

**MOLECULAR-LEVEL KINETIC MODELING OF THE UPGRADING
OF RESIDUAL OIL IN SUPERCRITICAL WATER**

by

Roel Smits

A thesis submitted to the Faculty of the University of Delaware in partial fulfillment
of the requirements for the degree of Master of Science in Chemical Engineering

Spring 2019

© 2019 Roel Smits
All Rights Reserved

**MOLECULAR-LEVEL KINETIC MODELING OF THE UPGRADING
OF RESIDUAL OIL IN SUPERCRITICAL WATER**

by

Roel Smits

Approved: _____
Michael T. Klein, Sc.D.
Professor in charge of thesis on behalf of Advisory Committee

Approved: _____
Eric M. Furst, Ph.D.
Chair of the Department of Chemical and Biomolecular Engineering

Approved: _____
Levi T. Thompson, Ph.D.
Dean of the College of Engineering

Approved: _____
Douglas J. Doren, Ph.D.
Interim Vice Provost for Graduate and Professional Education

ACKNOWLEDGMENTS

First and foremost, I would like to express my thanks of gratitude to my advisor Michael T. Klein for accepting me in his research group and mentoring me through this project. Secondly, I want to thank Pratyush Agarwal for all the things he taught me and for helping me with the problems I faced. I am very grateful to Norman Wagner, Isabelle Benoit, Peter Van Puyvelde and Ilse Smets for giving me the opportunity to do this dual degree exchange between the University of Delaware and the KU Leuven. I want to especially thank my parents, Jean Smits and Anne Matthys, for helping me to make this exchange possible. I also want to extend my thanks to my girlfriend, Febe Geebelen, this exchange has taken me a long time away from home, and I could not have done it without her support. A nal thank you to all the friends I have made during my American adventure, with a special mention for Alexander Tunnell and Mark Casagrande. All of you made my stay in the USA an amazing experience, it would not have been the same without all of you.

TABLE OF CONTENTS

LIST OF TABLES	vii
LIST OF FIGURES	ix
NOMENCLATURE	xiii
ABSTRACT	xiv
Chapter	
1 INTRODUCTION	1
2 OBJECTIVES AND METHODOLOGY	3
3 BACKGROUND	6
3.1 Residual Oil	6
3.1.1 Composition of Residual Oil	6
3.1.1.1 Aromatic Compounds	7
3.1.1.2 Hydrogenated Aromatics	7
3.1.1.3 Naphthenes	8
3.1.1.4 Paraffins	8
3.1.1.5 Sulfur Compounds	9
3.1.1.6 Nitrogen Compounds	9
3.1.1.7 Oxygen Compounds	10
3.1.1.8 Metals	10
3.2 Upgrading of Residual Oil	11
3.2.1 Conventional Technologies	12
3.2.2 Supercritical Water Treatment	14
3.2.2.1 Role as a Solvent	15
3.2.2.2 Role as a Reactant	17

3.2.2.3	Reasons to Investigate Supercritical Water Upgrading	18
4	MOLECULAR-LEVEL KINETIC MODELING & THE KINETIC MODELER’S TOOLBOX	19
4.1	Motivation for Molecular-level Modeling	19
4.2	General Structure of Molecular-level Kinetic Models	20
4.3	The Kinetic Modeler’s Toolbox	22
4.3.1	Molecular Representation	23
4.3.2	Interactive Network Generator	25
4.3.3	Property Generator	28
4.3.4	Initial Condition Generator	28
4.3.5	Kinetic Model Editor	30
5	MODEL EQUATIONS AND REACTION RATE LAWS	33
5.1	Model Equations	33
5.2	Rate Laws	34
5.2.1	Pyrolysis Reactions	34
5.2.2	Hydrolysis Reactions	37
5.2.3	Dehydrogenation Reactions	39
5.2.4	Coking Reactions	40
5.2.5	Graphical Representation Rate Laws	42
6	RESULTS AND DISCUSSION	48
6.1	Reaction Network Generation	48
6.1.1	Reaction Network Generated by Ingen	50
6.1.1.1	Reaction Families	50
6.1.1.2	Model Compounds	51
6.1.1.3	Assumptions	59
6.1.2	Manually Added Reactions	60
6.1.3	Diagnostics of the Reaction Network	63
6.2	Feed Composition Modeling	67
6.2.1	Residual Oil	68

6.2.2	VGO	73
6.3	Kinetic Model Evaluation	77
6.3.1	VGO	77
7	CONCLUSIONS	83
8	FUTURE WORK	85
8.1	Model Development	85
8.2	Model Usage	86
	BIBLIOGRAPHY	87
Appendix		
A	EXAMPLE OF A PDF TREE STRUCTURE	91
B	DERIVATION EQUILIBRIUM CONSTANT HYDROLYSIS REACTION	92
C	RATE OF HYDROLYSIS VS RATE OF PYROLYSIS	95
D	MANUAL ON HOW TO USE THE KINETIC MODEL	97
D.1	Ingen_Model	97
D.2	Manually_added_reactions	97
D.3	ICG_models	97
D.4	KME_model	98
D.4.1	Generating input stream	98
D.4.2	Include cage effect and the influence of the dielectric constant	98
D.4.3	Get product properties	99
E	KINETIC CONSTANTS	100
F	REPRINT PERMISSION DOCUMENTS	103

LIST OF TABLES

3.1	Hetero atom content residual oil originating from different geographical locations	6
3.2	Class fractions residual oil originating from different geographical locations	7
5.1	Critical point water	36
5.2	Coefficients a_k	36
5.3	Coefficients b_{ij}	37
5.4	Constants N_A , μ and α	38
5.5	Coefficients N_k , i_k and j_k	39
5.6	Data points to determine coefficients a and b in equation 5.21	41
5.7	Process conditions and parameter values	43
6.1	Reaction families	50
6.2	Examples of model compounds	52
6.3	Number of reactions for each reaction family	67
6.4	Reactor conditions experimental data	78
6.5	Comparison model results KME	79
6.6	Comparison between VGO feed-and product properties	81
B.1	Thermodynamic data to calculate the equilibrium constant	93
C.1	Data hydrolysis-and pyrolysis rate constants	95

E.1	Kinetic constants KME model	100
-----	---------------------------------------	-----

LIST OF FIGURES

1.1	Predictions of the global energy consumption by energy source . . .	1
3.1	Example of an aromatic compound	8
3.2	Example of a hydrogenated aromatic compound	8
3.3	Example of a naphthene	8
3.4	Example of a paraffin	9
3.5	Molecules containing easy and hard sulfur groups	9
3.6	Pyridine and Pyrrole	10
3.7	Example of a porphyrin metal compound	11
3.8	Phase diagram water	14
3.9	Phase structure of the residual oil-water mixture for different oil to water ratios	17
4.1	General structure of molecular-level kinetic models	21
4.2	Overview of KMT software packages	23
4.3	A bond-electron matrix representation of propane	24
4.4	Matrix operation for the hydro cracking of propane to methane and ethane	27
4.5	Example of a PDF	30
5.1	Lumped reaction network	42
5.2	Matlab simulation lumped model	43

5.3	Differences between simulations with extensive and simple kinetic rate laws	45
6.1	Hydrolysis/dehydration reaction network	49
6.2	Naphthene aromatization reaction	62
6.3	Olefin addition, cyclization and aromatization	62
6.4	Coking	63
6.5	ICG results residual oil	69
6.6	C-number distributions residual oil	72
6.7	ICG results VGO	74
6.8	C-number distributions VGO	76
6.9	Parity plots product properties	79
A.1	Example of a simple PDF tree structure	91
B.1	Hydrolysis reaction for the calculation of the equilibrium constant	92

NOMENCLATURE

α	Mean molecular polarizability water [$\frac{C^2}{Jm^2}$]
ϵ	Dielectric constant
ϵ_0	Permittivity of Vacuum [$\frac{F}{m}$]
η	Efficiency factor due to cage effect
η_p	Correction factor due to phase structure
μ	Dipole moment water [Cm]
μ_{ij}	Stoichiometric coefficient of component j in reaction i
ω_j	Weighing factor for measurement j
$\bar{\rho}$	Reduced density
\bar{P}	Reduced pressure
\bar{T}	Reduced temperature
ρ	Density [$\frac{kg}{m^3}$]
ρ_{crit}	Critical density [$\frac{kg}{m^3}$]
A_i	Pre exponential factor for reaction i
C_j	Concentration of component j [$\frac{mol}{m^3}$]
d_j	Molecular diameter component j [m]

D_{12}	Binary diffusivity of component 1 and component 2 [$\frac{m^2}{s}$]
Da	Damköhler number
E_i	Activation Energy for reaction i [$\frac{J}{mol}$]
N_A	Avogadro's number [$\frac{1}{mol}$]
N_j	Number of moles of component j [mol]
P_{crit}	Critical pressure [MPa]
R	Universal gas constant [$\frac{J}{K \cdot mol}$]
r_i	Reaction rate of reaction i per unit volume [$\frac{mol}{sm^3}$]
T	Temperature [K]
T_{crit}	Critical temperature [K]
V	Volume of the reacting system [m^3]
v_j	Molar volume of component j [$\frac{m^3}{mol}$]
y_{ij}^{exp}	Experimental data point value for property i in data set j
y_{ij}^{model}	Model prediction for property i in data set j
ICG	Initial Condition Generator
INGen	Interactive Network Generator
KME	Kinetic Model Editor
KMT	Kinetic Modeler's Toolbox
PDF	Probability Density Function
PropGen	Property Generator

SCW Supercritical water

VGO vacuum gas oil

ABSTRACT

The objective of this thesis is to develop a molecular-level kinetic model for the upgrading of residual oil in an environment of supercritical water. The Kinetic Modeler's Toolbox software, developed by the Klein research group, is used to make this kinetic model. A rank zero reaction network is created. This is necessary to limit the number of model compounds. The reaction network contains four major chemical pathways: pyrolysis, hydrolysis, aromatization and coking. The entire network consists of 10025 reactions between 2894 components. Besides creating a reaction network, formats for the rate laws are constructed. Because the system is in a pseudo single phase and no catalyst is used, the underlying principle for the rate laws is microkinetics. Supercritical water has three different solvent effects: solvent cage effect, the effect of the dielectric constant and the water-oil phase behavior. These solvent effects are incorporated into the rate laws. Due to the unavailability of product data for supercritical water upgrading of residual oil in literature, tuning of the kinetic parameters is not done in this thesis. Instead, two molecular representations of feed streams are made. One of them is a molecular representation of residual oil. This is done in order to show that the chosen model compounds can model a residual oil feed stream. The other is a molecular representation of VGO. VGO is a subset of residual oil, that contains the more volatile compounds. For VGO a product data set for supercritical water upgrading is available in literature. Kinetic parameters are tuned, such that the simulated properties of the output of the kinetic model are close to those reported in literature. This is done in order to show that the reactions, in the reaction network, and the format of the rate laws represent the physical and chemical phenomena that occur in supercritical water upgrading of oil fractions.

Chapter 1

INTRODUCTION

Energy is one of the main pillars of modern society. Utilization of available energy sources made it possible for our modern society to develop. But energy consumption also has negative aspects. Combustion of fossil fuels in large amounts is one of the main causes of global warming on our planet. A gradual transition towards more renewable energy sources is required in order to stop this phenomenon. Massive improvements have been made in the last few decades regarding renewable energy technologies. Predictions regarding the global energy consumption made by US Energy Information Administration are shown in Figure 1.1 [1]. It shows that however renewable energy has the biggest growth trajectory for the coming decades, hydrocarbons and especially petroleum-based products remain the main source of energy.

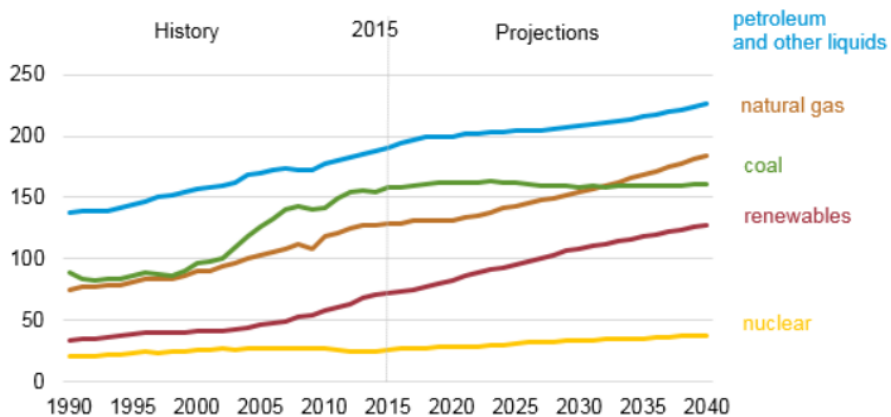


Figure 1.1: Predictions of the global energy consumption by energy source [1]

Crude oil reserves are finite. Extracting of conventional (light) feedstocks becomes harder and more expensive every year. Because of this, there is a growing interest in

extracting heavier forms of crude oil [2]. These heavier feedstocks contain a larger amount of the fraction called residual oil. This fraction is a lower value product that needs upgrading in order to be converted into useful products. As more heavier feedstocks are extracted, there is a growing supply of residual oil. This creates economic opportunities and increases the interest to find better and less expensive upgrading techniques. Upgrading of residual oil has two main goals. One is to crack the heavy molecules into smaller, low-boiling molecules that can be used as an energy source. The other is to remove the hetero-atoms (sulfur, nitrogen, and metals) in order to limit the production of toxic gasses during combustion. Experiments have indicated that supercritical water treatment has interesting characteristics for the upgrading of residual oil [3]. The exact phenomena behind these findings are still not clear. Therefore, more research, especially on the molecular level, is required in order to fully understand what mechanisms cause these interesting findings and to discover the full capacity of supercritical water treatment. This thesis describes the development of a molecular-level kinetic model for supercritical water upgrading of residual oil. Developing such a model creates more insight in the phenomena that are occurring on the molecular level. Once the model is fully developed and all its parameters are tuned, it can be used in order to predict better operating conditions to optimize the upgrading process.

Chapter 2

OBJECTIVES AND METHODOLOGY

The goal of this thesis is to develop a representative, molecular-level reaction network of the reactions occurring in a system where residual oil is upgraded in an atmosphere of SCW. The developed model should be able to simulate a supercritical water upgrading process within one minute. This is done by using the Kinetic Modeler's Toolbox (KMT). This is software, developed by the Klein Research Group, to do kinetic modeling of complex chemical systems on a molecular level. The entire toolbox consists of multiple software packages which are used in different stages of the model development.

First, a selection of reaction families is made based on literature [4, 5, 6, 7, 8, 9, 10, 11, 12, 13]. These reaction families represent all possible chemical reactions that are included in the model. Based on the chosen reaction families a selection of model compounds is made to represent the feed and the product. Combining the reaction families with the model compounds in the Interactive Network Generator (INGen) software creates a reaction network.

Subsequently, the mole fractions of the model compounds are determined in order to represent the reactant stream. This is done by using the Initial Condition Generator (ICG) software. The mole fractions for the different components and the associated properties of the stream are simulated by ICG. The set of mole fractions, which matches the experimental data found in literature [14, 15] best, will be used as a representation of the reactant stream.

