleiro, R.M., Sarup, B., Abildskov, J., Ceriani, R., Gani, R., J. Chem. Thermodyn., 2015, 91, 108–115.
N/A	N/A	N/A	N/A	0.02	Cunico, L.P., Damaceno, D.S., Matricarde Falleiro, R.M., Sarup, B., Abildskov, J., Ceriani, R., Gani, R., J. Chem. Thermodyn., 2015, 91, 108–115.
N/A	N/A	N/A	N/A	0.91	Wibawa, G., Mustain, A., Akbarina, M.F., Ruslim, R.M., J. Chem. Eng. Data, 2015, 60, 955–959
N/A	N/A	N/A	N/A	0.9	Wibawa, G., Mustain, A., Akbarina, M.F., Ruslim, R.M., J. Chem. Eng. Data, 2015, 60, 955–959
N/A	N/A	N/A	N/A	0.67	Veneral, J.G., Junior, D.L.R., Mazutti, M. a., Voll, F. a P., Cardozo-Filho, L., Corazza, M.L., Oliveira, J.V., J. Chem. Thermodyn., 2013, 60, 46–51.
N/A	N/A	N/A	N/A	0.67	Veneral, J.G., Junior, D.L.R., Mazutti, M. a., Voll, F. a P., Cardozo-Filho, L., Corazza, M.L., Oliveira, J.V., J. Chem. Thermodyn., 2013, 60, 46–51.
N/A	N/A	N/A	N/A	0.67	Veneral, J.G., Junior, D.L.R., Mazutti, M. a., Voll, F. a P., Cardozo-Filho, L., Corazza, M.L., Oliveira, J.V., J. Chem. Thermodyn., 2013, 60, 46–51.
N/A	N/A	N/A	N/A	0.67	Veneral, J.G., Junior, D.L.R., Mazutti, M. a., Voll, F. a P., Cardozo-Filho, L., Corazza, M.L., Oliveira, J.V., J. Chem. Thermodyn., 2013, 60, 46–51.
N/A	N/A	N/A	N/A	0.67	Veneral, J.G., Junior, D.L.R., Mazutti, M. a., Voll, F. a P., Cardozo-Filho, L., Corazza, M.L., Oliveira, J.V., J. Chem. Thermodyn., 2013, 60, 46–51.

Table B.2 Binary VLE data sets used for the systematic identification method application (Continued)

No.	System compounds 1	2	Data Type	Data points no	iso T, K	isoP, kPa	Q_{VLE} (TDE)
131	Glycerol	Ethanol	PTX	9	345.15	-	0.31
132	Glycerol	Ethanol	PTX	11	-	20.00	0.27
133	Glycerol	Ethanol	PTX	4	322.97	-	0.27
134	Glycerol	2-Propanol	PTX	9	333.15	-	0.26
135	Glycerol	Ethanol	PTX	8	343.15	-	0.24
136	Glycerol	Ethanol	PTX	4	347.97	-	0.23
137	Glycerol	Ethanol	PTX	20	-	101.33	0.25
138	Glycerol	Ethanol	PTX	11	-	13.30	0.21
139	Glycerol	Ethanol	PTX	11	-	26.70	0.19
140	Glycerol	Ethanol	PTX	11	-	6.70	0.17
141	Glycerol	Ethanol	PTX	11	-	33.30	0.15
142	Glycerol	Ethanol	PTX	4	297.98	-	0.082
143	Glycerol	Ethanol	PTX	8	353.15	-	0.055
144	Glycerol	Ethanol	PTX	8	293.15	-	0.036
145	Glycerol	Ethanol	PTX	8	303.15	-	0.025
146	Glycerol	Ethanol	PTX	8	313.15	-	0.013
147	Glycerol	Ethanol	PTX	8	323.15	-	0.011
148	Glycerol	Ethanol	PTX	8	333.15	-	0.01
149	Glycerol	Ethanol	PTX	9	273.15	-	0.034
150	Glycerol	Ethanol	PTX	9	283.15	-	0.017
151	Glycerol	1-Propanol	PTX	23	-	101.33	0.25
152	Glycerol	2-Propanol	PTX	20	-	101.33	0.25
153	Glycerol	1-Butanol	PTX	23	-	101.33	0.25

Individual consistency test results (TDE)					Reference
Q_1	Q_2	Q_3	Q_4	Q_5	
N/A	N/A	N/A	N/A	0.61	Wibawa, G., Mustain, A., Akbarina, M.F., Ruslim, R.M., J. Chem. Eng. Data, 2015, 60, 955–959
N/A	N/A	N/A	N/A	0.55	Veneral, J.G., Junior, D.L.R., Mazutti, M. a., Voll, F. a P., Cardozo-Filho, L., Corazza, M.L., Oliveira, J.V., J. Chem. Thermodyn., 2013, 60, 46–51.
N/A	N/A	N/A	N/A	0.54	Dulitskaya, K. A.; Vapor pressure of binary system: I; Zh. Obshch. Khim., 1945, 15, 9-21
N/A	N/A	N/A	N/A	0.52	Wibawa, G., Mustain, A., Akbarina, M.F., Ruslim, R.M., J. Chem. Eng. Data, 2015, 60, 955–959
N/A	N/A	N/A	N/A	0.48	Zaoui-Djelloul-Daouadji, M., Negadi, A., Mokbel, I., Negadi, L., J. Chem. Thermodyn., 2014, 69, 165–171.
N/A	N/A	N/A	N/A	0.47	Dulitskaya, K. A.; Zh. Obshch. Khim., 1945, 15, 9-21
N/A	N/A	N/A	N/A	0.49	Oliveira, M.B., Teles, A.R.R., Queimada, A.J., Coutinho, J.A.P., Fluid Phase Equilib., 2009, 280, 22–29.
N/A	N/A	N/A	N/A	0.41	Veneral, J.G., Junior, D.L.R., Mazutti, M. a., Voll, F. a P., Cardozo-Filho, L., Corazza, M.L., Oliveira, J.V., J. Chem. Thermodyn., 2013, 60, 46–51.
N/A	N/A	N/A	N/A	0.38	Veneral, J.G., Junior, D.L.R., Mazutti, M. a., Voll, F. a P., Cardozo-Filho, L., Corazza, M.L., Oliveira, J.V., J. Chem. Thermodyn., 2013, 60, 46–51.
N/A	N/A	N/A	N/A	0.35	Veneral, J.G., Junior, D.L.R., Mazutti, M. a., Voll, F. a P., Cardozo-Filho, L., Corazza, M.L., Oliveira, J.V., J. Chem. Thermodyn., 2013, 60, 46–51.
N/A	N/A	N/A	N/A	0.31	Veneral, J.G., Junior, D.L.R., Mazutti, M. a., Voll, F. a P., Cardozo-Filho, L., Corazza, M.L., Oliveira, J.V., J. Chem. Thermodyn., 2013, 60, 46–51.
N/A	N/A	N/A	N/A	0.16	Dulitskaya, K. A.; Zh. Obshch. Khim., 1945, 15, 9-21
N/A	N/A	N/A	N/A	0.11	Zaoui-Djelloul-Daouadji, M., Negadi, A., Mokbel, I., Negadi, L., J. Chem. Thermodyn., 2014, 69, 165–171.
N/A	N/A	N/A	N/A	0.07	Zaoui-Djelloul-Daouadji, M., Negadi, A., Mokbel, I., Negadi, L., J. Chem. Thermodyn., 2014, 69, 165–171.
N/A	N/A	N/A	N/A	0.05	Zaoui-Djelloul-Daouadji, M., Negadi, A., Mokbel, I., Negadi, L., J. Chem. Thermodyn., 2014, 69, 165–171.
N/A	N/A	N/A	N/A	0.03	Zaoui-Djelloul-Daouadji, M., Negadi, A., Mokbel, I., Negadi, L., J. Chem. Thermodyn., 2014, 69, 165–171.
N/A	N/A	N/A	N/A	0.02	Zaoui-Djelloul-Daouadji, M., Negadi, A., Mokbel, I., Negadi, L., J. Chem. Thermodyn., 2014, 69, 165–171.
N/A	N/A	N/A	N/A	0.02	Zaoui-Djelloul-Daouadji, M., Negadi, A., Mokbel, I., Negadi, L., J. Chem. Thermodyn., 2014, 69, 165–171.
N/A	N/A	N/A	N/A	0.07	Zaoui-Djelloul-Daouadji, M., Negadi, A., Mokbel, I., Negadi, L., J. Chem. Thermodyn., 2014, 69, 165–171.
N/A	N/A	N/A	N/A	0.03	Zaoui-Djelloul-Daouadji, M., Negadi, A., Mokbel, I., Negadi, L., J. Chem. Thermodyn., 2014, 69, 165–171.
N/A	N/A	N/A	N/A	0.49	Oliveira, M.B., Teles, A.R.R., Queimada, A.J., Coutinho, J.A.P., Fluid Phase Equilib., 2009, 280, 22–29.
N/A	N/A	N/A	N/A	0.49	Oliveira, M.B., Teles, A.R.R., Queimada, A.J., Coutinho, J.A.P., Fluid Phase Equilib., 2009, 280, 22–29.
N/A	N/A	N/A	N/A	0.49	Oliveira, M.B., Teles, A.R.R., Queimada, A.J., Coutinho, J.A.P., Fluid Phase Equilib., 2009, 280, 22–29.

Table B.2 Binary VLE data sets used for the systematic identification method application (Continued)

No.	System compounds 1	2	Data Type	Data points no	iso T, K	isoP, kPa	Q_{VLE} (TDE)
154	Glycerol	2-Propanol	PTX	18		53.33	0
155	Glycerol	2-Propanol	PTX	18		66.66	0
156	Glycerol	2-Propanol	PTX	18		79.99	0
157	Glycerol	2-Propanol	PTX	18		94.93	0.25
158	n-Hexane	Oleic acid	PTX	12	318.14	-	0.5
159	Hexadecanoic acid	Oleic acid	PTX	10	-	0.67	0.043
160	Hexadecanoic acid	Oleic acid	PTX	13	-	0.33	0.0068
161	Methyl hexadecanoate	Methyl linoleate	PTX	9	-	4.00	0.27
162	n-Hexane	Triolein	PTX	11	318.14	-	0.377
163	Ethyl hexadecanoate	Ethyl oleate	PTX	11	-	5.33	0.097
164	Glyceryl monooctanoate	Hexadecanoic acid	PTX	12	-	1.20	0.008
165	Glyceryl monooctanoate	Hexadecanoic acid	PTX	12	-	2.50	0.011
166	Methyl oleate	Methanol	PTX	16	-	101.33	0.25
167	Methyl oleate	Methanol	PTX	4	-	30.00	0.25
168	Methyl oleate	Ethanol	PTX	15	-	101.33	0.25
169	Triolein	2-Propanol	PTX	11	318.15	-	0.001
170	Oleic acid	Methanol	PTX	12	318.14	-	0.5
171	Oleic acid	2-Propanol	PTX	14	318.15	-	0.5
172	Oleic acid	Ethanol	PTX	13	318.15	-	0.008
173	Triolein	Acetone	PTX	11	318.14	-	0.476
174	Oleic acid	Acetone	PTX	14	318.15	-	0.5