Finally, the list of reactions generated by INGen, the composition of the reactant stream generated by ICG and chosen formats for the reaction rate laws are combined in the Kinetic Model Editor (KME) software. This software solves the mathematical

equations, that represent the change in concentrations due to chemical reactions, for a specified reactor type and reactor conditions. KME can be used to simulate the output of a chemical system if all the input parameters are known. KME can also be used to determine the numerical values for unknown input parameters that match experimental data points best.

Ideally, a complete data set is available which contains extensive data about a residual oil stream before and after SCW upgrading. This data set could then be used to determine the mole fractions of the model compounds for the feed stream in ICG, and the numerical values for the input parameters in KME. Unfortunately, this data is not available in literature. Therefore, a different approach is taken. Data regarding the properties of a residual oil stream before SCW treatment is available in literature. This data will be used in ICG to determine the mole fractions of the model compounds that match the feed stream. Tuning of the kinetic parameters in KME will not be done in this thesis. In order to validate that the reaction network and the chosen model compounds are representative, a second data set is used. This data set contains data about vacuum gas oil (VGO) before and after SCW treatment. VGO is a subset of residual oil that contains more volatile compounds. Using the same reaction network and model compounds, a second model is made in ICG which represents the VGO feed data. This stream is used in KME. The simulated properties of the SCW treated VGO stream are compared to the experimental data. Comparison of simulated-and experimental data indicates that the developed model contains the necessary chemistry to simulate the observed trends.

Chapter 3 contains background information regarding residual oil, conventional oil upgrading techniques and SCW upgrading. Chapter 4 will discuss the importance of (molecular-level) modeling and individual software packages of the KMT more deeply. Chapter 5 gives an overview of the model equations which describe the change in concentration of the model compounds. Chapter 5 also contains the formats of the rate laws, necessary to close the model equations and make them solvable. Chapter 6 shows how the KMT is used in order to develop the reaction network for the SCW

upgrading of residual oil. It also discusses the results of the modeling process. In Chapter 7 the conclusions of the modeling process are made. Chapter 8 highlights the questions that still have to be answered in future work.

Chapter 3

BACKGROUND

3.1 Residual Oil

Residual oil, or residue, is defined by Murray R. Gray in 1994 in his book 'upgrading petroleum residues and heavy oils' as the fraction of petroleum, heavy oil or bitumen that does not distill under vacuum. This corresponds to the fractions that have atmospheric boiling points of over 525 °C [2]. Note that this is not a universal definition. The book 'Oil Sands, Heavy Oil, and Bitumen: From Recovery to Refinery' by Dwijen K Banerjee refers in 2012 to residue as the fractions that have an atmospheric boiling point above 535 °C [16]. 10 To 30 % of all crude oil consists of residual oil [2]. This section takes a closer look at the molecular structures that are present in residual oil.

3.1.1 Composition of Residual Oil

The chemical composition of residue varies depending on the source of crude oil. Table 3.1 gives an example of elemental compositions of residual oil originating from crude oil extracted from two geographical locations.

Table 3.1: Hetero atom content residual oil originating from different geographical locations [2, 17]

location	molar ratio	wt %			ppm	
		H/C	S	N	O	Ni
Lloydminster (Canada)	1.47	4.69	0.53	0.99	140	190
Ishimbai (Russia)	/	3.9-5.25	0.61-1.01	2.76-3.69	/	/

The hydrocarbon fraction of residual oil can be subdivided in different class fractions (saturates, aromatics, resins, and asphaltenes). These class fractions are based on

solubility and adsorption characteristics. Saturates are soluble in n-pentane, and do not adsorb in a column chromatograph. Aromatics are soluble in n-pentane, and they adsorb from the solution to silica or alumina. Resins are soluble in n-pentane, and they adsorb from the solution to silica gel or clay. Asphaltenes are insoluble in n-pentane and soluble in benzene [2]. Table 3.2 gives an example of the class fractions of residual oil originating from crude oil extracted from two geographical locations.

Table 3.2: Class fractions residual oil originating from different geographical locations [2, 17]

Location	wt%			
	Saturates	Aromatics	Resin	Asphaltene
Lloydminster (Canada)	15.4	6.4	58.2	19.9
Ishimbai (Russia)	40.93	29.8	14.95	14.10

Further specification of the composition residual oil can be done by identifying which chemical structures (=functional groups) are present within the mixture. The following subsections discuss the different chemical structures that are found in residual oil.

3.1.1.1 Aromatic Compounds

In general, these compounds consist of clusters of aromatic rings which are connected by alkyl chains of varying lengths. The number of aromatic rings in a cluster varies and depends on the conditions the residual oil has encountered in the past. Aromatic groups in unprocessed residues contain mostly up to three rings while in processed residues they can contain up to ten aromatic rings depending on the processing. The length of the alkyl chains has a normal distribution [2]. Figure 3.1 shows an example of an aromatic compound.

3.1.1.2 Hydrogenated Aromatics

These compounds are very similar to the ones described in paragraph 3.1.1.1. The difference is that some, but not all the aromatic rings are hydrogenated [2]. Figure

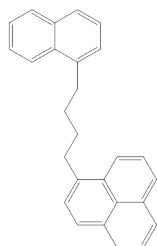


Figure 3.1: Example of an aromatic compound

3.2 shows an example of a hydrogenated aromatic compound.

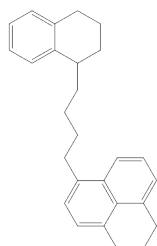


Figure 3.2: Example of a hydrogenated aromatic compound

3.1.1.3 Naphthenes

Naphthenes consist of fused, non-aromatic rings. The maximal number of fused rings in a group in residue molecules is six [2]. Figure 3.3 shows an example of a naphthene.

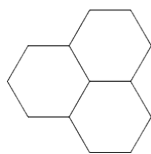


Figure 3.3: Example of a naphthene

3.1.1.4 Paraffins

Paraffins occur in two forms: straight-chain or branched. Low carbon paraffins are not present in residual oil [2]. The lowest paraffin carbon number found in [17] is 12. Figure 3.4 shows an example of a paraffin.

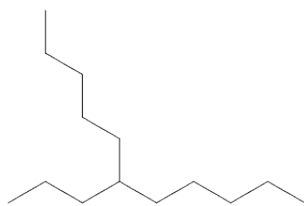


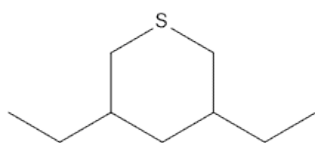
Figure 3.4: Example of a paraffin

3.1.1.5 Sulfur Compounds

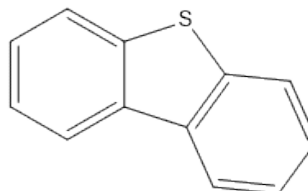
Besides hydrocarbons, sulfur is the most abundant element in residual oil. It is present in multiple forms. In general, these forms can be subdivided into two groups: easy sulfur and hard sulfur.

Easy sulfur can be easily removed from the residual oil. It is present as a sulfide, thioether, disulfide, sulfoxide or thiol [2]. Figure 3.5a shows a molecule containing an easy sulfur group.

Hard sulfur is hard to remove from residual oil. It requires aggressive environments (like hydroprocessing) in order to be removed. IT is present in thiophene and thiophene homologs [2]. Figure 3.5b shows a molecule containing a hard sulfur group.



(a) 3,5-diethyltetrahydro-2H-thiopyran



(b) Dibenzothiophene

Figure 3.5: Molecules containing easy and hard sulfur groups

3.1.1.6 Nitrogen Compounds

Residual oil contains two major types of nitrogen compounds: Nonbasic derivatives of pyrrole and basic derivatives of pyridine. Figure 3.6 shows both components. Both components require very aggressive environments in order to be removed. [2]



Figure 3.6: Pyridine and Pyrrole

Amines are not present in natural residual oil, but they are observed in the products of a thermal refinery. They are formed as products of degradation of higher molecular weight, nitrogen-containing compounds. Because of this, there will be a small fraction of primary and secondary amines present in residue coming from a thermal refinery process [18]. This is important regarding the supercritical water upgrading because amines form reactive sites for the hydrolysis reaction that occurs in supercritical water.

3.1.1.7 Oxygen Compounds

Oxygen is present in furan homologs, ethers, carboxylic acids, ketones, and aromatic hydroxyl groups. Out of all heteroatoms present in residue, oxygen is the one that is the least investigated [2]. This is mainly because of two reasons. First, oxygen does not produce highly toxic or polluting gasses during the combustion of the residue products (in contrast to sulfur). Second, oxygen does not poison refining catalysts or does not cause unwanted deposits (in contrast to nitrogen). [19]

3.1.1.8 Metals

Metals can be found in two organic forms. First, there are porphyrin metals. These metals are chelated in porphyrin structures. Second, there are nonporphyrin metals. These metals are thought of to be associated with the polar groups present in asphaltene [2]. Figure 3.7 shows an example of a porphyrin metal compound. It can be seen how the metal atom (M) is chelated by the four pyrrole groups.

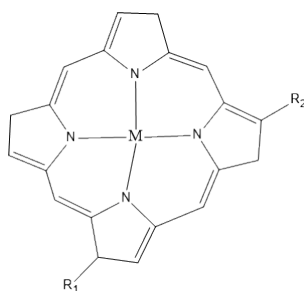


Figure 3.7: Example of a porphyrin metal compound

3.2 Upgrading of Residual Oil

As indicated above, residual oil is a complex mixture of many kinds of functional groups. In order to convert this crude mixture into a useful and clean fuel, upgrading processes are required.

Initially, the residual fractions were mostly used to produce asphalt [2]. As oil reserves shrink, heavier feedstocks are used to supply the growing demand for hydrocarbons. These days almost 70% of all fossil resources in the world are heavy oils [20]. These heavier feedstocks contain a larger fraction of residue (around 40%) [2]. Therefore, there has been a growing interest in upgrading these fractions to more valuable products over the last 30 years. Economic factors like the price of crude oil and the refinery cost play an important role in the economic feasibility of this upgrading process. [20]

Upgrading in general has three major objectives:

1. Converting large, high-boiling molecules into smaller, more volatile molecules [9, 16].
2. Decreasing the hetero atom content (mainly sulfur and nitrogen) [9, 16].
3. Changing the molar H/C ratio. Initially, this value will be around 1.5. The target value depends on the application of the final product. Diesel and jet fuels require high a H/C ratio (higher than 1.8), while for gasoline a H/C ration between 1 and 1.5 is desirable [9, 16].

In general, upgrading occurs in two phases.

In a primary phase, the residual oil undergoes a thermal or catalytic cracking treatment. This step lowers the heteroatom content and increases the number of small

molecules.

In a secondary upgrading phase, hydroprocessing is done. This is done in order to give the upgraded oil (from here on called syncrude) the required refinery feedstock specifications. In general, the heteroatom and metal content is lowered further, and aromatic compounds are saturated. [9, 16]

SCW treatment is an alternative for the primary upgrading phase. Therefore, an overview is given of the currently used technologies in this upgrading phase.

3.2.1 Conventional Technologies

Small organic molecules have more C-H bonds than large organic molecules for the same amount of carbon atoms. Therefore, if large molecules are cracked to smaller molecules, the H/C ratio of the cracked fraction must increase. This can be done in two ways:

1) Carbon rejection:

This technique separates the residual oil into a fraction that has a higher H/C ratio and a fraction that has a lower H/C ratio. Residual oil mainly consists of cyclic cores connected by alkyl chains. Thermal energy is used to separate the alkyl chains from the cyclic cores by thermal cracking. When the alkyl chains are cracked off the cyclic cores, a chemical bond is broken. Because the total amount of chemical bonds must remain constant, a double bond is induced in the alkyl chain, which creates an olefin. This makes the alkyl chain more carbon-dense (more hydrogen deficient). The olefins are cracked further into smaller olefins. Part of the olefins are added to the cyclic cores. The olefins that are not added to the cyclic cores are the fraction with the high H/C ratio and can be further upgraded to a valuable product. The olefins that are added to the cyclic cores will undergo cyclization and aromatization. Through this process, the olefins become part of the cyclic cores which makes the cores grow. Eventually, the cyclic cores become so large and fully aromatized. These large, carbon-dense molecules are called coke. Coke is a low-value waste product. [16]

The main advantage of this technique is that no external hydrogen source is required, which makes this technique economically attractive. The main disadvantage is that part of the organic fraction is degraded to the lower value product coke. [16]

The most commonly used technologies that use this principle are coking, delayed coking and flexicoking [16].

2) Hydrogen addition:

This technique adds hydrogen gas to the residual oil at high pressure and temperature in the presence of a catalyst. Note that this refers to a primary upgrading technique in which hydrogen gas is used. This can be mistaken for the hydroprocessing step which is done as a secondary upgrading step as described in section 3.2. Initially, the alkyl chains are cracked of the cyclic cores as described in the previous technique. Note that this is the same thermal process, so the catalyst does not play a role in this reaction. The cracked products (cyclic cores and olefins) are then hydrogenated by a catalytic reaction. The aromatic rings are saturated, the saturated rings are opened, and the olefins are saturated into paraffins. By adding hydrogen, the coke formation is lower than with the carbon rejection techniques. Coke mainly gets formed because of the presence of asphaltenes in residual oil. Asphaltenes contain large cyclic cores, which will still get turned into coke. This is an issue because the coke deposits on the catalyst, which deactivates the catalyst. Also, the present metals can deposit on the catalyst, causing deactivation. Because of the deactivation problem, almost all currently used technologies make the catalyst move through the reactor such that it can be regenerated and used again. By doing this the deactivation inside the reactor remains limited. [16]

The main advantage of this technique is that the loss of hydrocarbons to coke is limited. The main disadvantage is that this technique is more expensive because it requires hydrogen gas which is an expensive raw material. [16]

The most commonly used technologies that use this principle are Moving-bed hydrocracker, Ebullated-bed hydrocracker, and Slurry-phase hydrocracker. [16]

The conventional primary upgrading techniques both have a disadvantage. Experiments indicate that SCW upgrading cause less coke formation, without requiring hydrogen gas [3, 21, 22]. This is an interesting observation from an economic point of view. More useful product can be generated without an increase in production cost. Experiments also indicated that the upgraded products coming from SCW upgrading have better properties than those coming from carbon rejection techniques. However, the underlying mechanism which causes these promising results is still not identified. This asks for more research being done on this technique to understand the mechanism in order to fully exploit the possibilities. [3]

3.2.2 Supercritical Water Treatment

Supercritical water is water at a pressure and temperature higher than its critical values. The phase diagram in figure 3.8 shows the critical point and the supercritical region.

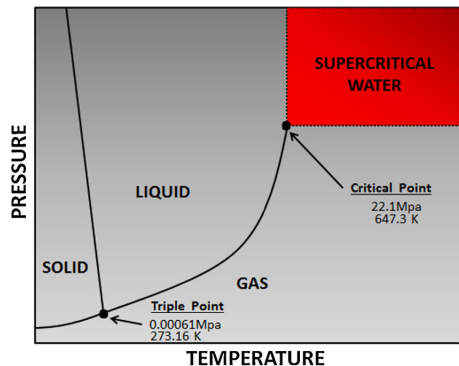


Figure 3.8: Phase diagram water [23]

At these high pressure and temperature values, the fluid is in the supercritical phase. This is a state where there is no clear distinction between liquid and vapor. Because of that, supercritical water is a medium which has unique properties. It combines liquidlike and gaslike behavior. It has a high ion product (liquidlike), and a low dielectric constant and high diffusivity (gaslike) [24]. Around the critical point, the fluid properties are very sensitive to variation in pressure or temperature. Besides the unique combination of properties, SCW also has the ability to act simultaneously

as a solvent and a reactant [10].

This unique combination of properties makes SCW an interesting medium for the upgrading of all kinds of oil. Due to the high temperature and high water concentration, two upgrading reaction mechanisms occur in parallel: hydrolysis and pyrolysis. Both reactions convert high boiling molecules into more volatile molecules. On top of that, the hydrolysis reaction occurs at heteroatoms locations and will remove some of the heteroatoms. This is of major interest for upgrading purposes. [20, 24]

3.2.2.1 Role as a Solvent

SCW influences the rate of reactions due to its solvent effects. All three solvent effects are explained in this subsection.

Effect of the dielectric constant

Changing the pressure or temperature will not only affect the water concentration, but also the solvent properties of water. One important solvent property is the dielectric constant. This will influence the rate of certain chemical reactions by influencing the electrostatic part of the activation energy. Reactions that have transition states that are more polar than the reactants will occur faster when the dielectric constant is higher. This is because a higher dielectric constant stabilizes the transition state more than the reactant [25]. The dielectric constant of SCW is very sensitive to the pressure near its critical point. Because of this, certain reaction pathways (that don't need to include water as a reactant or product) can be promoted/suppressed by altering the pressure. [10]

Cage effect

The presence of a solvent makes it more difficult for compounds to move. The reactants and products move through the solvent by diffusion. The denser the solvent (the more liquidlike) the harder it gets for them to move. This makes it harder for reactants to 'meet' each other and react, and for products to leave the reaction site (and therefore avoid reverse reaction). This phenomenon is described as the cage effect. [26]

Phase behavior of SCW-oil mixtures

The phase behavior of the water-oil mixture changes depending on the water density. Figure 3.9 shows two phase diagrams for a water-oil mixture for different water/oil ratios. The part of the phase diagram that is of most interest is the border between the partially miscible two-phase region and the pseudo single-phase region. SCW upgrading occurs at temperatures of 643 K and higher. Therefore, depending on the water to oil ratio, part of the SCW upgrading process might be in the two-phase region. This has major consequences for the coke production during the upgrading process. In a two-phase system, the water phase contains part of the molecules of the oil mixture. Far away from the border with the pseudo single phase zone, only the lightest fractions of the oil molecules will be in the water phase. As the temperature is increased (approaching the pseudo single phase region) more heavy molecules get transferred to the water phase, until finally, the composition of the oil fraction within the water phase is almost that of the residual oil. The only molecules that are still present in the oil phase are the very heavy asphaltene molecules. [27]

For SCW upgrading the pseudo single phase region is most favorable to operate. The part of the partially miscible two-phase region close to the border with the pseudo single phase region should be avoided. This has two main reasons: One is that asphaltene conversion is slowed down strongly in the two-phase region. The second is that coke production is strongly promoted in the two-phase region.

In the partially miscible two-phase region, the oil phase is rich in asphaltene molecules. In order to dealkylate these molecules, a C-C bond must be broken to form radicals. This requires, relatively to H abstraction, much more activation energy. The high viscosity of the oil phase makes diffusion hard for the aromatic radical and the olefin molecule. This favors in situ β -scission, creating locally elevated concentrations of olefins and methylated aromatics. This induces locally elevated concentrations of coke precursors and therefore will lead to high coke production.

In the pseudo single-phase region, all molecules are present in one phase which is characterized by a high diffusivity. Therefore, mass transfer limitations are no longer

present. Creating asphaltene radicals can now be done by H abstraction between other carbohydrate radicals and asphaltene molecules. This requires less activation energy and will, therefore, speed up the conversion of asphaltenes. The created aromatic radicals can diffusive away from the reaction site and get saturated by H abstraction with any other carbohydrate molecules. This avoids the creation of zones with elevated coke precursor concentrations and therefore suppresses coke production compared to the two-phase system. [27]

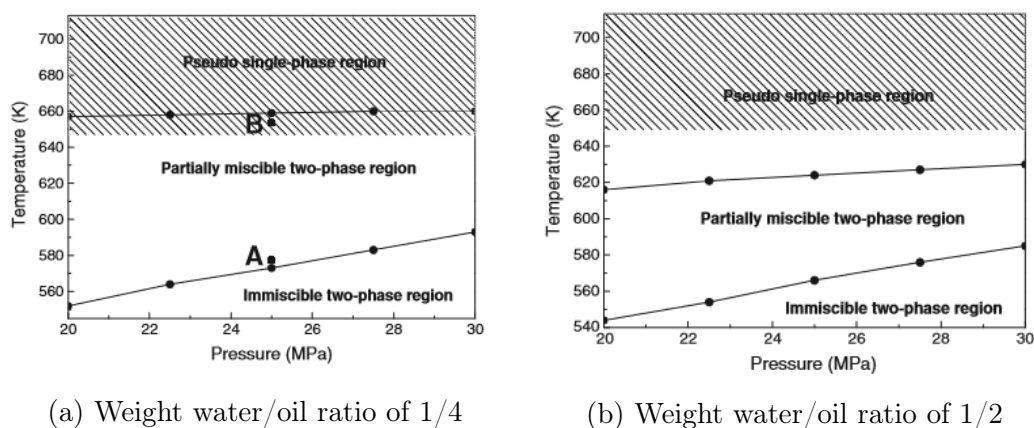


Figure 3.9: Phase structure of the residual oil-water mixture for different oil to water ratios [27]

3.2.2.2 Role as a Reactant

Besides influencing the rate of the reactions due to its solvent effects, SCW allows for a new type of reaction to take place, hydrolysis. The solvent reacts via a nucleophilic attack on a saturated carbon atom. This carbon atom needs to be attached to a leaving group which contains a hetero-atom. The rate of hydrolysis reaction increases more than linear with water concentration. This is because there are two effects influencing the rate of hydrolysis. First, there is an increase in rate because the concentration of one of the reactants increases. Second, the increase in water concentration also increases the second order reaction rate constant due to the solvent effect. This is because the hydrolysis reaction goes through a polar transition

state, which is more stabilized in solvents which have a higher dielectric constant (corresponds to a higher water concentration). Because hydrolysis is a parallel reaction pathway beside the thermal cracking (pyrolysis) reactions, the overall rate of reaction is higher than in a system without SCW (neat pyrolysis). [10]

3.2.2.3 Reasons to Investigate Supercritical Water Upgrading

The goal of upgrading residual oil is to convert as much as possible to high-value products for the lowest possible price. As indicated at the end of subsection 3.2.1, experiments have shown promising results for SCW treatment. The mechanism behind these findings is still not clear. As described in subsection 3.2.2, there are four main differences between pyrolysis in SCW and neat pyrolysis. The influence of the dielectric constant, the cage effect, the phase effect, and the hydrolysis reaction pathway. It is most likely that one or more of these phenomena are responsible for the observed results. Developing a molecular-level kinetic model creates a deeper insight in the phenomena that are occurring on the molecular scale. The model itself can also be used in an industrial setting to find better operating conditions or reactor settings to make more use of the interesting characteristics of SCW upgrading.

Chapter 4

MOLECULAR-LEVEL KINETIC MODELING & THE KINETIC MODELER'S TOOLBOX

This chapter discusses the importance of developing a kinetic model at the molecular level. The general structure and the types of molecular-level kinetic models are explained. The final paragraph discusses the software tools that are used during the model development.

4.1 Motivation for Molecular-level Modeling

Molecular-level modeling has many advantages over lumped modeling. In lumped models, many molecules are lumped together in one category, mainly determined by a physical property such as boiling point or solubility. The reaction network describes the transition from components in one lump to another. These models are simple and require low computational power, but they are also limited in functionality because they do not describe the actual chemistry. Lumped models also do not contain any information on what molecules are exactly present within the categories. Better models are required in order to improve product quality and meet environmental requirements. This in combination with developments in analytical chemistry and an increase in computational power paved the way for molecular-level kinetic modeling. In the case of SCW upgrading, there is the extra motivation of getting a deeper understanding of the process as explained in paragraph 3.2.2.3. [28]

A literature study is done in order to examine what kind of kinetic models were already made for SCW upgrading of oil. Two papers are found that discuss a kinetic model for SCW upgrading of oil:

1. "Heavy oil upgrading in the presence of high density water: Basic study" by Masaru Watanabe, Shin-nosuke Kato, Satoshi Ishizeki, Hiroshi Inomata and

Richard Lee Smith Jr. Published in 2010 [29].

This study developed a lumped kinetic model with three pseudo components: Maltenes, Asphaltenes and Coke. The kinetic parameters are determined for discrete values of water densities.

2. "Upgrading of crude oil in supercritical water: A five-lumped kinetic model" by Dongxiang Zhang, Zhong Ren, Die Wang and Kun Lu. Published in 2017 [30].

This study developed a complete kinetic model, with the determination of the kinetic parameters. The kinetic model is a lumped kinetic model which contains five pseudo components: Saturates, Aromatics, Resins, Asphaltenes, and Coke.

Multiple sources report a molecular-level kinetic model of one or a couple of model compounds that undergo supercritical water upgrading [4, 10, 31, 32]. A kinetic model that describes SCW upgrading of the entire mixture of compounds that are present in residual oil, on the molecular level, could not be found in literature. The reasons highlighted above what benefits can come from having a molecular-level kinetic model, and the absence of any kind of molecular-level kinetic model for SCW upgrading in literature form a strong motivation for this thesis research.

4.2 General Structure of Molecular-level Kinetic Models

Figure 4.1 gives the general structure of a molecular-level kinetic model. Based on experimental data of the feed stream, a selection of model compounds is made to describe the feed stream. A stochastic approach is used in order to determine the mole fractions of the different model compounds. In order to do so, software is used that simulates the properties of a mixture of molecules. The simulated properties of the molecular representation of the feed stream are matched to the experimental data that is available. Next, a reaction network is developed. The number of species in chemical systems can easily be as large as 10^5 . Because of this large number, it is not possible to write down all reactions by hand. Therefore, kinetic models are based on a few basic chemical principles. These basic principles are applied on all model compounds together with certain restrictions. This results in the development of a reaction network [33]. A reactor type is specified and for each type of reaction, a

format for the rate equation is chosen. This results in the description of the system as a set of mathematical equations, the kinetics model template. A simulation is done for the feed stream in a reactor type and process conditions which are the same as for the available experimental data. This generates a product stream. This mixture of products molecules is converted into product properties. These properties are compared to the experimental measurements that are available. Tuning of the kinetic model is done in order to make the simulated properties match as close as possible to the experimental data. Once this is done, the molecular-level kinetic model is finished and can be used to simulate the product properties for different situations. Examples are different reactor conditions and a different feed composition. [33]

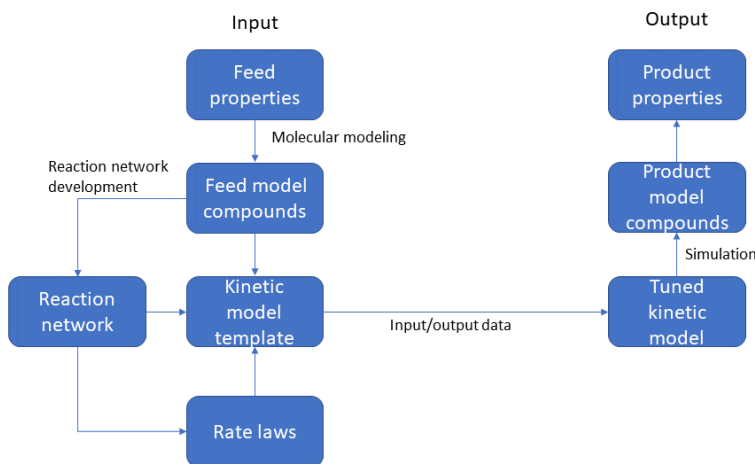


Figure 4.1: General structure of molecular-level kinetic models

Within molecular-level modeling, there are two main categories: pathway-level modeling and mechanistic-level modeling. Pathway-level models represent the system as molecule-to-molecule transitions. These models track most of the observable species, but neglect the non-observable intermediates. Because of this, pathways models require more a priori assumptions. For example, a rate-determining step is required in

order to get a rate law expression. [28]

Mechanistic-level models go one step further and also track the intermediate species. Because of this fewer a priori assumptions are required, but the complexity of the models increases drastically. [28]

In this work, the simultaneous pyrolysis and hydrolysis of residual oil are described. Residual oil is a very heavy fraction of hydrocarbons, carbon numbers can be as high as 120. The amount of species and the number of rate parameter increases exponentially with the carbon number for both pathway- and mechanistic-level models. The mechanistic models have the downside that the ODE's that describe the system are very stiff. This is because of the fast reactivity of the intermediates compared to the observable species. Pyrolysis is a reaction mechanism that occurs via free radicals. Because of this, many components can be formed. Because of the very high carbon number, the amount of species and intermediates is extremely high. All the above reasons justify why a pathway-model is used in order to describe this system. On top of that, the experimental data that is available is too limited for a mechanistic model to be accurately tuned. [28]

4.3 The Kinetic Modeler's Toolbox

The Kinetic Modeler's Toolbox (KMT) is a software package, developed by the Klein Research Group, to solve detailed molecular-level kinetic modeling problems. The following sections discuss the different software packages that are included in the KMT. The KMT software consists of four main software packages: Interactive Network Generator (INGen), Property Generator (PropGen), Initial Condition Generator (ICG) and Kinetic Model Editor (KME). Each software package is used in a different stage of the development of a kinetic model. How the different software packages work together is illustrated in figure 4.2. In INGen a selection of model compounds and reaction families are chosen. A reaction network is generated which creates a list of species and a list of reactions between these species. The list of species is loaded into ICG together with experimental data of the feed stream. In

ICG the mole fractions are determined that minimize the difference between the simulated properties and the experimental data. In KME a list of species, a list of reactions, a reactor type, reactor conditions and formats of the rate laws are specified. This generates a set of ordinary differential equations (ODE's) that describe the chemical system. The set of inlet stream mole fractions generated by ICG are the initial conditions necessary to solve this set of ODE's. In order to get physical and chemical properties for individual molecules, the PropGen software is used. The KMT can be used in different ways. It can be used to do once-through calculations, parameter estimation and goal seeking. [33]