Individual consistency test results (TDE)					Reference
Q_1	Q_2	Q_3	Q_4	Q_5	
N/A	N/A	N/A	N/A	0	Soujanya, J., Anvesh Reddy, C., Satyavathi, B., Sankarshana, T., Fluid Phase Equilib., 2016, 409, 327–333
N/A	N/A	N/A	N/A	0	Soujanya, J., Anvesh Reddy, C., Satyavathi, B., Sankarshana, T., Fluid Phase Equilib., 2016, 409, 327–333
N/A	N/A	N/A	N/A	0	Soujanya, J., Anvesh Reddy, C., Satyavathi, B., Sankarshana, T., Fluid Phase Equilib., 2016, 409, 327–333
N/A	N/A	N/A	N/A	0.5	Soujanya, J., Anvesh Reddy, C., Satyavathi, B., Sankarshana, T., Fluid Phase Equilib., 2016, 409, 327–333
N/A	N/A	N/A	N/A	1	Eduljee, G. H.; Boyes, A. P., J. Chem. Eng. Data, 1981, 26, 56
Failed	Failed	N/A	Failed	0.29	Hollo, J.; Lengyel, T., Fette, Seifen, Anstrichm., 1960, 62, 913-8
Failed	Failed	N/A	F	0.063	Naik, K. A.; Husain, A., Indian J. Technol., 1964, 2, 328-30
Failed	Failed	N/A	Failed	0.81	Monick, J. A.; Allen, H. D., Marlies, C. J.; Oil and Soap (Chicago), 1946, 23, 177
N/A	N/A	N/A	N/A	0.75	Eduljee, G. H.; Boyes, A. P., J. Chem. Eng. Data, 1981, 26, 58
Passed	Failed	N/A	Failed	0.14	Akisawa Silva, L.Y., Matricarde Falleiro, R.M., Meirelles, A.J. A., Krähenbühl, M. A., Thermochim. Acta, 2011, 512, 178–182.
N/A	N/A	N/A	N/A	0.02	Cunico, L.P., Damaceno, D.S., Matricarde Falleiro, R.M., Sarup, B., Abildskov, J., Ceriani, R., Gani, R., J. Chem. Thermodyn., 2015, 91, 108–115.
N/A	N/A	N/A	N/A	0.02	Cunico, L.P., Damaceno, D.S., Matricarde Falleiro, R.M., Sarup, B., Abildskov, J., Ceriani, R., Gani, R., J. Chem. Thermodyn., 2015, 91, 108–115.
N/A	N/A	N/A	N/A	0.5	Oliveira, M.B., Miguel, S.I., Queimada, A.J., Coutinho, J.A.P., Ind. Eng. Chem. Res., 2010, 49, 3452–3458.
N/A	N/A	N/A	N/A	0.49	Barreau, A., Brunella, I., de Hemptinne, J.-C., Coupard, V., Canet, X., Rivollet, F., Ind. Eng. Chem. Res., 2010, 49, 5800–5807.
N/A	N/A	N/A	N/A	0.5	Oliveira, M.B., Miguel, S.I., Queimada, A.J., Coutinho, J.A.P., Ind. Eng. Chem. Res., 2010, 49, 3452–3458.
N/A	N/A	N/A	N/A	0.01	Eduljee, G. H.; Boyes, A. P., J. Chem. Eng. Data, 1981, 26, 55
N/A	N/A	N/A	N/A	1	Eduljee, G. H.; Boyes, A. P., J. Chem. Eng. Data, 1981, 26, 55
N/A	N/A	N/A	N/A	1	Eduljee, G. H.; Boyes, A. P., J. Chem. Eng. Data, 1981, 26, 55
N/A	N/A	N/A	N/A	0.16	Eduljee, G. H.; Boyes, A. P., J. Chem. Eng. Data, 1981, 26, 55
N/A	N/A	N/A	N/A	0.95	Eduljee, G. H.; Boyes, A. P., J. Chem. Eng. Data, 1981, 26, 55
N/A	N/A	N/A	N/A	1	Eduljee, G. H.; Boyes, A. P., J. Chem. Eng. Data, 1981, 26, 55

Table B.3 Binary VLE data sets used for validation of the lipid-based parameters

No.	System compounds 1	2	Data Type	Data points no	iso T, K	Q_{VLE} (TDE)
1	Ethyl hexanoate	n-Tetradecane	TPX	7	373.15	0.5
2	Ethyl hexanoate	n-Tetradecane	TPX	7	383.15	0.5
3	Ethyl hexanoate	n-Tetradecane	TPX	7	393.15	0.5
4	Ethyl hexanoate	n-Tetradecane	TPX	7	403.15	0.5
5	Ethyl hexanoate	n-Tetradecane	TPX	7	413.15	0.5
6	Ethyl hexanoate	n-Tetradecane	TPX	7	423.15	0.5
7	Ethyl hexanoate	n-Tetradecane	TPX	7	433.15	0.5
8	Ethyl hexanoate	n-Tetradecane	TPX	7	443.15	0.5
9	Ethyl hexanoate	n-Tetradecane	TPX	7	453.15	0.5
10	Ethyl decanoate	n-Tetradecane	TPX	7	373.15	0.28
11	Ethyl decanoate	n-Tetradecane	TPX	7	383.15	0.27
12	Ethyl decanoate	n-Tetradecane	TPX	7	393.15	0.27
13	Ethyl decanoate	n-Tetradecane	TPX	7	403.15	0.28
14	Ethyl decanoate	n-Tetradecane	TPX	7	413.15	0.3
15	Ethyl decanoate	n-Tetradecane	TPX	7	423.15	0.34
16	Ethyl decanoate	n-Tetradecane	TPX	7	433.15	0.41
17	Ethyl decanoate	n-Tetradecane	TPX	7	443.15	0.5
18	Ethyl decanoate	n-Tetradecane	TPX	7	453.15	0.5
19	Ethyl tetradecanoate	n-Tetradecane	TPX	7	373.15	0.5
20	Ethyl tetradecanoate	n-Tetradecane	TPX	7	383.15	0.5
21	Ethyl tetradecanoate	n-Tetradecane	TPX	7	393.15	0.5
22	Ethyl tetradecanoate	n-Tetradecane	TPX	7	403.15	0.5
23	Ethyl tetradecanoate	n-Tetradecane	TPX	7	413.15	0.5
24	Ethyl tetradecanoate	n-Tetradecane	TPX	7	423.15	0.5
25	Ethyl tetradecanoate	n-Tetradecane	TPX	7	433.15	0.45
26	Ethyl tetradecanoate	n-Tetradecane	TPX	7	443.15	0.36
27	Ethyl tetradecanoate	n-Tetradecane	TPX	7	453.15	0.31

Individual consistency test results (TDE)					Reference
Q_1	Q_2	Q_3	Q_4	Q_5	
N/A	N/A	N/A	N/A	1	Benziane, M., Khimeche, K., Mokbel, I., Dahmani, A., Jose, J., J. Chem. Eng. Data, 2013, 58, 492–498.
N/A	N/A	N/A	N/A	1	Benziane, M., Khimeche, K., Mokbel, I., Dahmani, A., Jose, J., J. Chem. Eng. Data, 2013, 58, 492–498.
N/A	N/A	N/A	N/A	1	Benziane, M., Khimeche, K., Mokbel, I., Dahmani, A., Jose, J., J. Chem. Eng. Data, 2013, 58, 492–498.
N/A	N/A	N/A	N/A	1	Benziane, M., Khimeche, K., Mokbel, I., Dahmani, A., Jose, J., J. Chem. Eng. Data, 2013, 58, 492–498.
N/A	N/A	N/A	N/A	1	Benziane, M., Khimeche, K., Mokbel, I., Dahmani, A., Jose, J., J. Chem. Eng. Data, 2013, 58, 492–498.
N/A	N/A	N/A	N/A	1	Benziane, M., Khimeche, K., Mokbel, I., Dahmani, A., Jose, J., J. Chem. Eng. Data, 2013, 58, 492–498.
N/A	N/A	N/A	N/A	1	Benziane, M., Khimeche, K., Mokbel, I., Dahmani, A., Jose, J., J. Chem. Eng. Data, 2013, 58, 492–498.
N/A	N/A	N/A	N/A	1	Benziane, M., Khimeche, K., Mokbel, I., Dahmani, A., Jose, J., J. Chem. Eng. Data, 2013, 58, 492–498.
N/A	N/A	N/A	N/A	1	Benziane, M., Khimeche, K., Mokbel, I., Dahmani, A., Jose, J., J. Chem. Eng. Data, 2013, 58, 492–498.
N/A	N/A	N/A	N/A	0.55	Benziane, M., Khimeche, K., Mokbel, I., Dahmani, A., Jose, J., J. Chem. Eng. Data, 2013, 58, 492–498.
N/A	N/A	N/A	N/A	0.54	Benziane, M., Khimeche, K., Mokbel, I., Dahmani, A., Jose, J., J. Chem. Eng. Data, 2013, 58, 492–498.
N/A	N/A	N/A	N/A	0.55	Benziane, M., Khimeche, K., Mokbel, I., Dahmani, A., Jose, J., J. Chem. Eng. Data, 2013, 58, 492–498.
N/A	N/A	N/A	N/A	0.57	Benziane, M., Khimeche, K., Mokbel, I., Dahmani, A., Jose, J., J. Chem. Eng. Data, 2013, 58, 492–498.
N/A	N/A	N/A	N/A	0.61	Benziane, M., Khimeche, K., Mokbel, I., Dahmani, A., Jose, J., J. Chem. Eng. Data, 2013, 58, 492–498.
N/A	N/A	N/A	N/A	0.68	Benziane, M., Khimeche, K., Mokbel, I., Dahmani, A., Jose, J., J. Chem. Eng. Data, 2013, 58, 492–498.
N/A	N/A	N/A	N/A	0.81	Benziane, M., Khimeche, K., Mokbel, I., Dahmani, A., Jose, J., J. Chem. Eng. Data, 2013, 58, 492–498.
N/A	N/A	N/A	N/A	1	Benziane, M., Khimeche, K., Mokbel, I., Dahmani, A., Jose, J., J. Chem. Eng. Data, 2013, 58, 492–498.
N/A	N/A	N/A	N/A	1	Benziane, M., Khimeche, K., Mokbel, I., Dahmani, A., Jose, J., J. Chem. Eng. Data, 2013, 58, 492–498.
N/A	N/A	N/A	N/A	1	Benziane, M., Khimeche, K., Mokbel, I., Dahmani, A., Jose, J., J. Chem. Eng. Data, 2013, 58, 492–498.
N/A	N/A	N/A	N/A	1	Benziane, M., Khimeche, K., Mokbel, I., Dahmani, A., Jose, J., J. Chem. Eng. Data, 2013, 58, 492–498.
N/A	N/A	N/A	N/A	1	Benziane, M., Khimeche, K., Mokbel, I., Dahmani, A., Jose, J., J. Chem. Eng. Data, 2013, 58, 492–498.
N/A	N/A	N/A	N/A	1	Benziane, M., Khimeche, K., Mokbel, I., Dahmani, A., Jose, J., J. Chem. Eng. Data, 2013, 58, 492–498.
N/A	N/A	N/A	N/A	1	Benziane, M., Khimeche, K., Mokbel, I., Dahmani, A., Jose, J., J. Chem. Eng. Data, 2013, 58, 492–498.
N/A	N/A	N/A	N/A	1	Benziane, M., Khimeche, K., Mokbel, I., Dahmani, A., Jose, J., J. Chem. Eng. Data, 2013, 58, 492–498.
N/A	N/A	N/A	N/A	0.9	Benziane, M., Khimeche, K., Mokbel, I., Dahmani, A., Jose, J., J. Chem. Eng. Data, 2013, 58, 492–498.
N/A	N/A	N/A	N/A	0.73	Benziane, M., Khimeche, K., Mokbel, I., Dahmani, A., Jose, J., J. Chem. Eng. Data, 2013, 58, 492–498.
N/A	N/A	N/A	N/A	0.61	Benziane, M., Khimeche, K., Mokbel, I., Dahmani, A., Jose, J., J. Chem. Eng. Data, 2013, 58, 492–498.

Table B.4 Binary VLE data sets used for extrapolation of the lipid-based parameters

No.	System compounds		Data	Data points	iso P,	Reference
	1	2	Type	no	kPa	
1	Lauric acid	Monocaprylin	TPX	11	3.42	Damaceno, D.S., Ceriani, R., Fluid Phase Equilib., 2017, 452, 135–142.
2	Mononanoin	Monolaurin	TPX	11	2.06	Damaceno, D.S., Ceriani, R., Fluid Phase Equilib., 2017, 452, 135–142.
3	Hexadecanol	Mononanoin	TPX	11	2.02	Damaceno, D.S., Ceriani, R., Fluid Phase Equilib., 2017, 452, 135–142.
4	Octadecanol	Monolaurin	TPX	11	2.05	Damaceno, D.S., Ceriani, R., Fluid Phase Equilib., 2017, 452, 135–142.
5	Hexadecanol	Octadecanol	TPX	11	1.73	Damaceno, D.S., Ceriani, R., J. Chem. Eng. Data, 2018, 63, 2840−2847.
6	Methyl myristate	Hexadecanol	TPX	11	1.72	Damaceno, D.S., Ceriani, R., J. Chem. Eng. Data, 2018, 63, 2840−2847.
7	Tributyrin	Mononanoin	TPX	11	1.69	Damaceno, D.S., Ceriani, R., J. Chem. Eng. Data, 2018, 63, 2840−2847.
8	Dinanoin	Octacosane	TPX	11	1.7	Damaceno, D.S., Ceriani, R., J. Chem. Eng. Data, 2018, 63, 2840−2847.