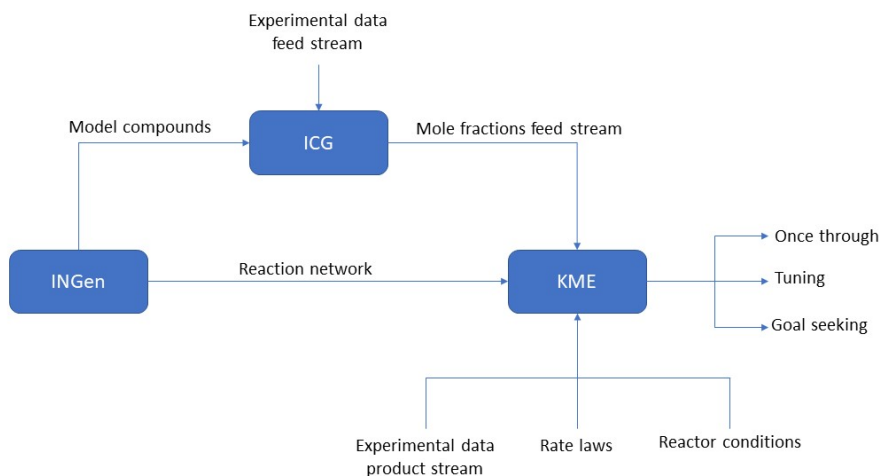


Figure 4.2: Overview of KMT software packages

4.3.1 Molecular Representation

For INGen to develop a list of reactions, it should first read all the chosen model compounds in order to find sites at which reactions can occur. In order to be able to do this, the molecules must be represented in a standardized way. The molecules are given by a NxN matrix called the bond-electron matrix. Each molecule that consists of N atoms is converted into a bond-electron matrix. One molecule can be represented

by multiple bond-electron matrices, but all these matrices can only be translated into the string code of one molecule. KMT software creates these bond-electron matrices from the molecule structure adjacency list. This is a representation of a molecule where the atoms are located at vertices of a graph and the bonds between atoms are the edges. In order to get a bond-electron matrix representation, each atom in the molecule corresponds to the number of a row and column in the matrix. The number that is at the intersection of a row and a column represents the number of bonds between the two atoms in the molecule. For example, if at the crossing of row 3 and column 4 there is the number 2 in the bond-electron matrix, this means that there is a double bond between the atoms corresponding to row/column numbers 3 and 4. An example of a bond-electron matrix is given in Figure 4.3. Note that the bond-electron matrix is symmetric because the atoms listed in both rows and columns are in the same order. The representation of a molecule as a matrix will be used in the reaction network generator software (INGen) in order to determine locations where certain reaction classes can occur. [33]

Propane

C	0	1	0	1	1	1	0	0	0	0	0
C ¹	1	0	1	0	0	0	1	1	0	0	0
C ²	0	1	0	0	0	0	0	0	1	1	1
H	1	0	0	0	0	0	0	0	0	0	0
H	1	0	0	0	0	0	0	0	0	0	0
H	1	0	0	0	0	0	0	0	0	0	0
H	0	1	0	0	0	0	0	0	0	0	0
H	0	1	0	0	0	0	0	0	0	0	0
H	0	0	1	0	0	0	0	0	0	0	0
H	0	0	1	0	0	0	0	0	0	0	0
H	0	0	1	0	0	0	0	0	0	0	0

Figure 4.3: A bond-electron matrix representation of propane [33]

4.3.2 Interactive Network Generator

The reaction network describes what kind of chemical reactions occur to the model compounds. Even if only one reaction family (e.g. a cracking reaction) can occur, this can lead to thousands of reactions occurring to all the model compounds. Note that the products of the first reactions (rank 1 products) can undergo a second, third,... reaction. Therefore, creating a complex reaction network by hand is not possible. The interactive network generator (Ingen) uses reaction families that can be applied to a specified set of the model compounds. A reaction family is a set of reactions that have the same bond transformation during the reaction. An example of a reaction family is 'Midchaincracking'. This reaction breaks the bond in the middle of an aliphatic carbon chain and creates two new chains. One of the new molecules contains a double bond. This reaction can happen to a lot of different molecules, resulting in a lot of different reactions. But all these reactions fall under the same reaction family. In order to describe thousands of reactions, one usually needs only up to 10 reaction families. A reaction family can be applied to all species in the system, but it could for example also be restricted to only happen to paraffins. [33, 34]

Ingen looks for reactive moieties within the model compounds for each reaction family. As described in subsection 4.3.1 the model compounds are represented as bond-electron matrices. Ingen searches for a specific chain of atoms and bonds in these matrices that represents a site where reaction may happen. Once it has found such a location, Ingen executes the reaction by doing a set of matrix operations. The bond-electron matrices of the reactants are combined into the augmented reactant matrix. This augmented reactant matrix is then permuted so that the atoms that are actively involved in the bond transformations of this reaction are arranged in the upper left corner of the matrix. The section of the permuted reactant matrix that contains the actively involved atoms is cut out of the permuted reactant matrix, forming the reduced reactant matrix. Then algorithms are performed on the reduced reactant matrix to ensure that it is always arranged in the prescribed manner. Because of

this, the reaction itself can be represented as a single reaction matrix (corresponding to a reaction family), regardless of the exact structure of the reactants. A matrix addition between the modified reduced reactant matrix and the reaction matrix is done resulting in the reduced product matrix. The reduced product matrix is then inserted in the upper left corner of the reactant matrix (replacing the elements of the reduced reactant matrix), forming the product matrix. The product matrix is analyzed and converted into the bond-electron matrices of the reaction products. Figure 4.4 show the matrix operation occurring in the hydrocracking reaction of propane to methane and ethane.[33, 34]

After the reaction has taken place and the products are identified, Ingen stores the reaction and continues to look for more reaction possibilities [34].

In systems where a lot of reaction families are occurring and different kinds of model compounds (different functional groups or different types of bonds) are present, it may be necessary to add limitations to the reaction families. This might be because certain reaction families should only occur to specific molecules, or to limit the number of different molecules that are formed and therefore the complexity of the kinetic model. There are four kinds of limitations that can be given to a reaction family:

1. Limitations on the kind of reactant molecule: e.g. a reaction family may only occur on normal olefins.
2. Limitations on the number of certain structures present in the reactant: e.g. a reaction family may only occur on molecules that have minimal 5 and maximal 15 carbon atoms.
3. Limitations on the number of certain structures present in the product: e.g. a reaction family may only occur when the formed product has minimal 0 and maximal 2 double bonds.
4. Limitation on the product rank: e.g. a reaction family may only occur at molecules that are rank 1 or lower.

4.3.3 Property Generator

Most oil-derived mixtures are highly complex. Experimental data on the concentration of every component is usually not available and is of less practical interest. Data is available in the form of values for physical and chemical properties of the mixtures. Examples of these properties are boiling point, melting point, viscosity index, cloud point, density, sulfur content, nitrogen content,... Process chemists-and engineers are usually interested in properties like octane number, cetane number, pour point, smoke point, freeze point, cloud point, diesel index, refractive index, viscosity index, and sulfur and nitrogen content. Because these properties indicate the combustion quality and so the value of their product. This indicates that the generation of properties is an important step in the development of the kinetic model. [28]

The PropGen software generates thermodynamic properties such as boiling point, free molecular volume, critical pressure,... For individual components by using the Gani and Benson group contribution methods [35, 36]. These group contribution methods give accurate results except for very small molecules like hydrogen, ammonia, water, carbon dioxide, and hydrogen sulfide. For these small molecules, the thermodynamic properties are manually added from the database in the book Chemical, Biochemical, and Engineering Thermodynamics by Stanley I. Sandler [37]. The pure component structural properties like carbon number, molecular weight,... are directly derived from the bond-electron matrices in INGen. [28]

The properties for individual molecules generated by PropGen are converted into properties for mixtures in ICG and KME by applying mixing rules.

4.3.4 Initial Condition Generator

In order to develop a molecular-level kinetic model, a molecular-level representation of the feed is required. Usually, only bulk properties of the feed stream are available. The Initial Condition Generator (ICG) generates mole fractions of a set of model compounds. The bulk properties of this mixture are simulated and compared to the

experimentally measured bulk properties. This is done by calculating a value for a chi-squared objective function F .

$$F = \sum_{i=1}^M \sum_{j=1}^N \left(\frac{y_{ij}^{model} - y_{ij}^{exp}}{\omega_j} \right)^2 \quad (4.1)$$

In Equation 4.1, y_{ij}^{model} refers to the simulated property value for the inlet stream for property i in data set j . y_{ij}^{exp} Refers to the experimental data point value for the inlet stream for property i in data set j . ω_j Is a weighing factor for property j .

The mole fractions are changed until an ideal composition is determined which has bulk properties that are as close as possible to the experimental data. This is mathematically represented as the mole fractions that minimize the value of the objective function. [28]

In order to find the mole fractions that match the measured bulk properties, the feed is represented in a statistical way. The molecules are viewed as a combination of structural attributes (number of aromatic rings, number of naphthenic rings, number of alkyl side chains, etc.), each of which is represented by a probability density function (PDF). An example of a PDF is given in figure 4.5. In this example, the PIONA (normal-paraffins, iso-paraffins, olefins, naphthenes, and aromatics) characteristics are represented as a cumulative PDF. Note that in this example the X-axis is discrete. This type of PDF has $n - 1$ parameters, with n the number of bars in the histogram. Each parameter is the weight of one of the bars. For quantities like molecular weight, carbon number, ... a continuous cumulative PDF is created by choosing a distribution and determining the parameters of this distribution based on the experimental data. A gamma distribution is chosen to describe the continuous PDF's in this work. This is because the gamma distribution describes most accurately the smooth distribution that is expected for these types of systems. The parameters for a gamma PDF are the mean value and the standard deviation. [33] A set of PDF's is created, which can be represented as a tree structure. figure A.1 in Appendix A gives an example of a simple PDF tree structure. Once the set of PDF's

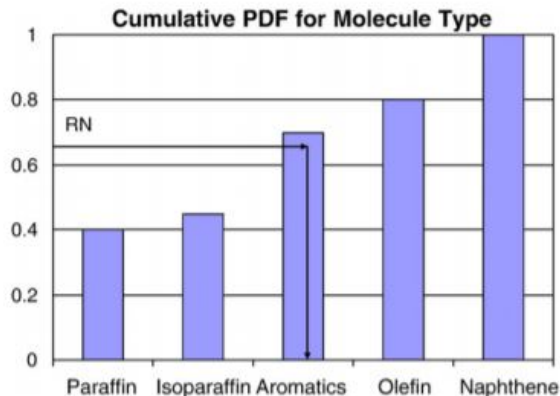


Figure 4.5: Example of a PDF [33]

is created, they are used to create a molecular representation of the feed by doing a Monte Carlo construction. A random number is chosen between 0 and 1. The number is plotted on the y-axis of a PDF. This will correspond to a certain X coordinate. In figure 4.5 this corresponds to aromatics. Based on the X coordinate there are more following PDF's to which random numbers are assigned. In figure A.1 the next PDF is the number of aromatic rings, followed by the number of naphthenic rings and the total carbon number. In the end, each Monte Carlo construction results in a final set of constraints. For example a molecule with 3 aromatic rings, 2 naphthenic rings and a total carbon number of 45. If there are multiple model compounds that satisfy these constraints, one of them is randomly chosen. This simulation is done more than 10^5 times in order to create an accurate molecular representation of the feed stream. By changing the PDF parameters, the mole fractions of the model compounds change. Minimizing the value of the objective function is done by changing the values of the PDF parameters. [28, 33]

4.3.5 Kinetic Model Editor

The Kinetic Model Editor (KME) is the last software package of the KMT. It combines the output of the previously described software packages. KME can be used in various ways, but the underlying mechanism is the same. KME solves the set of

ODE's that represent the change in concentration of the model compounds chosen in INGen. In order to be able to do this KME requires six forms of input:

1. A list of reactions that occur between species.
2. A list of molar flow rates for all the molecules that occur in the reaction list. These flow rates represent the molar flow rates of the input stream. This sets the initial conditions for the component mass balance model equations.
3. Specification of the reactor type. This determines how the overall format of the model equations looks like.
4. Specification of the reactor conditions. The pressure and temperature (profiles) in the reactor determine the values of thermodynamic properties that are required to calculate parameters that go in the model equations.
5. Specification of formats for the rate laws. The rate of production/consumption of a chemical species must be expressed as a function of concentrations, pressure, and temperature.
6. Numerical values for the physical-and chemical properties of the molecules that occur in the reaction list.

There are three modes in which KME can be used:

Mode 1: Once Through

This mode requires additionally the values for all kinetic constants in the chosen rate law format. The composition of the outlet stream of the reactor is simulated.

Mode 2: Tuning

This mode requires additionally experimental data about the product stream. This can either be data regarding the molecular composition or data regarding the physical properties of the product stream. In this mode, KME will estimate the set of kinetic parameters that go in the rate laws based on model predictions and experimental data of the product stream. The estimated set of kinetic parameters are the ones that minimize the value of an objective function. The objective function has the same format as the one given in equation 4.1.

Mode 3: Goal Seeking

This mode requires additional values for all kinetic constants and experimental data about the product stream. The general concept is very similar to the one of the

tuning mode. The value of the objective function given in equation 4.1 is again minimized. The minimization occurs by changing the operating conditions. This mode is used to determine the ideal operating conditions in order to get a set of specifications for the output stream.

Now all the used software packages have been explained, chapter 5 will give an overview of the mathematical equations that are solved in KME.

Chapter 5

MODEL EQUATIONS AND REACTION RATE LAWS

This chapter contains the general format of the mathematical equations that represent the kinetic model. Section 5.1 describes the general format of the component mass balance equations. In order to be able to solve the component mass balance equations, an expression for the reaction rate is required. Section 5.2 gives the reaction rate expression for the different kinds of chemical reactions that occur.

5.1 Model Equations

The mathematical representation of a chemical system is given by its model equations. A complete mathematical model consists of one component mass balance for each component and an overall energy balance. The general shape of the component mass balance equations is determined by the type of reactor. As described in chapter 2, there is no complete data set available that contains data on the upgrading of residual oil in a SCW environment. Therefore, there is also no specification of a reactor type. The data set that is available about the VGO upgrading in SCW, described in chapter 2, contains experimental data from experiments in an isothermal batch reactor. Therefore, the component mass balance equations that will be described in this paragraph are for an isothermal batch reactor. Besides a batch reactor, the KME software also allows simulation of plug flow reactors, continuously stirred tank reactors, side stream reactors, semi-batch reactors, and radial flow reactors.

Equation 5.1 gives the component mass balance for a batch reactor.

$$\frac{dN_j}{dt} = \sum_i^n \nu_{ij} r_i V \quad (5.1)$$

With N_j the total amount of moles of component j, ν_{ij} the stoichiometric coefficient of component j in reaction i, r_i the reaction rate of reaction i per unit volume and V the volume of the reacting system.

Because V is approximately constant for a pseudo single phase batch reactor, equation 5.1 can be simplified to:

$$\frac{dC_j}{dt} = \sum_i^n \nu_{ij} r_i \quad (5.2)$$

With C_j the concentration of component j.

Because the used data source contains data for an isothermal reactor there is no need to implement the overall energy balance.

5.2 Rate Laws

The set of equations given by equation 5.2 cannot be solved. An expression for the reaction rate of reaction i (r_i) in terms of the process conditions (pressure, temperature, and concentrations) is required to solve the component mass balances.

In section 6.1 the different types of chemical reactions that occur in the system are discussed in dept. This section discusses the format of the rate laws for each type of reaction. The reaction network consists of four main types of reactions. Pyrolysis reactions, hydrolysis reactions, dehydrogenation reactions, and coke formation reactions. All four reaction types have a different format for their rate laws. Note that no catalyst is used. Therefore, the derived rate laws originated from homogeneous microkinetic rate laws which are modified to include the solvent effects of SCW.

5.2.1 Pyrolysis Reactions

This set of reactions includes all thermal cracking reactions. The general format for the rate law is:

$$r_i = \eta A_p e^{\frac{-E_p}{RT}} C_{reactant} \quad (5.3)$$

A_p Is the pre-exponential factor and E_p is the activation energy of the Arrhenius equation. η Represents the efficiency factor due to the cage effect described in subsection 3.2.2.1. For the efficiency factor, a value can be calculated by using the expression given in [26].

$$\eta = \frac{1}{1 + Da} \quad (5.4)$$

Da Stands for the Damköhler number which is given by:

$$Da = \frac{\nu p_{-1} e^{\frac{-E_{-1}^*}{RT}} d_{ab}^2}{3D_{12}} \quad (5.5)$$

In this equation T is the temperature, D_{12} is the diffusion coefficient, d_{ab} is the diameter of the cage [26].

The diameter of the cage is taken proportional to the molecular diameter of the reactant. Because the reverse reaction is a radical recombination reaction, the approximation is made to set the activation energy for the reverse reaction (E_{-1}^*) equal to zero. ν Is the vibrational crossing frequency. This is proportional to the temperature [38]. By combining all the constants into one constant K , the following equation is obtained.

$$Da = \frac{KTd_r^2}{D_{12}} \quad (5.6)$$

With d_r the molecular diameter of the reactant.

Values for D_{12} and d_r are needed. d_r Can be approximated by the cubed root of the molecular volume of the reactant. This value will be off by a constant, but this can be captured by changing the value of the constant K . The reason that the molecular volume is used to calculate d_r is that the PropGen software generates values for the molar volume, which can easily be converted to the molecular volume (v_r).

$$d_r = \left(\frac{v_r}{N_A}\right)^{\frac{1}{3}} \quad (5.7)$$

For D_{12} a correlation is found in [39].

$$D_{12} = 7.4 \cdot 10^{-15} \frac{T \sqrt{\beta M_2}}{v_r^{0.6} \eta_2} \quad (5.8)$$

In this expression M_2 is the molecular weight of water, which is equal to 18,01528 $\frac{g}{mol}$ [37]. η_2 Is the viscosity of SCW and β is a constant equal to 2.6.

A value for the viscosity of the SCW is needed. This is found in [40].

$$\eta_2 = \eta_0 \cdot \eta_1 \quad (5.9)$$

$$\eta_0 = \frac{\eta^* \sqrt{\bar{T}}}{\sum_{k=0}^3 \frac{a_k}{\bar{T}^k}} \quad (5.10)$$

$$\eta_1 = \exp[\bar{\rho} \sum_{i=0}^5 \sum_{j=0}^4 b_{ij} (\frac{1}{\bar{T}} - 1)^i (\bar{\rho} - 1)^j] \quad (5.11)$$

In these expressions, \bar{T} is the reduced temperature and $\bar{\rho}$ is the reduced density of water. These reduced quantities are the absolute quantities divided by the critical temperature or density. For water these values are given in Table 5.1.

Table 5.1: Critical point water[37]

T_{crit} [K]	ρ_{crit} [kg/m ³]
647.3	322

The coefficients a_k and b_{ij} are given by tables 5.2 and 5.3.

Table 5.2: Coefficients a_k

a_0	0.0181583
a_1	0.0177624
a_2	0.0105287
a_3	-0.0036744

Table 5.3: Coefficients b_{ij}

i=	0	1	2	3	4	5
j=0	0.501938	0.162888	-0.130356	0.907919	-0.551119	0.146543
1	0.235622	0.789393	0.673665	1.207552	0.0670665	-0.0843370
2	-0.27463	-0.743539	-0.959456	-0.687343	-0.497089	0.195286
3	0.145831	0.263129	0.347247	0.213486	0.100754	-0.032932
4	-.0270448	0.0253093	- 0.0267758	- 0.0822904	0.0602253	-0.0202595

For pyrolysis reactions, there are three kinetic parameters in the rate expression that have to be determined: A_p , E_p and K .

Note that the reverse reaction is not explicitly present in the rate law. This phenomenon is captured by the efficiency factor due to the cage effect. Because the reaction products are in a cage between solvent molecules, the products must diffuse out of the cage in order to avoid reverse reaction from happening. How fast the diffusion of the products occurs compared to the reverse reaction is given by the Damköhler number, which determines the value of the efficiency factor.

5.2.2 Hydrolysis Reactions

This set of reactions includes the hydrolysis reactions at hetero atom reactive spots. The general format for the rate law is:

$$r_i = k_h e^{-\frac{E_h}{RT}} C_{reactant} C_{water} \quad (5.12)$$

In this equation E_h is the activation energy in the Arrhenius equation, but k_h is not the pre-exponential factor. This is because the hydrolysis reactions are influenced by the dielectric constant of the solvent as described in subsection 3.2.2.1. The dependence is captured in the value for k_h by the Kirkwood analysis found in [25].

$$\log(k_h) = \log(k_0) - \frac{\kappa N_A}{4\pi\epsilon_0 RT} \frac{\epsilon - 1}{\epsilon} \quad (5.13)$$

In this equation ϵ is the dielectric constant of the SCW, κ is an adjustable parameter, ϵ_0 is the permittivity of vacuum and k_0 is the rate constant in a condensed medium

with $\epsilon = 1$.

A correlation is found in [41] that links the dielectric constant of SCW to the reduced temperature and reduced density.

$$\epsilon = \frac{1 + A + 5B + \sqrt{9 + 2A + 18B + A^2 + 10AB + 9B^2}}{4 - 4B} \quad (5.14)$$

$$A = \frac{N_A \mu^2 \rho g}{\epsilon_0 k T} \quad (5.15)$$

$$B = \frac{N_A \alpha}{3\epsilon_0} \rho \quad (5.16)$$

In these equations N_A is Avogadro's number, μ is the dipole moment of water, k is the boltzmann constant and α is the mean molecular polarizability of water. Table 5.4 gives the numerical values for these constants.

Table 5.4: Constants N_A , μ and α [41]

N_A	$6.0221367 \cdot 10^{-23} \frac{1}{mol}$
μ	$6.138 \cdot 10^{-30} Cm$
k	$1.380658 \cdot 10^{-23} \frac{J}{K}$
α	$1.636 \cdot 10^{-40} \frac{C^2}{Jm^2}$

ρ Is the molar density of water, T is the temperature and g is a third variable. For g there is a second correlation [41].

$$g = 1 + \sum_{k=1}^{11} N_k \left(\frac{\rho}{\rho_c}\right)^{i_k} \left(\frac{T_c}{T}\right)^{j_k} + N_{12} \left(\frac{\rho}{\rho_c}\right) \left(\frac{T}{228} - 1\right)^{-q} \quad (5.17)$$

The coefficients that go in this correlation are given in Table 5.5. The constant q is equal to 1.2.

For hydrolysis reactions, there are three kinetic parameters in the rate expression that have to be determined: k_0 , E_h and κ .

Table 5.5: Coefficients N_k , i_k and j_k [41]

k	N_k	i_k	j_k
1	0.978224486826	1	0.25
2	-0.957771379375	1	1
3	0.237511794148	1	2.5
4	0.714692244396	2	1.5
5	-0.298217036956	3	1.5
6	-0.108863472196	3	2.5
7	$0.949327488264 \cdot 10^{-1}$	4	2
8	$-0.980469816509 \cdot 10^{-2}$	5	2
9	$0.165167634970 \cdot 10^{-4}$	6	5
10	$0.937359795772 \cdot 10^{-4}$	7	0.5
11	$-0.123179218720 \cdot 10^{-9}$	10	10
12	$0.196096504426 \cdot 10^{-2}$		

The reverse reaction is not present in the expression for the rate law. To be completely correct a term representing the reverse reaction should be included. But because this term is so small compared to the forward reaction this reverse term is neglected. To indicate this, the equilibrium constant of a model reaction is calculated. The model reaction is the hydrolysis reaction of dibenzyl ether to two benzyl alcohol molecules. At a temperature of $650K$ (minimal temperature for SCW upgrading), the equilibrium constant is equal to $2.124 \cdot 10^6$. The value for the equilibrium constant increases with increasing temperature. Therefore, the assumption to neglect the reverse reaction term is justified. The calculation of the equilibrium constant can be found in appendix B.

5.2.3 Dehydrogenation Reactions

These reactions include the reactions in which naphthenic rings are dehydrogenized and converted into aromatic rings. The general format for the rate law is:

$$r_i = A_d e^{\frac{-E_d}{RT}} C_{reactant} \quad (5.18)$$

A_d Is the pre-exponential factor and E_d is the activation energy of the Arrhenius equation. SCW will not have an influence on this reaction via one of its solvent effects.

The reverse reaction in which an aromatic ring gets saturated requires hydrogen partial pressures that range from 400 to 1200MPa to be significant [42]. The partial pressure of hydrogen is so far from these values that the reverse reaction is neglected. For dehydrogenation reactions, there are two kinetic parameters in the rate expression that have to be determined: A_d and E_d .

5.2.4 Coking Reactions

The format of the kinetic rate laws for coking reactions are still not fully understood [43, 44, 45]. In the developed molecular-level model there are two different kinds of coking mechanisms included. The first mechanism is the addition, cyclization, and dehydrogenation of an olefin molecule to an aromatic core, which creates a larger aromatic core. The second mechanism is the condensation of two aromatic cores into one bigger aromatic core. Why these mechanisms are chosen will be further explained in section 6.1.

Because no format for the kinetic rate law could be found in literature, the simplistic approach of homogeneous microkinetics is taken. As indicated in subsection 3.2.2.1, depending on the water density the phase behavior of the residual oil-SCW mixture changes from a two-phase to a pseudo-homogeneous mixture. This has a strong impact on the rate of coke formation. A correction factor is added to the microkinetic rate law in order to capture this effect. The general format of the rate law is:

$$r_i = \eta_p A_c e^{\frac{-E_c}{RT}} C_{reactant_1} C_{reactant_2} \quad (5.19)$$

In this equation, A_c and E_c are the pre-exponential factor and the activation energy in the Arrhenius equation. η_p Is the correction factor that takes the phase effect into account.

No mathematical expression for η_p could be found in literature. The effect is only described qualitatively. Therefore, an expression for η_p is created. As described in

subsection 3.2.2.1, this is not a continuous effect, but rather a sharp transition when the phase structure changes. That is why the following equation is used for η_p .

$$\eta_p = \begin{cases} \eta_{p1}, & \text{if } T < T_{trans} \\ \eta_{p2}, & \text{if } T \geq T_{trans} \end{cases} \quad (5.20)$$

The values for η_{p1} and η_{p2} become adjustable parameters of the kinetic model. In order to determine an expression for T_{trans} , the few experimental data points that are available in [27] are used. Figure 3.9 indicates that the temperature at which the phase structure changes (T_{trans}) can be approximately taken independent of the pressure. Therefore, only an expression in terms of the water to oil ratio is needed. Only two data points are available from the figures in figure 3.9. Therefore, only a two-parameter correlation can be created. A linear relationship is chosen between the temperature at which the phase structures changes and the water to oil ratio.

$$T_{trans} = a + b\omega_{wat,oil} \quad (5.21)$$

With $\omega_{wat,oil}$ the water to oil mass ratio. Table 5.6 gives the two data points extracted from Figure 3.9.

Table 5.6: Data points to determine coefficients a and b in equation 5.21

$T_{trans}[K]$	$\omega_{wat,oil}$
620	0.5
660	0.25

Based on this data, equation 5.21 becomes.

$$T_{trans} = 700 - 160\omega_{wat,oil} \quad (5.22)$$

The use of this equation is limited to the region of the experimental data that it is derived from. Extrapolation to higher water to oil ratios is no problem. Because all SCW upgrading processes operate at least at 650 K, T_{trans} will be lower than the

operating temperature for water to oil ratios higher than 0.5. Setting the value for η_p equal to η_{p2} .

In total for the coking reactions, there are four kinetic parameters in the rate expression that have to be determined: A_c , E_c , η_{p1} and η_{p2} . The product between A_c and η_p can be combined into a new parameter $A_{c,\eta}$. Therefore, only three parameters have to be determined.

5.2.5 Graphical Representation Rate Laws

The equations discussed in the previous subsections are implemented in a lumped kinetic model made in Matlab. This model is a strongly simplified version of the molecular-level kinetic model. It contains the parallel pyrolysis and hydrolysis pathways. Part of the pyrolysis products will be converted to coke. Figure 5.1 shows the reaction network.

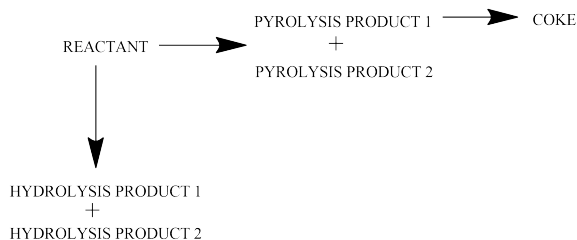


Figure 5.1: Lumped reaction network

A simulation for a batch reactor is done. Table 5.7 shows the process conditions and the parameter values that go in the rate equations. The process conditions are equal to the ones in the data source that is used for the product data of VGO upgrading in SCW [15]. The parameters are chosen such that the rate of hydrolysis, pyrolysis, and coking are within the same order of magnitude. The results of the simulation are shown in figure 5.2. For the molecular properties that are required, the properties of benzene are used.