APPENDIX C
SLE DATASETS

The binary SLE datasets used for parameters extrapolation testing are presented in Table C.1.

Table C.1 Binary SLE data sets used for extrapolation of the lipid-based parameters

No.	System compounds		Data points	Reference
	1	2	no	
1	Dodecanoic acid	Tetradecanoic acid	12	Costa, M.C., Rolemberg, M.P., Meirelles, A.J.A., Coutinho, J.A.P., Krähenbühl, M.A., Thermochim. Acta, 2009, 496, 30–37.
2	Dodecanoic acid	Tetradecanoic acid	11	Boros, L.A.D., PhD Thesis, University of Campinas, 2005
3	Dodecanoic acid	Tetradecanoic acid	12	Costa, M.C., Rolemberg, M.P., Boros, L.A.D., Krähenbühl, M.A., de Oliveira, M.G., Meirelles, A.J.A., J. Chem. Eng. Data, 2007, 52, 30–36.
4	Dodecanoic acid	Tetradecanoic acid	13	Costa, M.C., PhD Thesis, University of Campinas, 2008.
5	Dodecanoic acid	Hexadecanoic acid	12	Costa, M.C., Rolemberg, M.P., Boros, L.A.D., Krähenbühl, M.A., de Oliveira, M.G., Meirelles, A.J.A., J. Chem. Eng. Data, 2007, 52, 30–36.
6	Dodecanoic acid	Octadecanoic acid	13	Boros, L.A.D., PhD Thesis, University of Campinas, 2005
7	Dodecanoic acid	Octadecanoic acid	14	Costa, M.C., Rolemberg, M.P., Boros, L.A.D., Krähenbühl, M.A., de Oliveira, M.G., Meirelles, A.J.A., J. Chem. Eng. Data, 2007, 52, 30–36.
8	Dodecanoic acid	Octadecanoic acid	18	Costa, M.C., PhD Thesis, University of Campinas, 2008.
9	Tetradecanoic acid	Hexadecanoic acid	18	Costa, M.C., Rolemberg, M.P., Meirelles, A.J.A., Coutinho, J.A.P., Krähenbühl, M.A., Thermochim. Acta, 2009, 496, 30–37.
10	Tetradecanoic acid	Hexadecanoic acid	13	Rolemberg, M.P.,PhD Thesis, University of Campinas2002..
11	Tetradecanoic acid	Octadecanoic acid	13	Boros, L.A.D., PhD Thesis, University of Campinas, 2005
12	Tetradecanoic acid	Octadecanoic acid	11	Costa, M.C., PhD Thesis, University of Campinas, 2008.
13	Hexadecanoic acid	Octadecanoic acid	5	Costa, M.C., Rolemberg, M.P., Meirelles, A.J.A., Coutinho, J.A.P., Krähenbühl, M.A., Thermochim. Acta, 2009, 496, 30–37.
14	Hexadecanoic acid	Linoleic acid	12	Nishimura, K., Maeda, K., Kuramochi, H., Nakagawa, K., Asakuma, Y., Fukui, K., Osako, M., Sakai, S., J. Chem. Eng. Data, 2011 56, 1613–1616
15	Oleic acid	Octadecanoic acid	3	Rolemberg, M.P.,PhD Thesis, University of Campinas2002..
16	Octadecanoic acid	Acetone	11	Goff, M.J., Suppes, G.J., Dasari, M.A., Fluid Phase Equilib., 2005, 238, 149–156.
17	Linoleic acid	Oleic acid	5	Rolemberg, M.P.,PhD Thesis, University of Campinas2002..
18	Oleic acid	Hexadecanoic acid	25	Nishimura, K., Maeda, K., Kuramochi, H., Nakagawa, K., Asakuma, Y., Fukui, K., Osako, M., Sakai, S., J. Chem. Eng. Data, 2011 56, 1613–1616

Table C.1 Binary SLE datasets used for extrapolation of the lipid-based parameters (Continued)

No.	System compounds		Data points	Reference
	1	2	no	
19	2-Oleodipalmitin	Tripalmitin	11	Bruin, S., Fluid Phase Equilib., 1999, 158, 657–671.
20	Triolein	Tripalmitin	5	Costa, M.C., Boros, L.A.D., Souza, J.A., Rolemberg, M.P., Krähenbühl, M.A., Meirelles, A.J.A., J. Chem. Eng. Data, 2011, 56, 3277–3284.
21	Triolein	Tripalmitin	10	Nishimura, K., Maeda, K., Kuramochi, H., Nakagawa, K., Asakuma, Y., Fukui, K., Osako, M., Sakai, S., J. Chem. Eng. Data, 2011 56, 1613–1616
22	Oleic acid	Tripalmitin	12	Costa, M.C., Boros, L.A.D., Souza, J.A., Rolemberg, M.P., Krähenbühl, M.A., Meirelles, A.J.A., J. Chem. Eng. Data, 2011, 56, 3277–3284.
23	Oleic acid	Tripalmitin	5	Rolemberg, M.P.,PhD Thesis, University of Campinas2002..
24	Oleic acid	Tripalmitin	5	Nishimura, K., Maeda, K., Kuramochi, H., Nakagawa, K., Asakuma, Y., Fukui, K., Osako, M., Sakai, S., J. Chem. Eng. Data, 2011 56, 1613–1616
25	Linoleic	Tripalmitin	11	Nishimura, K., Maeda, K., Kuramochi, H., Nakagawa, K., Asakuma, Y., Fukui, K., Osako, M., Sakai, S., J. Chem. Eng. Data, 2011 56, 1613–1616
26	Triolein	Hexadecanoic acid	6	Costa, M.C., Boros, L.A.D., Rolemberg, M.P., Kra, M.A., J. Chem. Eng. Data, 2010, 55, 974–977.
27	Triolein	Hexadecanoic acid	10	Nishimura, K., Maeda, K., Kuramochi, H., Nakagawa, K., Asakuma, Y., Fukui, K., Osako, M., Sakai, S., J. Chem. Eng. Data, 2011 56, 1613–1616
28	Triolein	Hexadecanoic acid	10	Rolemberg, M.P.,PhD Thesis, University of Campinas2002..
29	Methyl dodecanoate	Methyl octadecanoate	13	Boros, L., Batista, M.L.S., Vaz, R. V., Figueiredo, B.R., Fernandes, V.F.S., Costa, M.C., Krahenbuhl, M.A., Meirelles, A.J.A., Coutinho, J.A.P., 2009. Crystallization behavior of mixtures of fatty acid ethyl esters with ethyl stearate. Energy and Fuels 23, 4625–4629.
30	Methyl tetradecanoate	Methyl hexadecanoate	11	Costa, M.C., Boros, L.A.D., Souza, J.A., Rolemberg, M.P., Krähenbühl, M.A., Meirelles, A.J.A., J. Chem. Eng. Data, 2011, 56, 3277–3284.
31	Methyl hexadecanoate	Methyl octadecanoate	11	Boros, L., Batista, M.L.S., Vaz, R. V., Figueiredo, B.R., Fernandes, V.F.S., Costa, M.C., Krahenbuhl, M.A., Meirelles, A.J.A., Coutinho, J.A.P., Energy and Fuels, 2009, 23, 4625–4629.
32	Methyl hexadecanoate	Methyl octadecanoate	13	Costa, M.C., Boros, L.A.D., Souza, J.A., Rolemberg, M.P., Krähenbühl, M.A., Meirelles, A.J.A., J. Chem. Eng. Data, 2011, 56, 3277–3284.
33	Methyl tetradecanoate	Methyl octadecanoate	11	Costa, M.C., Boros, L.A.D., Souza, J.A., Rolemberg, M.P., Krähenbühl, M.A., Meirelles, A.J.A., J. Chem. Eng. Data, 2011, 56, 3277–3284.
34	Methyl oleate	Methyl octadecanoate	11	Costa, M.C., Boros, L.A.D., Souza, J.A., Rolemberg, M.P., Krähenbühl, M.A., Meirelles, A.J.A., J. Chem. Eng. Data, 2011, 56, 3277–3284.
35	Mehyl linoleate	Methyl octadecanoate	11	Costa, M.C., Boros, L.A.D., Souza, J.A., Rolemberg, M.P., Krähenbühl, M.A., Meirelles, A.J.A., J. Chem. Eng. Data, 2011, 56, 3277–3284.
36	Ethyl dodecanoate	Ethyl hexadecanoate	11	Costa, M.C., Boros, L.A.D., Batista, M.L.S., Coutinho, J.A.P., Krähenbühl, M.A., Meirelles, A.J.A., Fuel, 2012, 91, 177–181.

Table C.1 Binary SLE data sets used for extrapolation of the lipid-based parameters (Continued)

No.	System compounds		Data points	Reference
	1	2	no	
37	Ethyl tetradecanoate	Ethyl hexadecanoate	11	Costa, M.C., Boros, L.A.D., Batista, M.L.S., Coutinho, J.A.P., Krähenbühl, M.A., Meirelles, A.J.A., Fuel, 2012, 91, 177–181.
38	Ethyl tetradecanoate	Ethyl octadecanoate	11	Costa, M.C., Boros, L.A.D., Souza, J.A., Rolemberg, M.P., Krähenbühl, M.A., Meirelles, A.J.A., J. Chem. Eng. Data, 2011, 56, 3277–3284.
39	Ethyl hexadecanoate	Ethyl oleate	11	Costa, M.C., Boros, L.A.D., Batista, M.L.S., Coutinho, J.A.P., Krähenbühl, M.A., Meirelles, A.J.A., Fuel, 2012, 91, 177–181.
40	Ethyl dodecanoate	Ethyl octadecanoate	10	Costa, M.C., Boros, L.A.D., Souza, J.A., Rolemberg, M.P., Krähenbühl, M.A., Meirelles, A.J.A., J. Chem. Eng. Data, 2011, 56, 3277–3284.
41	Ethyl linoleate	Ethyl octadecanoate	11	Costa, M.C., Boros, L.A.D., Souza, J.A., Rolemberg, M.P., Krähenbühl, M.A., Meirelles, A.J.A., J. Chem. Eng. Data, 2011, 56, 3277–3284.
42	Ethyl hexadecanoate	Ethyl linoleate	11	Costa, M.C., Boros, L.A.D., Batista, M.L.S., Coutinho, J.A.P., Krähenbühl, M.A., Meirelles, A.J.A., Fuel, 2012, 91, 177–181.
43	Triolinolein	Hexadecanoic acid	5	Nishimura, K., Maeda, K., Kuramochi, H., Nakagawa, K., Asakuma, Y., Fukui, K., Osako, M., Sakai, S., J. Chem. Eng. Data, 2011 56, 1613–1616
44	Trilinolein	Octadecanoic acid	12	Costa, M.C., Boros, L.A.D., Rolemberg, M.P., Kra, M.A., J. Chem. Eng. Data, 2010, 55, 974–977.

APPENDIX D

LLE DATASETS AND MODELLING

The lipid-based parameters were tested for LLE prediction capabilities, and their performance was compared with other sets of parameters for the Original and Linear UNIFAC models. The LLE data sets used for evaluation are presented in Table D.2. The lipid parameters were not able to be tested for the water-acid (system number 1-10 in Table D.2), and water-ester (system number 11 – 30 in table D.2) data sets since some of the parameters are missing for both type of systems (e.g. H_2O-COOH, H_2O-CH_2COO). The two sets of parameters from Bessa (Bessa et al., 2016) dedicated to deacidification process (*Bessa 1* parameters in Table D.1) and biodiesel processing (*Bessa 2* parameters in Table D.1)[9] were not tested for the acetone – acid systems (systems number 31 – 35) since the parameter table did not include the CH_3CO group. The *Other* group covers systems with methanol and n-hexane (systems number 36 and 37). The LLE is described by equation Eq. D.1

$$x_i^I \gamma_i^I = x_i^{II} \gamma_i^{II} \tag{D.1}$$

Where x_i represents the composition of compound i in liquid phase I and in liquid phase II, and γ_i represents the activity coefficient of compound i in the liquid phase I and II. The results of all the tested model and parameters variants are given in Table D.1

For the water – acid systems the best results are given by Linear UNIFAC with published parameters followed by Original UNIFAC with LLE parameters and parameters from Bessa, which have similar performances. The best results for water – ester systems are given by the Linear UNIFAC with published parameters, Original UNIFAC with LLE and published (VLE) parameters.

The performance of the models for the acetone – acid systems is significant lower compared to the two previously mentioned type of systems, and the best results are given by Linear UNIFAC model with published parameters. For the last category, Linear UNIFAC with NIST-KT parameters gives the best results. When available, the lipid-based parameters have similar or lower performance compared to the other parameters. A conclusion cannot be drawn since only a few systems are investigated, and further testing is necessary.

[9] The parameters for biodiesel processing (Bessa 2 in Table D.1) do not include the COOH group.

Table D.1 Performance of different UNIFAC models using lipid-based and other parameters

Model	Original UNIFAC					Linear			
Parameters	Pub. [1]	LLE [2]	Lip. [3]	Bessa [4]	Bessa 2 [5]	NIST [5]	Pub. [6]	Lip. [7]	NIST-KT [5]
System Type									
Water - Acid	71.9	60.4	-	61.0	-	65.3	60.3	-	117.8
Water - Ester	19.9	19.0	-	20.8	30.0	24.2	18.3	-	38.0
Acetone - Acid	95.9	124.3	131.8	-	-	91.4	79.1	89.7	105.5
Others	35.1	21.1	35.1	21.1	21.0	23.9	24.4	34.9	17.7
$ARD_2(\%)$[b]	44.4	43.8	99.8	33.0	29.2	43.8	37.7	74.0	65.4

[1] (Hansen et al., 1991), [2] (Magnussen et al., 1981), [3] (Perederic et al., 2018b), [4] (Bessa et al., 2016), [5] (Kang et al., 2011), [6] (Hansen et al., 1992), [7] (Damaceno et al., 2018b), *Lip – Lipid-based parameters, Pub. – Published parameters.*

[a] $ARD_0 = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{x_i^{experimental} - x_i^{calculated}}{x_i^{experimental}}\right|$, N data points number, x – molar fraction

$ARD_1(\%) = \frac{100}{M}\sum_{j=1}^{M} ARD_0$, M – data sets number within a category-group

[b] $ARD_2(\%) = \frac{100}{Tt}\sum_{k=1}^{T} ARD_1$, T– total data sets number

Table D.2 Binary SLE data sets used for extrapolation of the lipid-based parameters

No.	System compounds		Data points	Reference
	1	2	no	
1	Hexanoic acid	Water	5	Ralston and Hoerr, 1942 / DECHEMA[a]
2	Hexanoic acid	Water	8	Oliveira, M.B., Pratas, M.J., Marrucho, I.M., Queimada, A.J., Coutinho, J.A.P., AIChE J., 2009, 55, 1604–1613.
3	Hexanoic acid	Water	11	Oliveira, M.B., Pratas, M.J., Marrucho, I.M., Queimada, A.J., Coutinho, J.A.P., AIChE J., 2009, 55, 1604–1613.
4	Octanoic acid	Water	10	Othmer and Serrano, 1940 / DECHEMA
5	Octanoic acid	Water	7	Oliveira, M.B., Pratas, M.J., Marrucho, I.M., Queimada, A.J., Coutinho, J.A.P., AIChE J., 2009, 55, 1604–1613.
6	Octanoic acid	Water	5	Kholkin, 1965 / TDE[b]
7	Octanoic acid	Water	5	Kholkin, 1965 / TDE[b]
8	Decanoic acid	Water	4	Oliveira, M.B., Pratas, M.J., Marrucho, I.M., Queimada, A.J., Coutinho, J.A.P., AIChE J., 2009, 55, 1604–1613.
9	Decanoic acid	Water	5	Ralsoton and Hoerr, 1942 / DECHEMA
10	Dodecanoic acid	Water	7	Oliveira, M.B., Pratas, M.J., Marrucho, I.M., Queimada, A.J., Coutinho, J.A.P., AIChE J., 2009, 55, 1604–1613.
11	Methyl Hexanoate	Water	7	Oliveira, M.B., Varanda, F.R., Marrucho, I.M., Queimada, A. J., Coutinho, J. A. P., Ind. Eng. Chem. Res., 2008, 47, 4278–4285.
12	Methyl Hexanoate	Water	10	Stephenson et al., 1986 / TDE[b]
13	Methyl Hexanoate	Water	10	Stephenson et al., 1986 / TDE[b]
14	Methyl Octanoate	Water	8	Oliveira, M.B., Varanda, F.R., Marrucho, I.M., Queimada, A. J., Coutinho, J. A. P., Ind. Eng. Chem. Res., 2008, 47, 4278–4285.

Table D.2 Binary SLE data sets used for extrapolation of the lipid-based parameters (Continued)

No.	System compounds		Data points	Reference
	1	2	no	
15	Methyl Octanoate	Water	5	Kuramochi, H., Maeda, K., Kato, S., Osako, M., Nakamura, K., Sakai, S., Fuel, 2009, 88, 1472–1477.
16	Methyl Octanoate	Water	8	Oliveira, M.B., Varanda, F.R., Marrucho, I.M., Queimada, A. J., Coutinho, J. A. P., Ind. Eng. Chem. Res., 2008, 47, 4278–4285.
17	Methyl Dodecanoate	Water	7	Oliveira, M.B., Varanda, F.R., Marrucho, I.M., Queimada, A. J., Coutinho, J. A. P., Ind. Eng. Chem. Res., 2008, 47, 4278–4285.
18	Methyl Hexadecanoate	Water	4	Oliveira, M.B., Varanda, F.R., Marrucho, I.M., Queimada, A. J., Coutinho, J. A. P., Ind. Eng. Chem. Res., 2008, 47, 4278–4285.
19	Methyl Hexadecanoate	Water	2	Bassil et al., 2012 / *Lipids Database*
20	Methyl Hexadecanoate	Water	3	Kuramochi, H., Maeda, K., Kato, S., Osako, M., Nakamura, K., Sakai, S., Fuel, 2009, 88, 1472–1477.
21	Methyl Octadecanoate	Water	3	Oliveira, M.B., Varanda, F.R., Marrucho, I.M., Queimada, A. J., Coutinho, J. A. P., Ind. Eng. Chem. Res., 2008, 47, 4278–4285.
22	Ethyl Hexanoate	Water	10	Stephenson, R., Stuart, J., J. Chem. Eng. Data, 1986, 31, 56–70.
23	Ethyl Hexanoate	Water	10	Stephenson, R., Stuart, J., J. Chem. Eng. Data, 1986, 31, 56–70.
24	Ethyl Hexanoate	Water	3	Hong et al., 2002 / TDE[b]
25	Ethyl Hexanoate	Water	3	Hong et al., 2002 / TDE[b]
26	Ethyl Hexanoate	Water	3	Lin, H.; Hong, G.-B.; Yeh, C.-E.; Lee, M. J. 2003 / TDE
27	Ethyl Octanoate	Water	7	Stephenson, R., Stuart, J., J. Chem. Eng. Data, 1986, 31, 56–70.
28	Ethyl Decanoate	Water	7	Oliveira, M.B., Varanda, F.R., Marrucho, I.M., Queimada, A. J., Coutinho, J. A. P., Ind. Eng. Chem. Res., 2008, 47, 4278–4285.
29	Methyl Oleate	Water	8	Oliveira, M.B., Varanda, F.R., Marrucho, I.M., Queimada, A. J., Coutinho, J. A. P., Ind. Eng. Chem. Res., 2008, 47, 4278–4285.
30	Methyl Oleate	Water	4	Kuramochi, H., Maeda, K., Kato, S., Osako, M., Nakamura, K., Sakai, S., Fuel, 2009, 88, 1472–1477.
31	Octanoic Acid	Acetone	3	Ralsoton and Hoerr, 1942 / DECHEMA[a]
32	Decanoic acid	Acetone	5	Ralsoton and Hoerr, 1942 / DECHEMA[a]
33	Tetradecanoic acid	Acetone	6	Ralsoton and Hoerr, 1942 / DECHEMA[a]
34	Hexadecanoic acid	Acetone	6	Ralsoton and Hoerr, 1942 / DECHEMA[a]
35	Stearic acid	Acetone	6	Ralsoton and Hoerr, 1942 / DECHEMA[a]
36	Methyl Oleate	Methanol	11	Barreau, A., Brunella, I., de Hemptinne, J.C., Coupard, V., Canet, X., Rivollet, F.,Ind. Eng. Chem. Res., 2010, 49, 5800–5807.
37	Methyl Oleate	n-Hexane	1	Barreau, A., Brunella, I., de Hemptinne, J.C., Coupard, V., Canet, X., Rivollet, F.,Ind. Eng. Chem. Res., 2010, 49, 5800–5807.

[a] (Westhaus et al., 1999)
[b] (Diky et al., 2009)

APPENDIX E
DSC EXPERIMENTAL RESULTS

E.1 Introduction

This part of the work shows the applicability of the systematic identification method, presented in Chapter 3, for experimental planning and UNIFAC model extension for lipid systems. Using the method's calculation sequence and the UNIFAC lipid based parameter matrix, a list of necessary experimental binary phase equilibria measurements was proposed (see Table E.4, available also in (Perederic et al., 2018b)). Four parameters from the proposed list, which are of high importance in modelling and design of lipid related process, were identified: GLY-CH_2COO, GLY-COOH, GLY-CH=CH, GLY-OH_{acyl}. Using Table E.4 and properties of lipid compounds of interest, three systems were identified and measured experimentally, which could provide the four interaction parameters mentioned above. The identified systems are presented in Table E.1. Based on the interactions involved in each identified binary system, as well as, the interaction available already from the method/*Lipids Database* (see Figure E.1 and Table E.3), the calculation sequence was updated with the new identified binary group interaction parameters as it is presented in Figure E.1.

Table E.1. Application of the Systematic Identification Method for experimental design and UNIFAC model extension

System type		System Compounds		Structural groups	Binary interaction	Assigned Category Group
Glycerol	Saturated Acid	Glycerol	Palmitic acid	GLY CH_2 COOH	GLY-CH_2, **GLY-COOH**, CH_2-COOH	3.1.2
Glycerol	Unsaturated Ester	Glycerol	Methyl Oleate	GLY CH_2 CH=CH CH_2COO	GLY-CH_2,**GLY-CH=CH**, **GLY-CH_2COO**, CH_2-CH=CH, CH_2-CH_2COO, CH=CH-CH_2COO	6.2.1
Glycerol	Mono-,di-acylglycerol	Glycerol	Mono-caprylin	GLY CH_2 CH2COO OH_{acyl}	GLY-CH_2, GLY-CH_2COO, **GLY-OH_{acyl}**, CH_2-CH_2COO, CH_2-OH_{acyl}, CH_2COO-OH_{acyl}	6.1.6

* Text in Bold from Binary Interactions column highlights the parameters to be estimated.

Within the method, only the VLE data was considered for the regression of the lipid based binary interaction parameters, as presented in Chapters 3 and 4. The validation results of the UNIFAC model variants with the lipid-based parameters resulted from the method, showed improvements for VLE prediction (see Table 4.5) and only slight to no improvements for SLE prediction (see Table 5.3). Considering the equipment available at the Centre for Energy Resources Engineering at the Department of Chemical and Biochemical Engineering, DTU, it was decided to measure the solid-liquid equilibrium data for the selected binary systems presented in Table E.1. Vapour-liquid equilibria measurements for lipid systems require high temperatures and low pressures, which the available equipment could not handle.

In the following sections, the experimental method and the results obtained are presented and discussed. Since the project was mainly focused on phase equilibria modelling, more work has to be done for the experimental data gathering.