Table 5.7: Process conditions and parameter values

Process conditions										
Temperature			Pressure		Water-oil mass ratio			Water density		
693 K			25 MPa		2			150 $\frac{kg}{m^3}$		
Parameter values										
R	K	κ	η_{p1}	η_{p2}	A_p	E_p	k_0	E_h	A_c	E_c
8,3145	10^{11}	$-5 \cdot 10^{-30}$	1.5	0.5	10^{11}	$1.6 \cdot 10^5$	10^2	$1.15 \cdot 10^5$	$5 \cdot 10^9$	$1.6 \cdot 10^9$

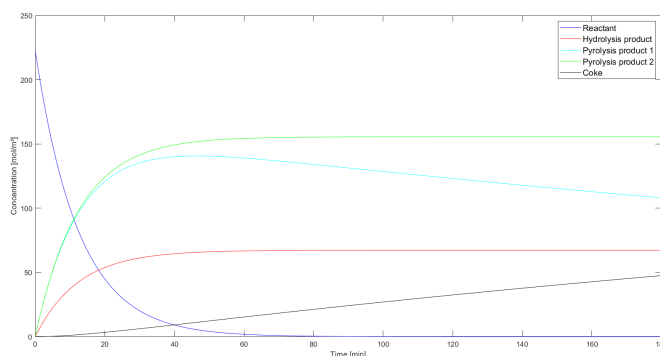
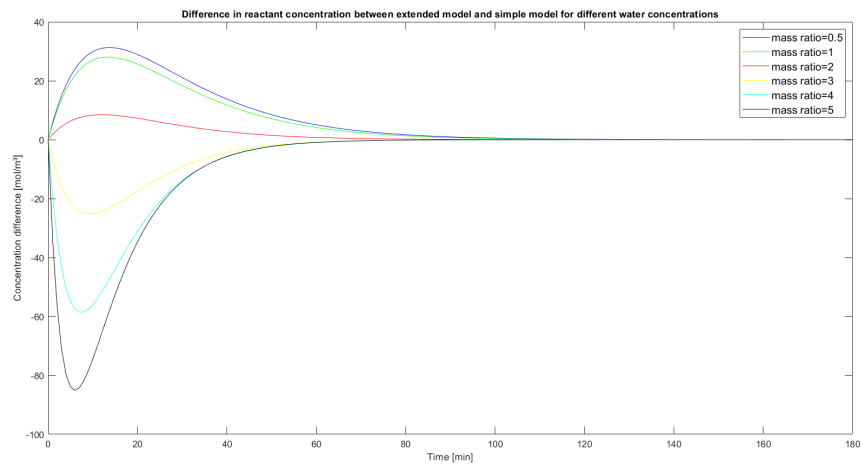


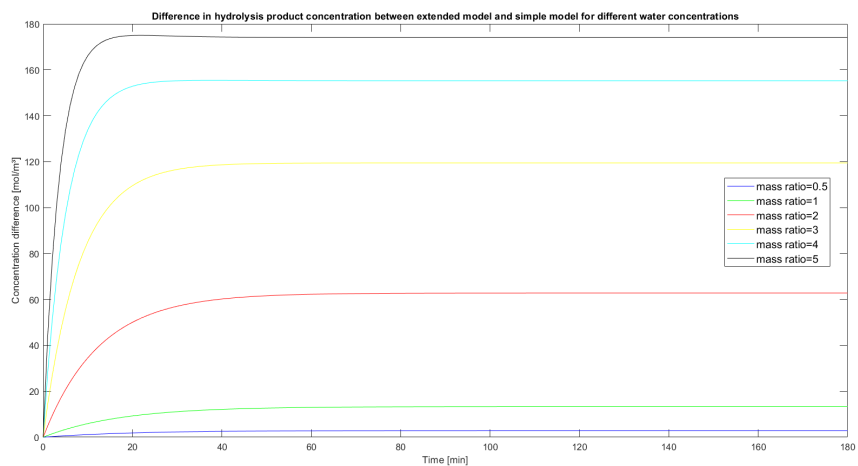
Figure 5.2: Matlab simulation lumped model

The simulation results show that reactant is consumed and converted into hydrolysis- and pyrolysis products. The hydrolysis products and pyrolysis product 2 reach a steady state concentration when all reactant is consumed. Pyrolysis product 1 gets converted into coke as time increases.

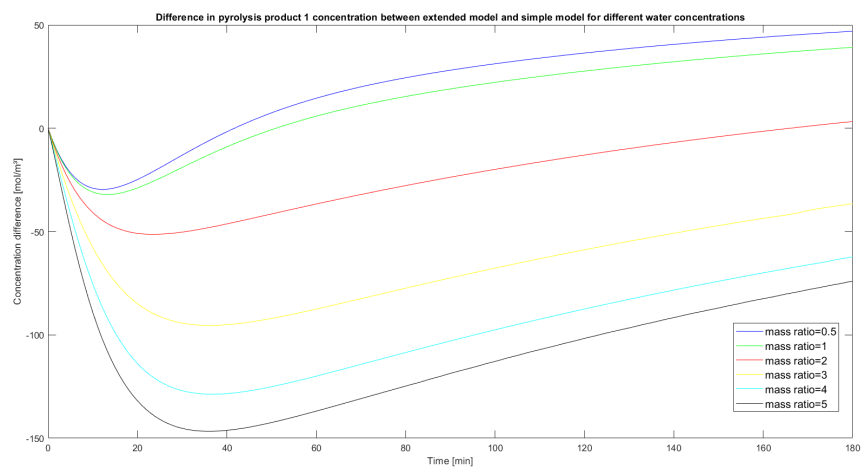
The basic principle behind the rate laws is microkinetics. The rate laws are extended because of the solvent effects of SCW. In order to show the effect of the extensive rate laws, a second model is made in Matlab. The reaction network is the same as the one shown in figure 5.1, but in the second model, the rate laws are microkinetic rate laws. Simulations are made for both models and for different water-oil mass ratios. The difference between the concentrations of the model compounds simulated by both models is plotted in figure 5.3. Simulations are made with different water-oil mass ratios in order to show the effect of SCW as a solvent. Note: "the difference" means concentration simulated by the model with extensive rate laws - concentration simulated by the model with microkinetic rate laws.



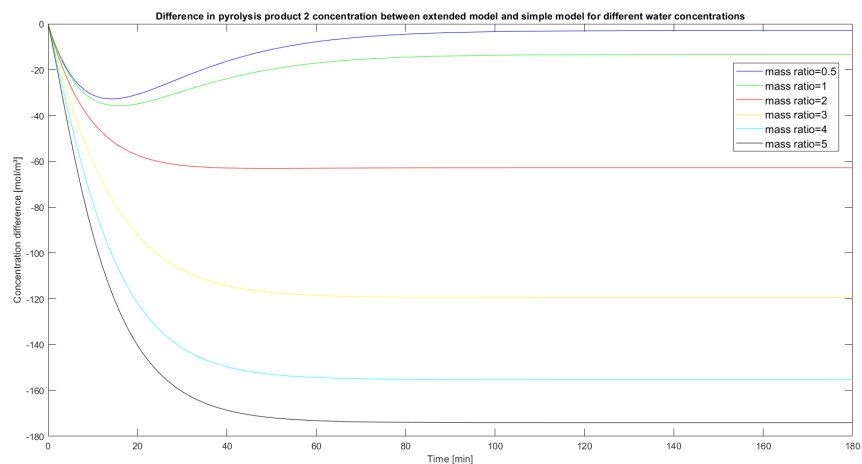
(a) Difference in reactant concentration



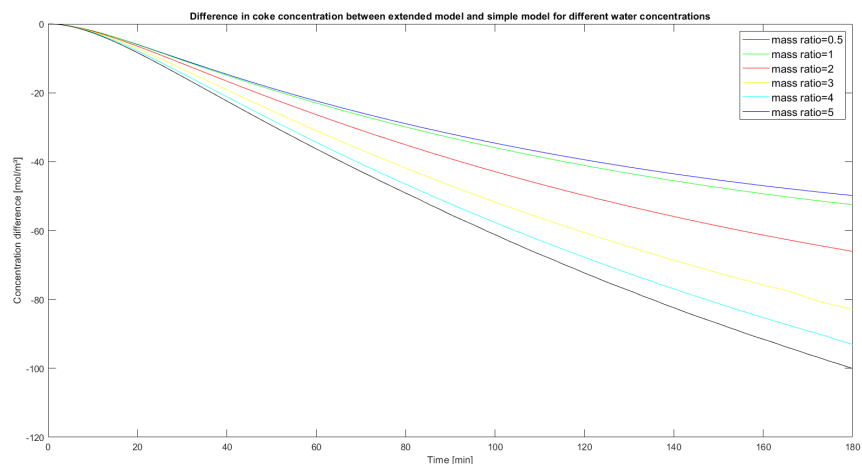
(b) Difference in hydrolysis product concentration



(c) Difference in pyrolysis product 1 concentration



(d) Difference in pyrolysis product 2 concentration



(e) Difference in coke concentration

Figure 5.3: Differences between simulations with extensive and simple kinetic rate laws

In order to be able to interpret the results shown in figure 5.3 it is necessary to understand what phenomena are included in the extensive rate laws that are excluded in the microkinetic rate laws. These are three phenomena: the solvent cage effect, the effect of the dielectric constant and the phase behavior. These phenomena are explained in depth in subsection 3.2.2.1.

In figure 5.3b it is shown that the difference is always positive. This means that

the extensive model has a higher hydrolysis product concentration. This is since the hydrolysis rate constant is increased, because of the effect of the dielectric constant ($\kappa < 0$), and the pyrolysis rate constant is decreased, because of the solvent cage effect. Both these effects get stronger as the water concentration increases, which is also shown in the figure.

Figure 5.3d displays that the difference is always negative. This corresponds to a lower concentration of pyrolysis product 2 in the extended model. This is again due to the increase of the hydrolysis rate constant and the decrease of the pyrolysis rate constant. Some curves have a minimum. This is because over time the difference in reactant concentration increases. At the minimum point of the curve, the relative increase in reactant concentration exactly compensates the decrease of the pyrolysis rate constant due to the solvent cage effect.

Figure 5.3c shows curves that are quite similar to the ones in figure 5.3d. The same explanation that was given for pyrolysis product 2 also holds for pyrolysis product 1. The difference is that pyrolysis product 1 can be converted to coke. In figure 5.3e it can be seen that the coke production in the extensive model is lower. Therefore, less of pyrolysis product 1 is converted to coke. Because of this, some of the curves become positive at long reaction times. Figure 5.3d shows that the production of pyrolysis product is lower in the extended model. But for some water-oil mass ratios, the difference in coke production is even more negative which causes the difference in concentration of pyrolysis product 1 to be positive.

In figure 5.3e it is displayed that the coke concentration is always lower in the extended model. This is partly because of the lower concentration of pyrolysis product 1 (but this is not always the case, as described in the previous paragraph). It is also partly because of the lower coking rate constant due to the phase structure. Figure 5.3a shows the difference in reactant concentration. These curves can either be positive or negative. The solvent cage effect slows down the rate of reactant consumption, while the effect of the dielectric constant speeds up the rate of reactant consumption. Depending on the water-oil mass ratio, one of these effects is more

dominant. This causes the curves that correspond to lower water-oil mass ratios to be positive and the ones corresponding to high ratios to be negative. At long reaction times, all reactant gets consumed. Note that no backward reaction term is present in the rate laws. Therefore, all curves will eventually go to zero.

This comparison shows that the extensive rate laws have the mathematical format to simulate trends that are expected due to the solvent effect of SCW.

Chapter 6

RESULTS AND DISCUSSION

This chapter describes how the software tools described in chapter 4 are used to develop the molecular-level kinetic model.

6.1 Reaction Network Generation

Reaction network generation has the final goal to create a list of chemical reactions between model components. The components are represented as 'Speciesxxxxxx', with xxxxxx representing the species number. An example of a reaction in the reaction list could be 'Species000001 -> Species000002 + Species000003.

There are two ways to develop the reaction network. First, the software package InGen is used to develop most of the reaction network. Some reactions cannot be generated by InGen. Therefore, the reaction list is manually extended with the reactions that couldn't be generated by InGen. As indicated in section 3.1.1, residual oil consists of a variety of molecular structures. Besides that, the carbon number of the molecules can be as high as 120. Because of these reasons, there are a lot of spots where InGen can let a chemical reaction take place. This creates a large number of species. Every new species generates a new model equation in the set of ODE's that describe the system. In order to keep the simulation time limited, the number of species must remain limited too. The goal is to develop a model that can be simulated within one minute. Therefore, the objective is to keep the total amount of species bound to 3000. In order to keep the number of components that low, major limitations must be given to INGen. Because of the complexity of the molecules and the severeness of the limitations that are required, a rank zero network is developed. A rank zero network means that only chemical reactions can occur between molecules that are seeded to

INGen. This is an effective way to limit the number of species, without losing much valuable information [46]. The choice of the model compounds determines which reactions can take place. Therefore, this determines all the assumptions that are made regarding the reaction network. The assumptions will be listed in subsection 6.1.1.3. An example of the power of a rank zero network is given in figure 6.1. By seeding the five molecules present in figure 6.1b into a rank zero network, the same chemistry can be shown as in figure 6.1a with four components less. This is almost half the components.

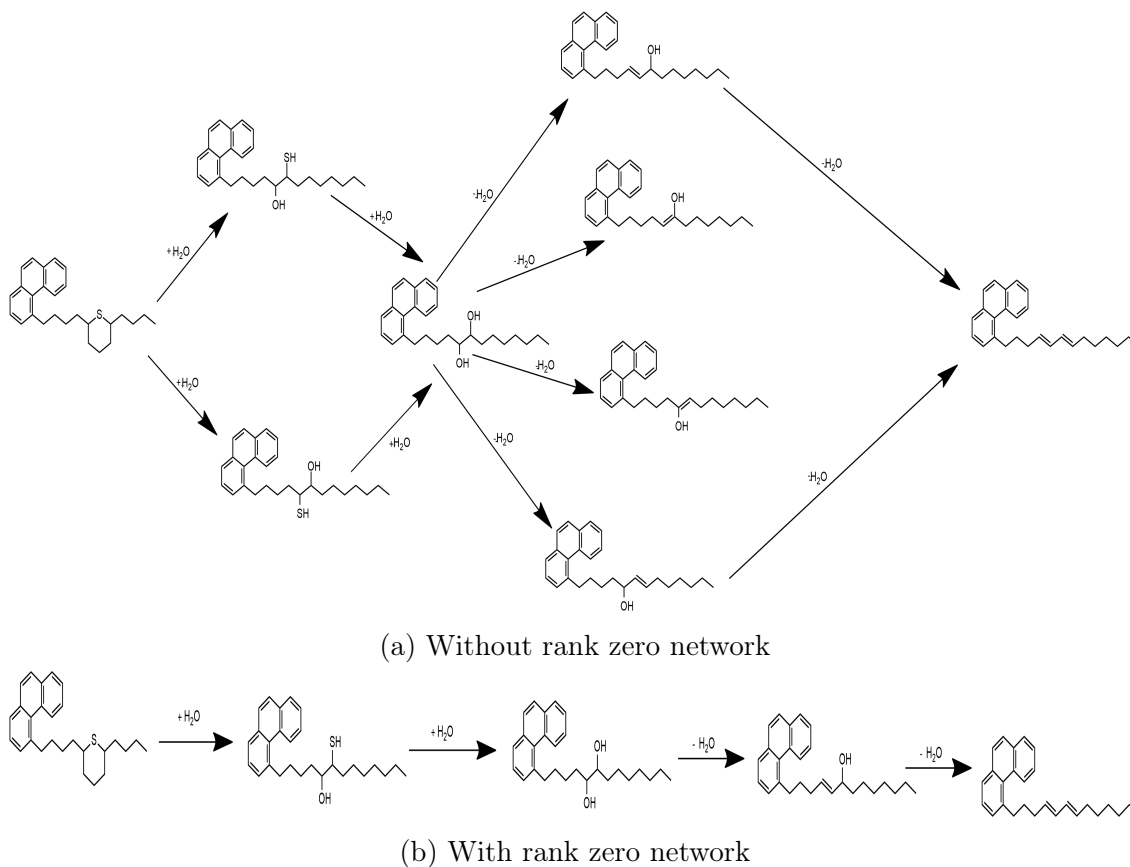


Figure 6.1: Hydrolysis/dehydration reaction network

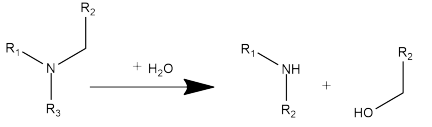
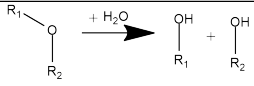
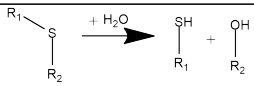
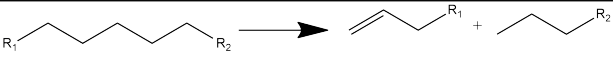
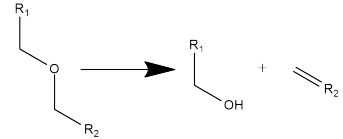
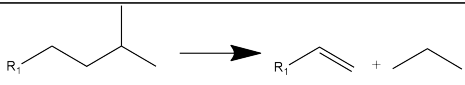

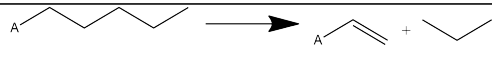
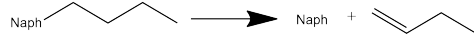
Subsection 6.1.1 discusses the part of the reaction network generated by INGen. Subsection 6.1.2 handles the part of the reaction network that is manually added. In subsection 6.1.3 the reaction network as a whole is analyzed.