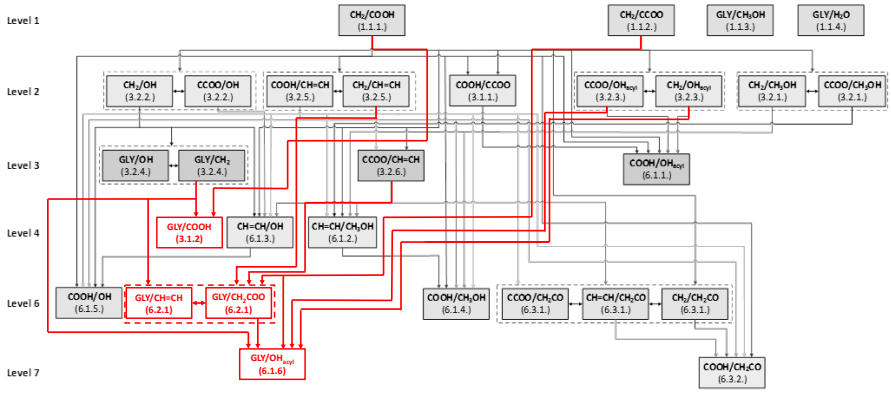


Figure E.1. Extended calculation sequence resulted from Systematic Identification Method and selected data to be measured

E.2 Experimental Method

E.2.1 Reagents

The materials used for calibration of the apparatus are naphthalene (99.9%) certified by Setaram Instrumentation (SI), deionized water (Mili-Q, Milipore), biphenyl (TraceCERT®). The chemicals used to prepare the samples (glycerol, palmitic acid, methyl oleate) were from Merck/Sigma-Aldrich and they were used without any further purification. All the reagents used in this work are listed in Table A5.2 along with CAS registry number, IUPAC name, Purity, Supplier, molecular mass (MW) and melting point (T_m). All chemicals were used with no further purification. Instrument grade nitrogen 5.0 (≥ 99.99 % purity) provided by Linde was used to purge the calorimeter chamber.

E.2.2 Apparatus

The differential scanning calorimetry analysis is performed with µDSC 7 EVO calorimeter (Setaram Instrumentation), France. The calorimeter is equipped with Julabo F-32 cooling system. Standard batch cells made of Hastelloy C276 (Setaram Instrumentation) with a 1 mL useful volume were used for both reference and measurement cells. All the samples were first added in a glass sample holder, which was introduced into the sample cell. An empty glass sample holder was used in the reference cell. Sample weighing was performed with a $2 \cdot 10^{-4}$ g precision on an Adam Nimbus 214 i analytical balance. The water sampling was done using a 50 µL Hamilton syringe, while ambient temperature and pressure were recorded.

E.2.3 Method

The calibration method follows the ASTM standard for DSC calibration and it is described in the following section. The preparation and measurements for the mixtures that were studied followed the ASTM standard test method for melting and crystallization temperature by thermal analysis and the procedure provided by Costa et al. (Costa et al., 2007).

E.2.3.1 Mixture sample preparation

The mixtures (Glycerol – Palmitic acid) were prepared in a 0.2 g amount in a glass tube and weighed on the microbalance. The mixture was heated up until the solid melted. The mixture weight was checked on the microbalance to ensure no material loss.

All the samples were measured on the analytical balance and added to the glass sample holder. The weight of the samples varied between 3-5 mg. In the case of water, the sampling was done by injecting 5 µL with the syringe in the glass sample holder.

E.2.3.2 Calibration and DSC procedure

The DSC was calibrated following the ASTM E967-08 (2014) (ASTM, 2014) and the apparatus software calibration method. Three standard substances were used for performing the calibration: water, biphenyl, and naphthalene. The samples were prepared following the procedure described in Section E.2.3.1, except the naphthalene sample that is provided sealed in a crucible (Setaram Instrumentation). The list of all samples and measurements performed are listed in Table E.4 and E.5 from Results section. The reference and measuring cell along with the glass sample holder were weight was checked to match to 10^{-3} decimal (mg). Before performing the calibration, the baseline of the apparatus was checked for the working temperature range (- 40 °C to 120 °C) for adjusting the power output ratio. The program for the solid samples at room temperature consists of following steps: thermal history removal at a 1 °C/minute heating rate, stabilisation, crystallization by cooling at 1 °C/minute rate, and melting using heating speeds lower than 1 °C/minute. In case of samples that are liquid at room temperature, the sample is cooled down with 1 °C/minute. Below the freezing point, it is stabilised and then, the sample is heated to a temperature 15 °C higher than the melting temperature. The details of each scanning program are presented in Table E.6. The accuracy of the experimental data was evaluated based on several repeated runs, while the repeatability was checked by measuring different samples in different days.

Material type	Reagent	IUPAC Name	CAS No.	Purity, wt.% / Certification	Supplier	Mw, g/mol	Tm, °C	Reference
Calibration materials	Naphthalene	Naphthalene, Bicyclo[4.4.0]deca-1,3,5,7,9-pentaene	91-20-3	≥99.9%, Setram Instrumentation certification	Setaram instrumentation, France	128.171	80.23	(Richardson and Charsley, 1998)
	Water	Water	7732-18-5	Type 1, Mili-Q Ultra Pure Water (18.2 mΩ)	Merck Milipore	18.0153	0.01	(ASTM, 2014)
	Biphenyl	1,1'-Biphenyl	92-52-4	TraceCERT®	Sigma-Aldrich	154.212	68.93	(Richardson and Charsley, 1998)
Measurements materials	Glycerol	propane-1,2,3-triol	56-81-5	≥99.5%	Sigma-Aldrich	92.0938	17, 18 , 18.17, 17.19*	(Lane, 1925), (Ralf et al., 2006), (Morrison, 2000), (NIST Chemistry WebBook.)
	Palmitic acid	Hexadecanoic acid	57-10-3	≥99%	Sigma-Aldrich	256.43	61.85 ± 1	(NIST Chemistry WebBook.)
	Methyl oleate**	methyl (Z)-octadec-9-enoate	112-62-9	≥98.5%	Sigma-Aldrich	296.495	-19.9	(Lide, 1995)
	Monocaprylin**	2,3-Dihydroxypropyl octanoate	19670-49-6, 502-54-5		Sigma-Aldrich	218.293	39.5-40.5	(Larodan.)

E.3 RESULTS

E.3.1 Calibration

The calibration was done using Naphthalene, Water, and Biphenyl standard substances. The calibration was performed in the Calisto Software, provided by Setaram Instrumentation. The temperature correction equation is given in Eq.E.1.The real temperature, $T_{corrected}$, is given by the difference of the measured temperature and the correction (Eq. E.2). Up to 15 data points can be used to get the correction coefficients in the calibration procedure.

$$C = B_0 + B_1 \cdot T + B_2 \cdot R + B_3 \cdot R^2 \quad \text{(Eq. E.1)}$$

$$T_{corrected} = T - C \quad \text{(Eq. E.2)}$$

Where:

B_i – Correction coefficients, and i=1, 2, 3

C – Correction, °C

R – Heating speed, °C /min

T – Measured temperature, °C

$T_{corrected}$ – corrected temperature, °C

The experimental data considered for the calibration is presented in Table E.2. The coefficients given in Table E.3, were obtained using only the average results for Naphthalene and Biphenyl. When using the water results, significant deviations from the corrected temperature were noticed. In order to obtain a full set of data, more measurements are necessary.

Table E.3. Coefficients for the temperature correction (Eq. E.1) for the DSC calibration

Coefficient, UM	B_0, °C	B_1	B_2, minute	B_3, minute^2/°C
Value	-11.6	0.148	2.85	0

E.3.2 Experimental measurements for calibration

The list of all the experiments, samples and runs for calibration, as well as, pure compounds measurements are presented in Table E.4. The main results used for calibration and for pure compounds are presented in Table E.5. Table E.6 provides information regarding the temperature-scanning program that was performed for each type of sample.

For all the pure compounds, which are described as crystalline substances, the melting temperature is considered at the T_{eim} temperature (see Figure E.1). For mixtures or semi-crystalline substances, melting temperature measurement is done

at T_{pm} (ASTM, 2014). In Costa et al. (Costa et al., 2007) the temperature measurement of fatty acids was done at both onset and peak temperature. The best agreement with the literature is for the onset temperature. Charsley and Richardson (Richardson and Charsley, 1998) report the melting temperature as the extrapolated onset temperature for naphthalene and other standards.

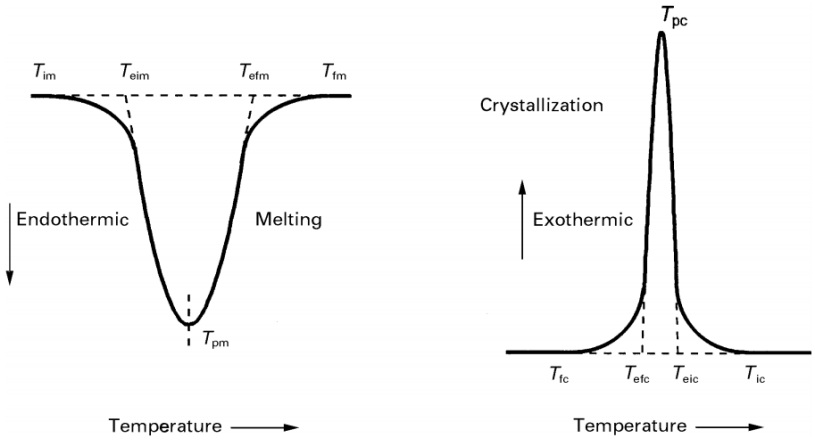


Figure E.2. Melting peak parameters for endothermic (left) and exothermic (right) processes; T_{ei} – onset temperature, T_{ef} – offset temperature, T_p – peak temperature, m – melting, c-crystallization (ASTM, 2014)

E.3.2.1. Naphthalene

The run for the naphthalene standard sample, one sealed crucible containing 4.02 mg of Naphthalene, was performed several times, as follows:

- R=0.7 °C/min (10 runs)
- R =0.5 °C/min (1 run)
- R=0.25 °C/min (1 run)
- R=0.1 °C/min (1 run)

Selected results are presented in Table E.3. The heat flow vs furnace temperature for the melting process of naphthalene is presented in Figure E.3. The melting peak moves from lower to higher temperature with the increase of the scanning temperature.

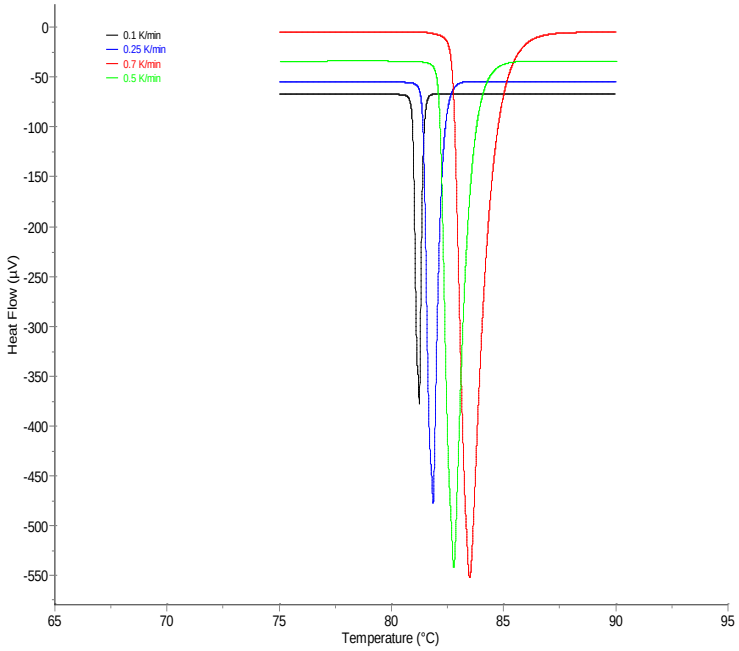


Figure E.3. Naphthalene melting peak for different scanning speeds (temperature correction was not used for the graph generation; signal cutting and slope correction were performed for each signal): — 0.1 °C/min, — 0.25 °C /min, — 0.5 °C /min, — 0.7 °C /min

E.3.2.2 Biphenyl

The biphenyl was analysed though 7 different samples. The same scanning speeds were used as in the case of Naphthalene (0.1, 0.25, 0.5, 0.7 K/minute). The best results obtained from the measurements are presented in Table 3. Two different scanning programs were used for Biphenyl (see Table E.4). The first scanning program (B) had 3 isotherms, 2 heating cycles and one cooling cycle. Due to the high temperature selected to finish the scanning program, 85 °C (and the isotherm at this temperature), the sample decomposed. In the second scanning program used, the intermediary and final isotherms were removed, and the heating cycle was stopped at 74 °C. No decomposition was observed.

The melting diagram of the biphenyl sample 7 before the temperature correction is presented in Figure E.2.

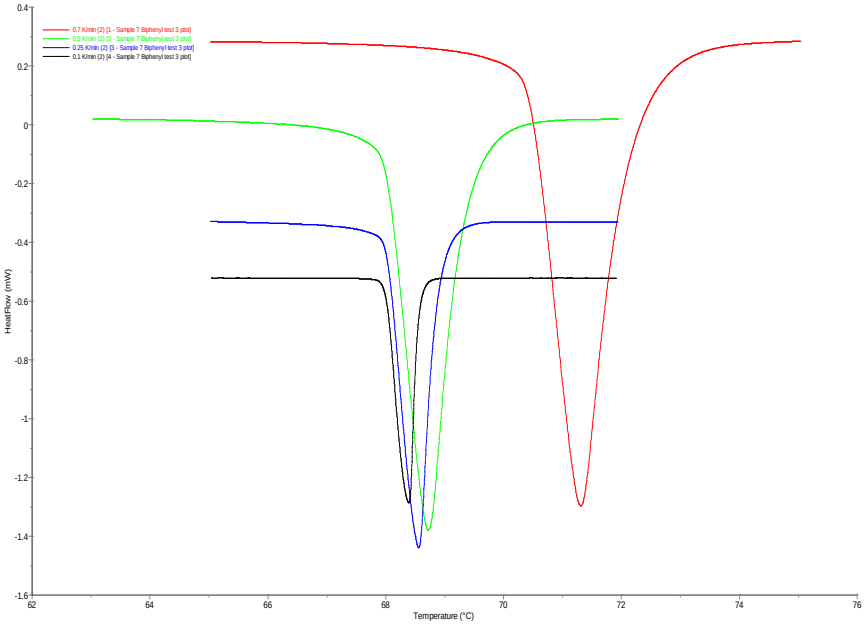


Figure E.4. Biphenyl melting peak for different scanning speeds (temperature correction was not used for the graph generation; signal cutting and slope correction were performed for each signal): — 0.1 °C/min, — 0.25 °C /min, — 0.5 °C /min, — 0.7 °C /min

E.3.2.3 Water

The water was tested within 10 samples: 3 of these samples were using deionised (DI) Water from DTU System, while the other 7 samples were using Type 1 Mili-Q, Milipore water. All the results presented in Table E.3 are for the MiliQ Type 1 water, considered a standard. The same scanning speeds were used as for all the other materials as was used for the calibration. The best results along with all the other relevant details are presented in Table E.3 and E.4. The water thermogram of sample 7, (second set of runs) before the temperature correction is presented in Figure E.5.

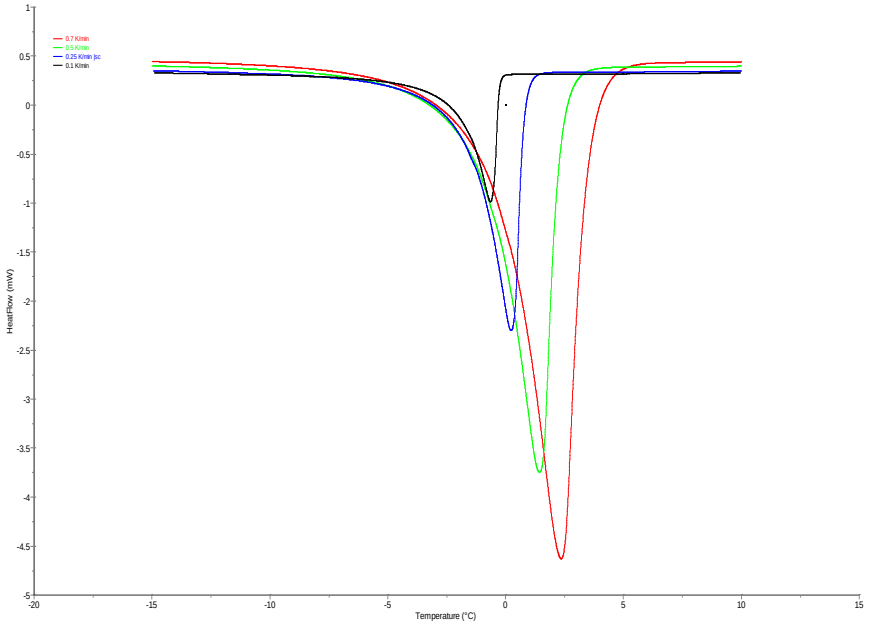


Figure E.5. Water melting peak for different scanning speeds (temperature correction was not used for the graph generation; signal cutting and slope correction were performed for each signal): — 0.1 °C/min, — 0.25 °C /min, — 0.5 °C /min, — 0.7 °C /min

E.3.3 Pure Compounds Measurements

E.3.3.1 Palmitic acid

Four samples of palmitic acid were measured. Sample 2 and 3 gave the best results. For each sample several melting-crystallization cycles (runs) were performed. The first run performed on a sample, using the same scanning program as for measurements, was used for sample thermal history removal.

The results before the temperature correction are presented in Table E.3, while the corrected values using Eq. E.1 and values form Table E.1 are presented in Table E.5. The average corrected onset temperature for palmitic acid is 63.34 °C, while the literature reported one is 61.85+/-1 °C.

E.3.3.2 Glycerol

Six samples of glycerol were analysed. The first 5 samples were taken from a glycerol fraction added in a separate glass after the glycerol regent bottle was open (normal room atmospheric conditions) first time. The last sample was collected in nitrogen atmosphere: a sample from the bottle was added in a small glass and then transferred with a 1 mL plastic syringe to the glass sample holder.

In all the measurements, no crystallization-melting peak could be observed. Several scanning programs were used: cooling from 1 K/min to 0.5 K/min; heating from 0.01 to 0.05 K/min rates, cooling till -20 or -10 °C, and with isotherm at -10 °C from 30 minutes up to 2 hours.

Glycerol is classified as a glassy substance exhibiting different properties than other types of liquids. In most of the cases, glycerol exist in a liquid, supercooled or glassy/amorphous state, and only when dehydrated and a special thermal treatment is applied, glycerol can form crystals (Ryabov et al., 2003).

In the paper of Ryabov et al. (Ryabov et al., 2003), it is stated that the glycerol, which is handled in normal atmospheric condition, does not crystallize due to a change in liquid structure as a result of water absorption (glycerol is highly hygroscopic).

The conditions to get the glycerol to crystallize are:

- very high purity. Traces of water absorbed from the atmosphere will change the liquid structure and will prevent the crystallization (Ryabov et al., 2003). The different dynamics of the anhydrous (nitrogen atmosphere handled) glycerol vs. glycerol handled in normal atmospheric conditions suggest two different structural organizations of glycerol in supercooled liquid state.
- very slow heating rates to allow for crystallization. Ryabov et al. (Ryabov et al., 2003) cooled the glycerol sample to 133 K and then heat up 303 K using a 0.1 K/min heating rate. The crystallization occurred at 293 K, while the melting occurred at 263 K. At higher hating rates, not even the fastest crystallization rates (see (Ryabov et al., 2003) for more details) are able to provide glycerol crystallization.
- Seeding the sample with a glycerol crystal (Hass, 1939; Lane, 1925).

E.3.4 Palmitic acid – Glycerol mixture(s)

The preparation of the Palmitic acid – Glycerol mixture was intended to be done under nitrogen atmospheric conditions. However, weighing the mixture with high precision is very difficult under these conditions.

Since the Palmitic acid is in the solid phase, the mixture was heated up to 70-75 °C. After melting the mixture it was noticed (the glass tub sample was put out in normal atmospheric conditions) that the two substances form two liquid phases (very difficult to notice while working in the box to ensure nitrogen atmosphere). The mixture was very difficult to handle since palmitic acid is crystallizing almost instantly at the temperature drop.

Table E.4 Experiments details for standard substances used for calibration and Palmitic acid

Reagent	Sample	Experiment No.	Scanning program	Scanning speed, K/min	Melting parameters				Crystallizing parameters			
					T Oneset, °C	T peak, °C	T Ofset, °C	Peak high, mW	T Oneset, °C	T peak, °C	T Ofset, °C	Peak high, mW
Naphthalene	Naphthalene (Setaram Standard)	1	Naphthalene	0.7	82.73	83.51			-	-	-	-
		2	Naphthalene	0.7	82.74	83.51	84.59		-	-	-	-
		3	Naphthalene	0.7	82.73	83.52	84.61	-5.46	-	-	-	-
		4	Naphthalene	0.7	82.74	83.5	84.55		-	-	-	-
		5	Naphthalene	0.5	82.14	82.78	83.54	-5.236	-	-	-	-
		6	Naphthalene	0.25	81.41	81.86	82.24	-4.35	-	-	-	-
		7	Naphthalene	0.1	80.95	81.24	81.40	-3.194	-	-	-	-
Water MILI Q Type 1	Sample 5	1	A	0.25	-1.31	0.39	0.83	-3.098	-25.539	-25.85	-26.952	21.67
	Sample 7	1	A	0.1	-2.02	-0.63	-0.24	-1.246	-22.37	-22.73	-24.05	17.87
		2	A	0.25	-1.89	0.02	0.57	-2.498	-20.2	-20.58	-21.9	17.79
		3	A	0.5	-1.21	1.26	2.11	-3.97	-22.4	-22.75	-24.05	17.87
		4	A	0.7	-0.66	2.11	3.22	-4.856	-22.3	-22.65	-23.93	17.74
		5	A	0.1	-1.96	-0.639	-0.27	-109.11	-21.633	-22.01	-23.318	1348.45
		6	A	0.25	0.722	0.238	-1.57	-222.16	-22.047	-22.40	-23.669	1344.91
		7	A	0.5	-0.922	1.444	-0.92	-349.55	-21.853	-22.21	-23.439	1372.52
		8	A	0.7	3.449	2.367	-0.35	-430.67	-21.819	-22.16	-23.45	1382.16
	Sample 8	1	A	0.1	-1.47	-0.142	0.18	-135.5	-	-	-	-
		2	A	0.25	-0.877	0.796	1.26	-282.06	-	-	-	-
		3	A	0.5	-0.09	2.07	2.83	-446.95	-	-	-	-
		4	A	0.7	0.44	2.99	4.03	-539.53	-	-	-	-

Table E.5 Scanning programs used in the experiments from Table 5

Scanning program	Interval	T_{in}, °C	T_{fin},°C	Speed, K/min	Time, s	Total time, min
Naphthalene	↗	25	50	1	1500	133
	↗	50	95	0.7*	3857	
	↘	95	25	3	1400	
	→	25	25	-	1200	
A	↘	20	-25	1	2700	235
	→	-25	-25		1200	
	↗	-25	10	0.25*	8400	
	↗	10	20	1	600	
	→	20	20	-	1200	
B	→	20	20	-	1200	197
	↗	20	45	1	1500	
	→	45	45	-	600	
	↗	45	85	0.7	3429	
	→	85	85	0	1200	
	↘	85	20	1	3900	
New	→	20	20	-	1200	389
	↗	20	45	1	1500	
	↗	45	74	0.1*	17400	
	↘	74	20	1	3240	
C	→	25	25	-	1200	157
	↗	25	35	1	600	
	↗	35	75	0.7	3429	
	→	75	75	-	1200	
	↘	75	25	1	3000	

* Other scanning speeds were used as well: 0.7 0.5, 0.25 and 0.1 (for calibration)
** Total time is calculated for the scanning speed shown in the table

Table E.6 Palmitic acid experimental results

Speed, K/min	T Onset, °C	T Peak, °C	T_{lit}, °C (literature)	$T_{corrected}$ (Onset), °C	AAD(1)	AAD(2)	ARD
0.7	62.3	64.1	61.85	62.68	0.67	0.83	1.34
0.7	61.9	64.01		62.39	0.96	0.54	0.87
0.7	62.1	64.09		62.48	0.86	0.63	1.02
0.7	63.2	65.36		63.48	0.13	1.63	2.63
0.7	63.2	65.29		63.43	0.08	1.58	2.55
0.7	64	65.96		64.10	0.76	2.25	3.64
0.7	63.8	65.84		63.99	0.65	2.14	3.46
0.7	64.1	66.31		64.21	0.87	2.36	3.81
Average	*63.1*	*65.12*		*63.34*	*0.62*	*1.49*	*2.41*

$$AAD(1) = \sum_{i=1}^{n} \left| \overline{T} - T_i \right| \qquad \overline{T} = \frac{1}{n} \sum_{i=1}^{n} T_i \qquad AAD(2) = \sum_{i=1}^{n} \left| T_{lit} - T_i \right| \qquad ARD = \sum_{i=1}^{n} \frac{\left| T_{lit} - T_i \right|}{T_{lit}}$$

APPENDIX F
SHEA OIL FRACTIONATION SIMULATION RESULTS

In this appendix the most important results that were not covered in Chapter 6 are given. Table F.1 presents thee mass and energy balance for the base case scenario of the Shea oil fractionation process.