6.1.1 Reaction Network Generated by Ingen

6.1.1.1 Reaction Families

Table 6.1 gives an overview of which reaction families are used in Ingen. It shows what kind of chemistry is represented by this reaction family and gives the sources that report that this chemistry occurs in SCW upgrading.

Table 6.1: Reaction families

reaction family	Chemistry	sources
CNHydrolysis		[4]
COHydrolysis		[5]
CSHydrolysis		[6],[7], [8]
MidChainCracking		[9]
OxideThermalCracking		[10], [11]
PathCCracking		[9]
ThermalPostAllylicBetaScission		[9]
ThermalSideChainCrackingAromGamma		[9]
ThermalSideChainCrackingNaphAlpha		[9]

ThermoChainMercap- tonDesulurization	$\text{R}_1\text{-CH}_2\text{-CH}_2\text{-S-CH}_2\text{-CH}_2\text{-R}_2 \longrightarrow \text{R}_1\text{-CH=CH}_2 + \text{H}_2\text{S} + \text{CH}_2\text{=CH-R}_2$	[12]
ThermoChainSulfid- eDesulfurization	$\text{R-CH}_2\text{-CH}_2\text{-SH} \longrightarrow \text{R-CH=CH}_2 + \text{H}_2\text{S}$	[13]

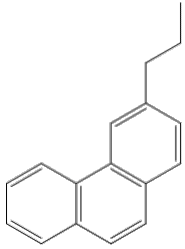
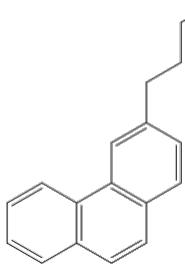
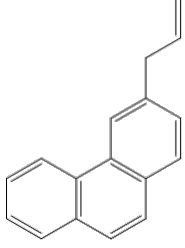
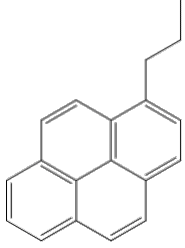
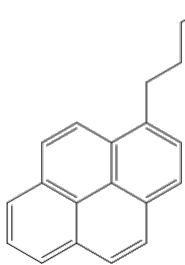
6.1.1.2 Model Compounds

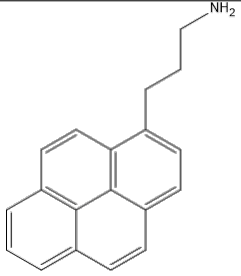
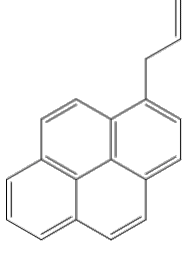
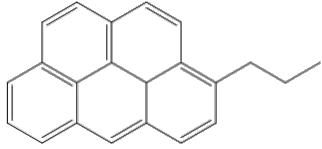
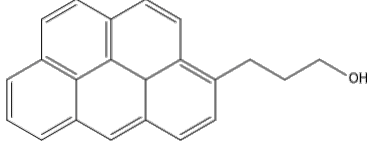
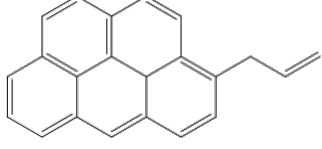
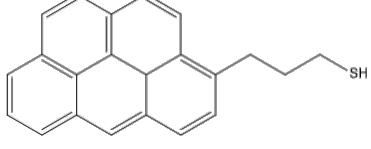
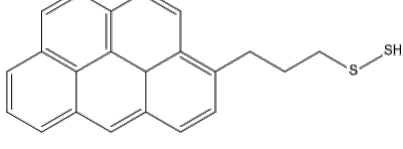
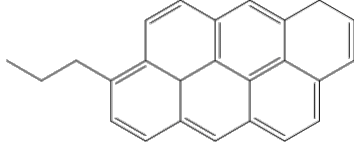
For the reaction families to generate reactions, the right reactive spots should be present. Therefore, the functional groups, present in the model compounds, are chosen in function of the reaction families. Literature is consulted in order to confirm that these functional groups are present within the molecules in residual oil [2]. The ratio between aromatic-and aliphatic carbons, the number of heteroatoms and the carbon numbers are tuned during the modeling process. As a starting point, data is used from a paper that did modeling of the molecular composition of vacuum residue [14]. A PDF structure is made in ICG. The model predictions are compared to the experimental data in [14] and [15]. Adaptions to the chosen model compounds are made. This modifies the ratio between aromatic-and aliphatic carbons, the heteroatom content and the carbon numbers. A new PDF is made. This process is repeated until a final set of model compounds is obtained which can model the feed accurately. During this process, the number of model compounds must remain limited. Since a rank zero network is used, every molecule that is present in the reaction network must be created by the modeler and added as a seed in Ingen.

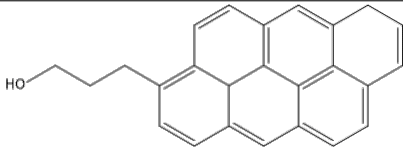
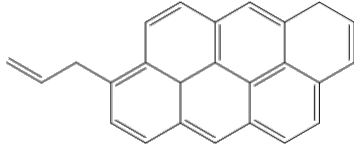
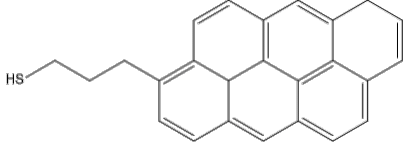
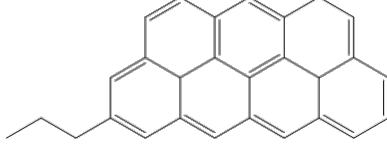
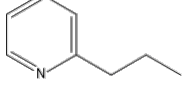
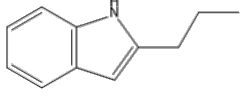
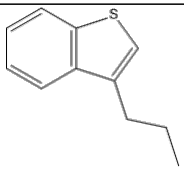
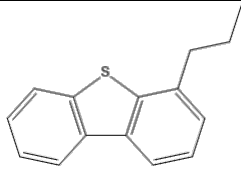
The model compounds can be subdivided into categories. Molecules within the same category contain the same functional groups. They only differ by the length of an alkyl chain. This is done to get the functional groups distributed over all carbon numbers. Table 6.2 gives an overview of the chosen model compounds, the categories, and the carbon number range. In the category names, "A" refers to aromatic rings and "N" refers the naphthenic rings.

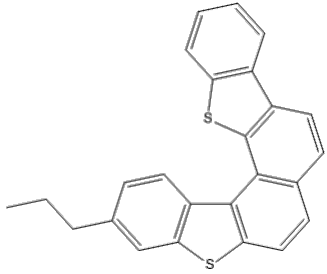
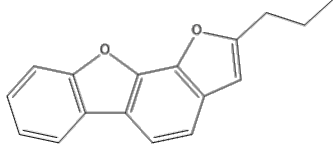
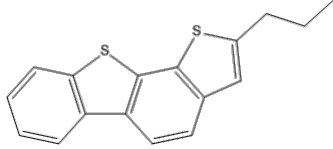
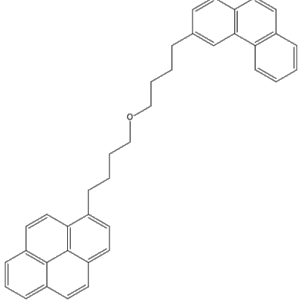
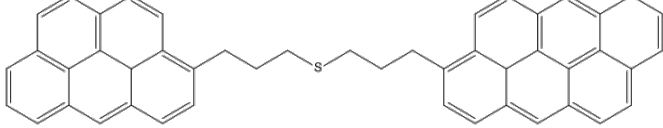
Table 6.2: Examples of model compounds

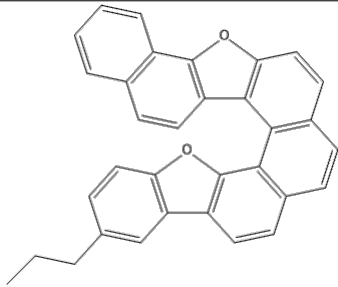
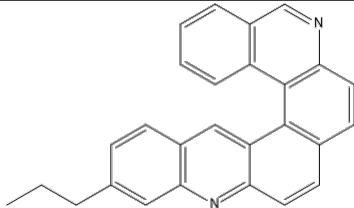
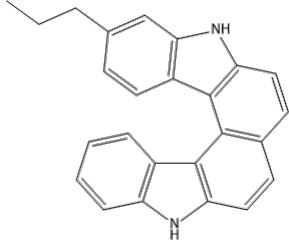
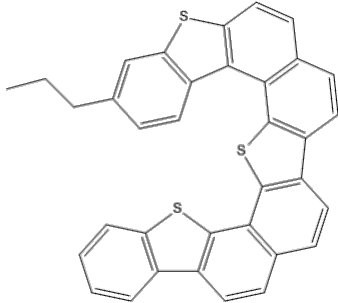
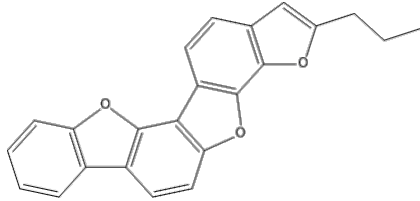
Category name	Example model compound	Carbon number range
normal paraffins		1-100
iso paraffins		4-100
1-olefins		2-100
2-olefins		4-49
alcohols		4-49
1N		6-60
2N		10-60
3N		14-80
4N		16-80
1A		6-60
2A		10-65

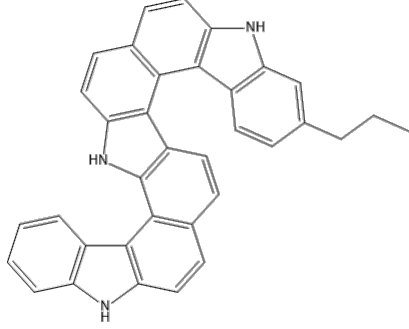
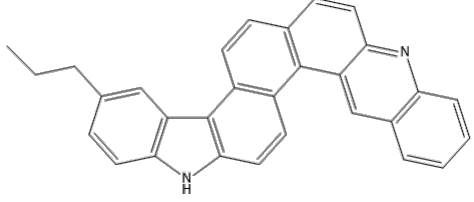
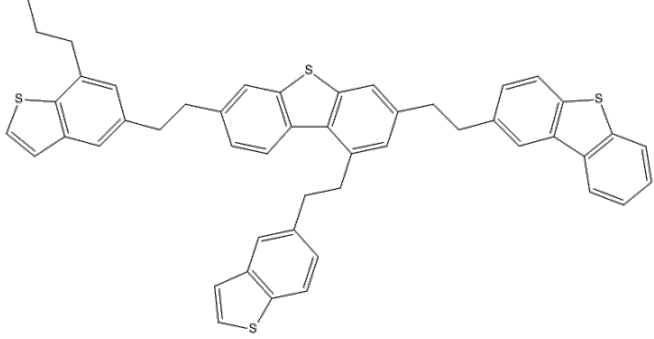
3A		14-80
3A alcohol		16-60
3A dehydrated		16-60
4A		16-80
4A alcohol		18-80

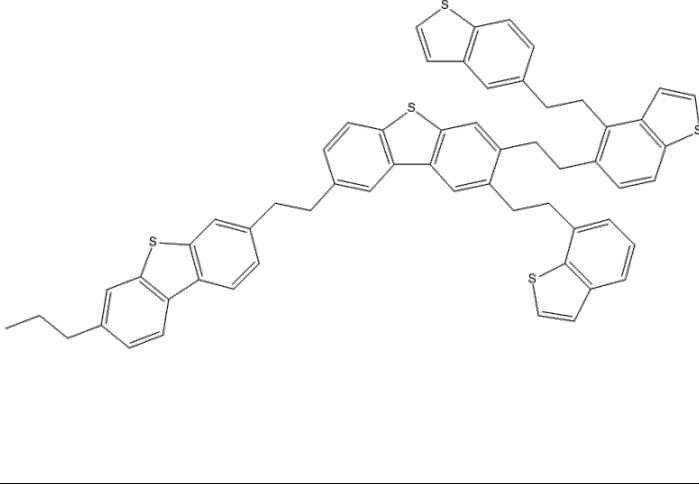
4A amine		18-80
4A dehydrated		18-80
5A		19-80
5A alcohol		22-80
5A dehydrated		22-80
5A thiol		22-80
5A dithiol		20-80
6A		22-80

6A alcohol		24-65
6A dehydrated		24-65
6A thiol		24-65
7A		25-80
Pyridine		5-80
Indole		8-80
BenzoThiophene (BT)		8-65
DiBenzoThio- phene (DBT)		12-80

<p>Double DiBen- zoThiophene (DDBT)</p>		<p>22-80</p>
<p>Double Benzo- Furan (DBF)</p>		<p>14-80</p>
<p>Double Ben- zoThiophene</p>		<p>14-80</p>
<p>Ether</p>		<p>38-80</p>
<p>Thioether</p>		<p>45-80</p>

<p>Extended BenzoFuran (EBF)</p>		<p>30-80</p>
<p>DiAcridine</p>		<p>24-80</p>
<p>DiCarbazole</p>		<p>22-95</p>
<p>Triple DiBenzoThiophe (TDBT)</p>		<p>32-120</p>
<p>Triple BenzoFuran (TBF)</p>		<p>20-80</p>

Triple Carbazole		32-80
Pyridine Carbazole Combo (PCC)		27-95
Quadruple DiBenzoThiophene (QDBT)		47-120

Quin DiBen- zoThiophene (QuinDBT)		57-110
Small inorganic molecules	Water; Hydrogen; Hydrogen sulfide; Hydrogen disulfide; Ammonia; Carbon dioxide	/

6.1.1.3 Assumptions

As indicated earlier, the choice of the model compounds determines which assumptions are made regarding the reaction network. The assumptions that are made for the Ingen part of the reaction network are:

- Only reactions that have a reaction chemistry like the ones that are given in table 6.1 can be included in the reaction network.
- In order for a reaction to occur all reactant-and product molecules must satisfy both of the following rules. The molecules belong to one of the categories in table 6.2. The molecules have a total carbon number that is within the carbon number range in the third column of table 6.2 for their category.
- Removing of aliphatic carbon structures from aromatic clusters by thermal cracking (=thermal dealkylation) only occurs via a mechanism where a radical is formed on the alpha position. The following beta scission reaction creates an aromatic core with an alkyl chain that is two carbon atoms long and has a double bond as a final bond in the alkyl chain, and a normal paraffin or alcohol. This mechanism is chosen because the formed radical is stabilized in the aromatic ring, which makes this the most likely pathway [9, 47].
- Removing of aliphatic carbon structures from aromatic clusters or cracking within these aliphatic carbon structures, only occurs to side chains that are

normal paraffins, olefins with one double bond at the end of the alkyl chain or primary alcohols. Thiols or amines are first converted to one of the three above structures before thermal cracking occurs. This pathway is chosen because the hydrolysis of an amine and thiol is more likely to occur than thermal cracking. Appendix C shows a calculation that strengthens this assumption.