Table F.1. Shea oil fractionation base case mass and energy balance

Stream Name	FEED_OIL	FEED_OIL_HOT	MAKE_UP_SOLV	OLEIN	RECYFLASH	S-00
Temperature, °C	25.0	50.0	20.0	40.0	60.0	-0.8
Pressure, bar	1.0	1.0	1.0	0.3	1.0	1.0
Enthalpy, ´MW	1.6E-02	4.9E-02	3.4E-07	1.9E-02	1.4E+00	-2.1E-02
Liquid Weight Fraction	1.0000	1.0000	1.0000	1.0000	0.0000	1.0000
S-S-S, kg/h	88.4	88.4	0.0	43.6	0.0	88.4
O-O-O, kg/h	566.3	566.3	0.0	279.1	0.0	566.3
P-O-S, kg/h	1079.6	1079.6	0.0	532.1	0.0	1079.6
P-P-P, kg/h	35.4	35.4	0.0	17.5	0.0	35.4
O-O-OH, kg/h	10.0	10.0	0.0	5.3	0.0	10.0
P-S-OH, kg/h	10.0	10.0	0.0	5.3	0.0	10.0
O-OH-OH, kg/h	1.2	1.2	0.0	0.6	0.0	1.2
P-OH-OH, kg/h	0.4	0.4	0.0	0.2	0.0	0.4
P-OOH, kg/h	7.0	7.0	0.0	6.0	0.0	7.0
S-OOH, kg/h	86.0	86.0	0.0	73.9	0.0	86.0
O-OOH, kg/h	88.0	88.0	0.0	75.6	0.0	88.0
LI-OOH, kg/h	13.0	13.0	0.0	11.2	0.0	13.0
A-OOH, kg/h	6.0	6.0	0.0	5.2	0.0	6.0
B-TOCOPH, kg/h	2.4	2.4	0.0	1.3	0.0	2.4
CHOLSTRL, kg/h	4.8	4.8	0.0	2.5	0.0	4.8
SITOSTRL, kg/h	0.2	0.2	0.0	0.1	0.0	0.2
STRC12.0, kg/h	1.0	1.0	0.0	0.5	0.0	1.0
SQUALNE, kg/h	0.1	0.1	0.0	0.0	0.0	0.1
ACETONE, kg/h	0.0	0.0	0.0	0.0	7715.5	8000.0
WATER, kg/h	0.0	0.0	0.0	3.3	13.7	15.0

Table F.1. Shea oil fractionation base case mass and energy balance (Continued)

Stream Name	S-01A	S-01C	S-01VAP	S-02A	S-02B	S-02VAP
Temperature, °C	-5.0	56.5	56.5	56.5	61.8	61.8
Pressure, bar	1.0	1.0	1.0	1.0	1.0	1.0
Enthalpy, ´MW	-3.2E-02	7.8E-01	6.2E-01	1.5E-01	6.1E-01	5.7E-01
Liquid Weight Fraction	1.0000	0.5652	0.0000	1.0000	0.3077	0.0000
S-S-S, kg/h	43.6	43.6	0.0	43.6	43.6	0.0
O-O-O, kg/h	279.1	279.1	0.0	279.1	279.1	0.0
P-O-S, kg/h	532.1	532.1	0.0	532.1	532.1	0.0
P-P-P, kg/h	17.5	17.5	0.0	17.5	17.5	0.0
O-O-OH, kg/h	5.3	5.3	0.0	5.3	5.3	0.0
P-S-OH, kg/h	5.3	5.3	0.0	5.3	5.3	0.0
O-OH-OH, kg/h	0.6	0.6	0.0	0.6	0.6	0.0
P-OH-OH, kg/h	0.2	0.2	0.0	0.2	0.2	0.0
P-OOH, kg/h	6.0	6.0	0.0	6.0	6.0	0.0
S-OOH, kg/h	73.9	73.9	0.0	73.9	73.9	0.0
O-OOH, kg/h	75.6	75.6	0.0	75.6	75.6	0.0
LI-OOH, kg/h	11.2	11.2	0.0	11.2	11.2	0.0
A-OOH, kg/h	5.2	5.2	0.0	5.2	5.2	0.0
B-TOCOPH, kg/h	1.3	1.3	0.0	1.3	1.3	0.0
CHOLSTRL, kg/h	2.5	2.5	0.0	2.5	2.5	0.0
SITOSTRL, kg/h	0.1	0.1	0.0	0.1	0.1	0.0
STRC12.0, kg/h	0.5	0.5	0.0	0.5	0.5	0.0
SQUALNE, kg/h	0.0	0.0	0.0	0.0	0.0	0.0
ACETONE, kg/h	7060.0	7060.0	3530.0	3530.0	3530.0	3177.0
WATER, kg/h	8.0	8.0	4.7	3.3	3.3	3.0
Stream Name	S-03A	S-03B	S-03VAP	S-04A	S-04B	S-04 BOTTOM
Temperature, °C	61.8	74.5	74.5	74.5	58.7	80.7
Pressure, bar	1.0	1.0	1.0	1.0	0.2	0.3
Enthalpy, ´MW	4.8E-02	9.3E-02	4.5E-02	4.8E-02	4.8E-02	4.8E-02
Liquid Weight Fraction	1.0000	0.8250	0.0000	1.0000	0.9262	1.0000
S-S-S, kg/h	43.6	43.6	0.0	43.6	43.6	43.6
O-O-O, kg/h	279.1	279.1	0.0	279.1	279.1	279.1
P-O-S, kg/h	532.1	532.1	0.0	532.1	532.1	532.1
P-P-P, kg/h	17.5	17.5	0.0	17.5	17.5	17.5
O-O-OH, kg/h	5.3	5.3	0.0	5.3	5.3	5.3
P-S-OH, kg/h	5.3	5.3	0.0	5.3	5.3	5.3
O-OH-OH, kg/h	0.6	0.6	0.0	0.6	0.6	0.6
P-OH-OH, kg/h	0.2	0.2	0.0	0.2	0.2	0.2
P-OOH, kg/h	6.0	6.0	0.0	6.0	6.0	6.0
S-OOH, kg/h	73.9	73.9	0.0	73.9	73.9	73.9
O-OOH, kg/h	75.6	75.6	0.0	75.6	75.6	75.6
LI-OOH, kg/h	11.2	11.2	0.0	11.2	11.2	11.2
A-OOH, kg/h	5.2	5.2	0.0	5.2	5.2	5.2
B-TOCOPH, kg/h	1.3	1.3	0.0	1.3	1.3	1.3
CHOLSTRL, kg/h	2.5	2.5	0.0	2.5	2.5	2.5
SITOSTRL, kg/h	0.1	0.1	0.0	0.1	0.1	0.1
STRC12.0, kg/h	0.5	0.5	0.0	0.5	0.5	0.5
SQUALNE, kg/h	0.0	0.0	0.0	0.0	0.0	0.0
ACETONE, kg/h	353.0	353.0	247.1	105.9	105.9	0.0
WATER, kg/h	0.3	0.3	0.2	0.1	0.1	3.3

Table F.1. Shea oil fractionation base case mass and energy balance (Continued)

Stream Name	S-04C	S-04 STEAM	S-04STRIP	S-04 STRIP-VP	S-04VAP	S-05A
Temperature, °C	79.3	120.3	79.3	79.6	79.3	-5.0
Pressure, bar	0.2	2.0	0.2	0.2	0.2	1.0
Enthalpy, ´MW	6.5E-02	1.3E-02	4.7E-02	1.2E-02	1.8E-02	-1.4E-02
Liquid Weight Fraction	0.9182	0.0000	1.0000	0.0000	0.0000	1.0000
S-S-S, kg/h	43.6	0.0	43.6	0.0	0.0	44.9
O-O-O, kg/h	279.1	0.0	279.1	0.0	0.0	287.2
P-O-S, kg/h	532.1	0.0	532.1	0.0	0.0	547.6
P-P-P, kg/h	17.5	0.0	17.5	0.0	0.0	18.0
O-O-OH, kg/h	5.3	0.0	5.3	0.0	0.0	4.7
P-S-OH, kg/h	5.3	0.0	5.3	0.0	0.0	4.7
O-OH-OH, kg/h	0.6	0.0	0.6	0.0	0.0	0.6
P-OH-OH, kg/h	0.2	0.0	0.2	0.0	0.0	0.2
P-OOH, kg/h	6.0	0.0	6.0	0.0	0.0	1.0
S-OOH, kg/h	73.9	0.0	73.9	0.0	0.0	12.1
O-OOH, kg/h	75.6	0.0	75.6	0.0	0.0	12.4
LI-OOH, kg/h	11.2	0.0	11.2	0.0	0.0	1.8
A-OOH, kg/h	5.2	0.0	5.2	0.0	0.0	0.8
B-TOCOPH, kg/h	1.3	0.0	1.3	0.0	0.0	1.1
CHOLSTRL, kg/h	2.5	0.0	2.5	0.0	0.0	2.3
SITOSTRL, kg/h	0.1	0.0	0.1	0.0	0.0	0.1
STRC12.0, kg/h	0.5	0.0	0.5	0.0	0.0	0.5
SQUALNE, kg/h	0.0	0.0	0.0	0.0	0.0	0.0
ACETONE, kg/h	105.9	0.0	10.6	10.6	95.3	940.0
WATER, kg/h	0.1	16.8	0.0	13.5	0.1	7.1
Stream Name	S-04C	S-04STEAM	S-04STRIP	S-04STRIP-VP	S-04VAP	S-05A
Temperature, °C	79.3	120.3	79.3	79.6	79.3	-5.0
Pressure, bar	0.2	2.0	0.2	0.2	0.2	1.0
Enthalpy, ´MW	6.5E-02	1.3E-02	4.7E-02	1.2E-02	1.8E-02	-1.4E-02
Liquid Weight Fraction	0.9182	0.0000	1.0000	0.0000	0.0000	1.0000
S-S-S, kg/h	43.6	0.0	43.6	0.0	0.0	44.9
O-O-O, kg/h	279.1	0.0	279.1	0.0	0.0	287.2
P-O-S, kg/h	532.1	0.0	532.1	0.0	0.0	547.6
P-P-P, kg/h	17.5	0.0	17.5	0.0	0.0	18.0
O-O-OH, kg/h	5.3	0.0	5.3	0.0	0.0	4.7
P-S-OH, kg/h	5.3	0.0	5.3	0.0	0.0	4.7
O-OH-OH, kg/h	0.6	0.0	0.6	0.0	0.0	0.6
P-OH-OH, kg/h	0.2	0.0	0.2	0.0	0.0	0.2
P-OOH, kg/h	6.0	0.0	6.0	0.0	0.0	1.0
S-OOH, kg/h	73.9	0.0	73.9	0.0	0.0	12.1
O-OOH, kg/h	75.6	0.0	75.6	0.0	0.0	12.4
LI-OOH, kg/h	11.2	0.0	11.2	0.0	0.0	1.8
A-OOH, kg/h	5.2	0.0	5.2	0.0	0.0	0.8
B-TOCOPH, kg/h	1.3	0.0	1.3	0.0	0.0	1.1
CHOLSTRL, kg/h	2.5	0.0	2.5	0.0	0.0	2.3
SITOSTRL, kg/h	0.1	0.0	0.1	0.0	0.0	0.1
STRC12.0, kg/h	0.5	0.0	0.5	0.0	0.0	0.5
SQUALNE, kg/h	0.0	0.0	0.0	0.0	0.0	0.0
ACETONE, kg/h	105.9	0.0	10.6	10.6	95.3	940.0
WATER, kg/h	0.1	16.8	0.0	13.5	0.1	7.1

Table F.1. Shea oil fractionation base case mass and energy balance (Continued)

Stream Name	S-05C	S-05VAP	S-05 VAPCOL	S-05 VAPRECY	S-06A	S-06B
Temperature, °C	60.2	60.2	60.2	60.2	60.2	72.6
Pressure, bar	1.0	1.0	1.0	1.0	1.0	1.0
Enthalpy, ´MW	1.5E-01	1.0E-01	1.5E-02	8.8E-02	4.3E-02	9.4E-02
Liquid Weight Fraction	0.6988	0.0000	0.0000	0.0000	1.0000	0.7846
S-S-S, kg/h	44.9	0.0	0.0	0.0	44.9	44.9
O-O-O, kg/h	287.2	0.0	0.0	0.0	287.2	287.2
P-O-S, kg/h	547.6	0.0	0.0	0.0	547.6	547.6
P-P-P, kg/h	18.0	0.0	0.0	0.0	18.0	18.0
O-O-OH, kg/h	4.7	0.0	0.0	0.0	4.7	4.7
P-S-OH, kg/h	4.7	0.0	0.0	0.0	4.7	4.7
O-OH-OH, kg/h	0.6	0.0	0.0	0.0	0.6	0.6
P-OH-OH, kg/h	0.2	0.0	0.0	0.0	0.2	0.2
P-OOH, kg/h	1.0	0.0	0.0	0.0	1.0	1.0
S-OOH, kg/h	12.1	0.0	0.0	0.0	12.1	12.1
O-OOH, kg/h	12.4	0.0	0.0	0.0	12.4	12.4
LI-OOH, kg/h	1.8	0.0	0.0	0.0	1.8	1.8
A-OOH, kg/h	0.8	0.0	0.0	0.0	0.8	0.8
B-TOCOPH, kg/h	1.1	0.0	0.0	0.0	1.1	1.1
CHOLSTRL, kg/h	2.3	0.0	0.0	0.0	2.3	2.3
SITOSTRL, kg/h	0.1	0.0	0.0	0.0	0.1	0.1
STRC12.0, kg/h	0.5	0.0	0.0	0.0	0.5	0.5
SQUALNE, kg/h	0.0	0.0	0.0	0.0	0.0	0.0
ACETONE, kg/h	940.0	564.0	84.6	479.4	376.0	376.0
WATER, kg/h	7.1	4.4	0.7	3.7	2.7	2.7
Stream Name	S-06VAP	S-07A	S-07B	S-07 BOTTOM	S-07C	S-07 STEAM
Temperature, °C	72.6	72.6	56.3	76.8	75.8	120.3
Pressure, bar	1.0	1.0	0.2	0.2	0.2	2.0
Enthalpy, ´MW	5.3E-02	4.1E-02	4.1E-02	3.9E-02	5.5E-02	1.0E-02
Liquid Weight Fraction	0.0000	1.0000	0.9255	1.0000	0.9177	0.0000
S-S-S, kg/h	0.0	44.9	44.9	44.9	44.9	0.0
O-O-O, kg/h	0.0	287.2	287.2	287.2	287.2	0.0
P-O-S, kg/h	0.0	547.6	547.6	547.6	547.6	0.0
P-P-P, kg/h	0.0	18.0	18.0	18.0	18.0	0.0
O-O-OH, kg/h	0.0	4.7	4.7	4.7	4.7	0.0
P-S-OH, kg/h	0.0	4.7	4.7	4.7	4.7	0.0
O-OH-OH, kg/h	0.0	0.6	0.6	0.6	0.6	0.0
P-OH-OH, kg/h	0.0	0.2	0.2	0.2	0.2	0.0
P-OOH, kg/h	0.0	1.0	1.0	1.0	1.0	0.0
S-OOH, kg/h	0.0	12.1	12.1	12.1	12.1	0.0
O-OOH, kg/h	0.0	12.4	12.4	12.4	12.4	0.0
LI-OOH, kg/h	0.0	1.8	1.8	1.8	1.8	0.0
A-OOH, kg/h	0.0	0.8	0.8	0.8	0.8	0.0
B-TOCOPH, kg/h	0.0	1.1	1.1	1.1	1.1	0.0
CHOLSTRL, kg/h	0.0	2.3	2.3	2.3	2.3	0.0
SITOSTRL, kg/h	0.0	0.1	0.1	0.1	0.1	0.0
STRC12.0, kg/h	0.0	0.5	0.5	0.5	0.5	0.0
SQUALNE, kg/h	0.0	0.0	0.0	0.0	0.0	0.0
ACETONE, kg/h	282.0	94.0	94.0	0.0	94.0	0.0
WATER, kg/h	2.1	0.6	0.6	2.6	0.6	13.2

Table F.1. Shea oil fractionation base case mass and energy balance (Continued)

Stream Name	S-07STRIP	S-07STRIP-VP	S-07VAP	S-08B	S-08BOTTOM	S-08VAP
Temperature, °C	75.8	76.2	75.8	73.0	73.0	13.1
Pressure, bar	0.2	0.2	0.2	0.2	0.4	0.2
Enthalpy, ´MW	3.9E-02	9.6E-03	1.6E-02	7.0E-02	2.1E-03	2.2E-03
Liquid Weight Fraction	1.0000	0.0000	0.0000	0.0000	1.0000	1.0000
S-S-S, kg/h	44.9	0.0	0.0	0.0	0.0	0.0
O-O-O, kg/h	287.2	0.0	0.0	0.0	0.0	0.0
P-O-S, kg/h	547.6	0.0	0.0	0.0	0.0	0.0
P-P-P, kg/h	18.0	0.0	0.0	0.0	0.0	0.0
O-O-OH, kg/h	4.7	0.0	0.0	0.0	0.0	0.0
P-S-OH, kg/h	4.7	0.0	0.0	0.0	0.0	0.0
O-OH-OH, kg/h	0.6	0.0	0.0	0.0	0.0	0.0
P-OH-OH, kg/h	0.2	0.0	0.0	0.0	0.0	0.0
P-OOH, kg/h	1.0	0.0	0.0	0.0	0.0	0.0
S-OOH, kg/h	12.1	0.0	0.0	0.0	0.0	0.0
O-OOH, kg/h	12.4	0.0	0.0	0.0	0.0	0.0
LI-OOH, kg/h	1.8	0.0	0.0	0.0	0.0	0.0
A-OOH, kg/h	0.8	0.0	0.0	0.0	0.0	0.0
B-TOCOPH, kg/h	1.1	0.0	0.0	0.0	0.0	0.0
CHOLSTRL, kg/h	2.3	0.0	0.0	0.0	0.0	0.0
SITOSTRL, kg/h	0.1	0.0	0.0	0.0	0.0	0.0
STRC12.0, kg/h	0.5	0.0	0.0	0.0	0.0	0.0
SQUALNE, kg/h	0.0	0.0	0.0	0.0	0.0	0.0
ACETONE, kg/h	9.4	9.4	84.6	284.5	0.0	284.5
WATER, kg/h	0.1	10.7	0.5	25.5	24.2	1.3

Stream Name	S-09A-RECY-T	S-09C	SOLVENT_FEED	STEARIN	WASTEWATER
Temperature, °C	29.4	29.4	-15.0	50.0	30.0
Pressure, bar	1.0	1.0	1.0	0.2	0.4
Enthalpy, ´MW	1.4E-01	1.4E-01	-7.0E-02	2.3E-02	8.4E-04
Liquid Weight Fraction	1.0000	1.0000	1.0000	1.0000	1.0000
S-S-S, kg/h	0.0	0.0	0.0	44.9	0.0
O-O-O, kg/h	0.0	0.0	0.0	287.2	0.0
P-O-S, kg/h	0.0	0.0	0.0	547.6	0.0
P-P-P, kg/h	0.0	0.0	0.0	18.0	0.0
O-O-OH, kg/h	0.0	0.0	0.0	4.7	0.0
P-S-OH, kg/h	0.0	0.0	0.0	4.7	0.0
O-OH-OH, kg/h	0.0	0.0	0.0	0.6	0.0
P-OH-OH, kg/h	0.0	0.0	0.0	0.2	0.0
P-OOH, kg/h	0.0	0.0	0.0	1.0	0.0
S-OOH, kg/h	0.0	0.0	0.0	12.1	0.0
O-OOH, kg/h	0.0	0.0	0.0	12.4	0.0
LI-OOH, kg/h	0.0	0.0	0.0	1.8	0.0
A-OOH, kg/h	0.0	0.0	0.0	0.8	0.0
B-TOCOPH, kg/h	0.0	0.0	0.0	1.1	0.0
CHOLSTRL, kg/h	0.0	0.0	0.0	2.3	0.0
SITOSTRL, kg/h	0.0	0.0	0.0	0.1	0.0
STRC12.0, kg/h	0.0	0.0	0.0	0.5	0.0
SQUALNE, kg/h	0.0	0.0	0.0	0.0	0.0
ACETONE, kg/h	8000.0	8000.0	8000.0	0.0	0.0
WATER, kg/h	15.0	15.0	15.0	2.6	24.2

The economic analysis is performed with ECON. The analysis considers the costs for Europe region. The prices used for the for the raw materials and products are given in Table F.2 based on suggestions from Alfa Laval, online available prices and prices available in ECON. The assumed number of operating days per year is 288. The CEPCI is updated with the factor from 2016 (Plant Cost Index, 2017). The results for the capital cost and operating cost for the base case scenario are given in Table F.3 and F.4. The cost distribution for equipment and utility cost for the base case are presented in Figure F.1 and Figure F.2.

Table F.2 Raw material and products prices used in the economic analysis for Base case, Alternative 1 and Alternative 2

Material	Quantity, t/yr	Price, €/kg
Shea Oil	2680	1.5[a]
Solvent	0.024[b]	2.3[c]
Process water	207	0.2
Shea Stearin	7563	3.0
Shea Oleine	8530	1.5
Ammonia	-[d]	0.8

[a] (CBI Market Intellingence, 2015)
[b] The solvent quantity considered here represents the solvent make-up. The first batch of solvent needed for the process used the same price and considered the amount for two hours of continuous feed.
[c] High purity acetone was considered for the process (Chembid).
[d] The amount of ammonia needed for the cooling system was obtained from the flowrate (see Table F.5) and 1.5 h residence time and the price was considered as double of the maximum production cost (Boulamanti and Moya, 2017).

Table F.3 Economic analysis results for the capital cost for the Base case

Indicator	Value, M€
Total Direct Cost	3.6
Total indirect cost	1.4
Fixed-capital Investment (FCI)	5.1
Working Capital Investments (WC)	0.0
Total Capital Investment (TCI)	5.1

Table F.4 Economic analysis results for the operating cost for the base case

Indicator	Value, M€/yr
Raw Material	4.1
Utilities	0.1
Variable cost	5.3
Fixed charges	0.1
Manufacturing cost	5.5
General expenses	0.6
Total product cost	6.2

Table F.5 Economic analysis results for all the process alternatives.

	Utility Cost, k€/yr		Heat exchanger		Distillation Column
	Hot Utility	Cold utility *	Area, m^2	Cost, k€	Cost, k€
Base case	241.2	8.4	524.6	106.6	62.6
Process alternative 1	187.9	6.0	534.9	116.1	62.6
Process alternative 2	92.5	3.7	515.6	115.0	62.6
Process alternative 3	101.5	3.8	511.2	105.7	49.7

*only cooling water (CW) is reported here. The cooling with ammonia is the same in all process alternatives.

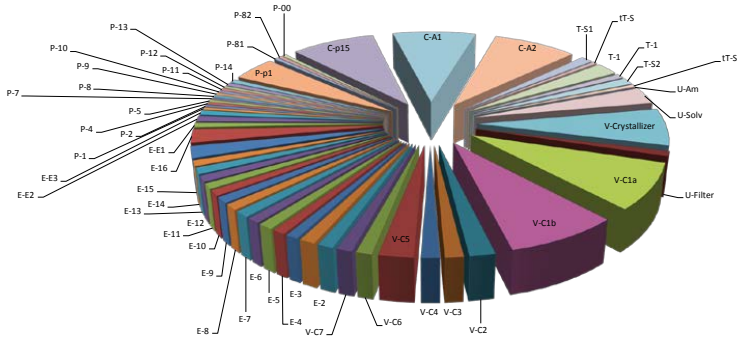


Figure F.1 Equipment cost distribution for the base case

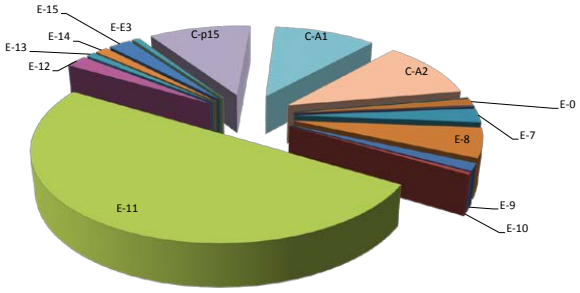


Figure F.2 Utility cost distribution for the base case

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