- Cracking of side chains on cyclic carbon structures only occurs as a mid-chain cracking. In reality, cracking will occur at multiple positions within the chain, but this assumption is a necessity to limit the number of components because of the large carbon number.
- The maximum amount of double bonds that can occur in an olefin are two [47].
- Removing of aliphatic carbon structures from naphthenic clusters by thermal cracking (=thermal dealkylation) only occurs via a mechanism where a radical is formed on the beta position. The following beta scission reaction creates a naphthenic core with a methyl side chain and an olefin. This mechanism is chosen because the radicals in reactants and products are most stabilized, which makes this pathway the most favorable [9, 47].
- No ring opening of cyclic compounds occurs. For aromatic compounds this assumption is valid [47]. Naphthenic rings could be opened by thermal cracking. This reaction pathway is not included in the model to limit to the number of components.
- Heteroatoms that are part of an aromatic system do not react [9, 11].
- Iso paraffins are first cracked via thermal cracking such that a radical is formed on the carbon atom that is bound to three other carbon atoms. The following beta scission reaction creates an olefin and a normal paraffin that can be further cracked [47].

6.1.2 Manually Added Reactions

Some reaction pathways cannot be modeled with Ingen. Therefore, a list of reactions is added to the list that is generated by Ingen. The added list contains reactions that can be categorized in three reaction families: Naphthene aromatization, olefin addition, cyclization and aromatization, and coking. To a broader extent, the last two of these reaction families can be captured under the name coking chemistry.

Coking chemistry includes a wide variety of reactions. In general, it can be described as carbon and heteroatoms, coming from a variety of molecular structures, being condensed into large aromatic clusters. These clusters contain almost no

hydrogen[43, 44, 45]. Two different reaction pathways are modeled to represent this chemistry: addition, cyclization and aromatization of olefins to aromatic clusters; condensation of small aromatic clusters into larger, more carbon-dense aromatic clusters.

For the manually added reactions, it is much more complicated to formulate a list of assumptions that are made. The manner how certain the chemistry is incorporated in the model is one large assumption. Therefore, the assumptions for each of the manually added reaction families are given within the description of the reaction families.

Naphthene aromatization

This reaction family represents the reactions in which naphthenic rings are dehydrogenized, resulting in the formation of aromatic rings [43, 44]. An aromatization reaction family is present in Ingen. It creates reactions where one naphthenic ring is aromatized at a time. This shows the reaction pathway most accurately, but it also creates a lot of model compounds. An example is given for a naphthenic compound that consists of four naphthenic rings (4N). If no approximations are made, aromatizing this component creates 16 new components per carbon number. Considering that the carbon number for 4N components goes from 16 to 80, aromatizing only the 4N components would generate 1040 new components. This is too much. A simplification could be made that, says that only one component with a certain amount of naphthenic-and aromatic rings can exist. This fixes the relative locations between the naphthenic-and aromatic rings. The number of components per carbon number is limited to 5. This still generates 325 components which is quite a lot for one reaction pathway of one category of molecules. Therefore, aromatization is modeled as one reaction where all the naphthenic rings present in a molecule are aromatized. An example of this reaction is given in figure 6.2. This reaction chemistry is not present in Ingen and is therefore added manually to the reaction list.

Olefin addition, cyclization and aromatization

This reaction family is added in order to include a reaction pathway for non-cyclic,

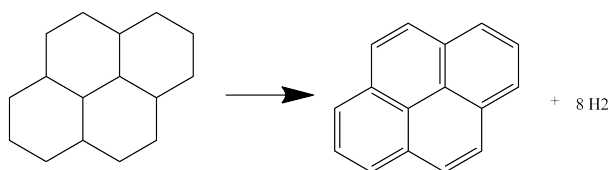


Figure 6.2: Naphthene aromatization reaction

aliphatic carbons to become aromatic carbons. The reaction is bimolecular. One reactant is an aromatic core with a small paraffin side chain. The side chain has a carbon number going from zero to five. The other reactant is an olefin, that has one double bond between the first and the second carbon atom and has no other side chains or heteroatoms. The carbon number of the olefin is limited such that the highest carbon number of the product is 80. The reaction products are an aromatic core, with a paraffin side chain and one extra aromatic ring, and hydrogen [43, 44]. An example is given in figure 6.3.

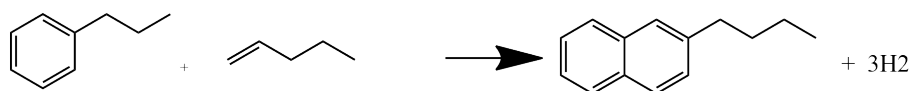


Figure 6.3: Olefin addition, cyclization and aromatization

Coking

This reaction family represents the chemistry where aromatic molecules are combined into large aromatic clusters, called coke. The exact reaction pathway that leads to coke formation is complex, and not fully understood. There is also no molecular representation for a 'coke molecule' [45, 48]. The following approach is taken in order to model this chemistry. The reactants are all aromatic cores that contain one side chain that is two carbon atoms long and has a double bond between the two carbon atoms in the side chain (a dealkylated aromatic core). These cores are divided into four groups, based on their heteroatom content. The four groups are pure hydrocarbon, nitrogen-containing, sulfur-containing and oxygen-containing. In the first step, each reactant reacts with itself. This creates a bond between two carbon atoms of the aromatic cores. The product is a molecule that is twice as large

as the reactants and hydrogen. The products of step one that belong to the same group combine in binary reactions. In each reaction, a bond between two aromatic carbons is created, producing larger aromatic clusters and hydrogen. This continues until there are two molecules per group. In the final step, these two molecules combine and a large quantity of hydrogen is removed to give a product that has a H/C ratio that is representative for a coke molecule [48]. The product of the final reaction is called coke. Note that no chemical structure for the coke molecule is created. It is only represented as an elemental composition. Each group has its own "coke molecule". The combination of the elemental compositions of the four "coke molecules" can be compared to an experimental elemental composition of coke, if present in the data source. An example of this reaction pathway is given in figure 6.4.

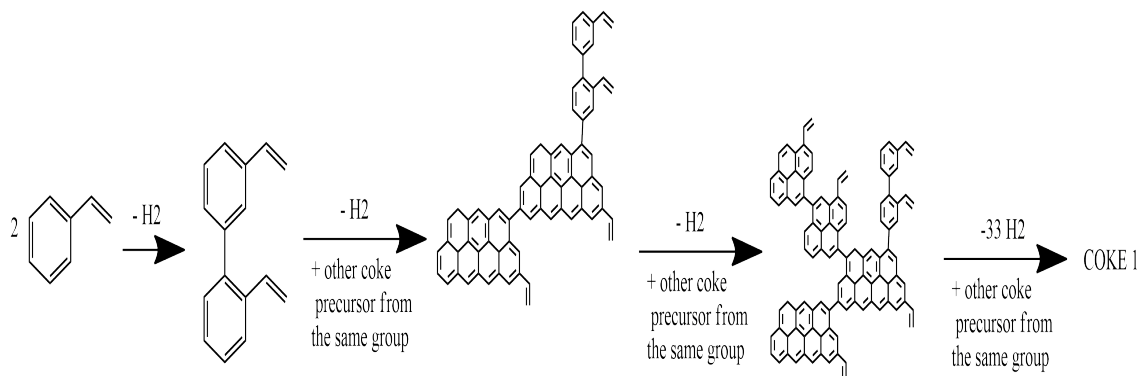


Figure 6.4: Coking

6.1.3 Diagnostics of the Reaction Network

The observed reaction pathways for each type of reactant are given.

Normal paraffins

- Normal paraffins can be cracked via mid-chain cracking into smaller paraffins and olefins. These products can be cracked further. The olefins can react further as described below.

Olefins

- Olefins can be cracked into smaller paraffins and olefins through mid-chain cracking. They can also be added to aromatic cores, forming larger aromatic cores. These large aromatic cores can be converted to coke. The side chain can be cracked off the larger aromatic cores, forming a normal paraffin and a dealkylated aromatic core. The normal paraffin can react further as described above. The dealkylated aromatic core can react further as described below.

Iso paraffins

- Iso paraffins are first cracked such that the side chain is removed as a paraffin. This results in normal paraffins and olefins, which can react further as described above.

Alcohols

- Alcohols can be dehydrated, creating olefins. The olefins can react further as described above.
- Alcohols can be cracked by mid-chain cracking. This creates a smaller alcohol and an olefin. The olefin can react further as described above. The smaller alcohol can react further as described in this paragraph.

Pure hydrocarbon aromatic compounds

- The side chains can be cracked off these compounds, creating two products. One is an aromatic compound with a two-carbon side chain with a double bond between the two carbons in the side chain. These kinds of components will be referred to as dealkylated aromatics. The second is a normal paraffin or olefin, depending on whether there is a double bond in the side chain or not. The normal paraffin or olefin can react further as described above. The dealkylated aromatic compound can react further through reactions described in **coking** to form coke.
- Mid-chain cracking can occur in the side chain of these compounds. This can always create an olefin and an aromatic compound with a shorter paraffin chain. If the aromatic compound with an olefin side chain is present as a seed in the rank zero network, then this reaction can also create a paraffin and an aromatic compound with a shorter olefin side chain. The aromatic compound can react further as described in this paragraph. The paraffin and olefin can react further as described above.
- Olefins can be added to these compounds. Creating larger pure hydrocarbon aromatic compounds which can react further as described above.

Naphthenic compounds

- The side chains can be cracked of naphthenic compounds, creating methylated naphthenic clusters and olefins. The olefins can react further as described above.
- Mid-chain cracking can occur in the side chain of these compounds. This creates a naphthenic compound with a shorter paraffin side chain and an olefin. The olefin can react further as described above. The naphthenic compound can react further as described in this paragraph.
- Naphthenic compounds can get aromatized to pure hydrocarbon aromatic compounds. These pure hydrocarbon aromatic compounds can react further as described above.

Aromatic compound with aromatic heteroatoms, but no aliphatic heteroatoms

- The side chains can be cracked of these compounds, creating a dealkylated aromatic compound and a normal paraffin. The normal paraffin can react further as described above. The dealkylated aromatic compound can react further through reaction described in **coking** to form coke.
- Mid-chain cracking can occur in the side chain of these compounds. This creates an aromatic compound with a shorter paraffin side chain and an olefin. The olefin can react further as described above. The aromatic compound can react further as described in this paragraph.

Aromatic compounds with an alcohol group in a side chain

- The side chains can be cracked of these compounds, creating a dealkylated aromatic compound and an alcohol. The dealkylated aromatic compound and the alcohol can further react as described above.
- The alcohol group in the side chain can be dehydrated, creating a side chain with a double bond. The aromatic compound with the dehydrated side chain can react further as described above.
- Midchain cracking can occur in the side chain, creating a linear alcohol and an aromatic compound with an olefin side chain. Both products can react further as described above.

Aromatic compounds with an amine group in a side chain

- The amine group in the side chain can get hydrolyzed to an alcohol group and ammonia. The aromatic compound with the alcohol group in the side chain can react further as described above.

Aromatic compounds with a thiol group in a side chain

- The thiol group in the side chain can get hydrolyzed to an alcohol group and hydrogen sulfide. The aromatic compound with the alcohol group in the side chain can react further as described above.
- The thiol group can be removed from the side chain, creating a side chain with a double bond and hydrogen sulfide. The aromatic compound with the dehydrated side chain can react further as described above.

Aromatic compound with a disulfide group in a side chain

- The disulfide group in the side chain can get hydrolyzed to an alcohol group and hydrogen disulfide. The aromatic compound with the alcohol group in the side chain can react further as described above.

Aromatic rings connected by a side chain that contains an ether

- The ether bond can get hydrolyzed, creating two aromatic compounds with an alcohol group in the side chain. The aromatic compounds with an alcohol group in the side chain can react further as described above.
- The ether bond can get thermally cracked, creating an aromatic compound with an alcohol in the side chain and an aromatic compound with a double bond in the side chain. Both products can react further as described above.

Aromatic rings connected by a side chain that contains a thioether

- The thioether bond can get hydrolyzed, creating an aromatic compound with an alcohol group in the side chain and an aromatic compound with a thiol group in the side chain. Both products can react further as described above.
- The thioether bond can get thermally cracked, creating two aromatic compounds with a double bond in the side chain and hydrogen sulfide. The aromatic compounds can react further as described above.

In total, the reaction network consists of 10025 reactions between 2894 species. Out of the 10025 reactions, 7615 are created by Ingen and 2410 are manually added. Table 6.3 shows the amount of reactions for each reaction family.

Table 6.3: Number of reactions for each reaction family

Reaction family	Number of reactions
CNHydrolysis	63
COHydrolysis	43
CSHydrolysis	193
MidChainCracking	4187
OxideThermalCracking	372
PathCCracking	95
ThermalPostAllyticBetaScission	509
ThermalSideChainCrackingAromGamma	1471
ThermalSideChainCrackingNaphAlpha	546
ThermoChainMercaptonDesulfurization	101
ThermoChainSulfideDesulfurization	35
Naphthene aromatization	237
Olefin addition, cyclization and aromatization	2133
Coking	40

Based on the numbers in table 6.3, the thermal reactions are the dominant reaction types. This is because thermal reactions have much more reactive spots compared to the hydrolysis reactions. The amount of hydrolysis reactions corresponds to the number of aliphatic heteroatoms that are present in the model compounds.

6.2 Feed Composition Modeling

In order to solve the set of ODE's generated by KME, a set of initial conditions is required. In this molecular-level kinetic model, this means that the number of moles, of each molecule in the batch reactor before reactions take place, should be known. ICG models the composition of the feed stream that goes into the reactor. The result of the ICG simulation sets the initial conditions for KME.

As described earlier in chapter 2, only product data for VGO is available. Therefore,

two models in ICG are made. One model simulates the molecular composition of residual oil data [14]. This is done in order to validate that with the chosen model compounds the physical properties of residual oil can be obtained. The second model simulates the molecular composition of VGO data [15]. This model is made to set the initial condition of the KME model.

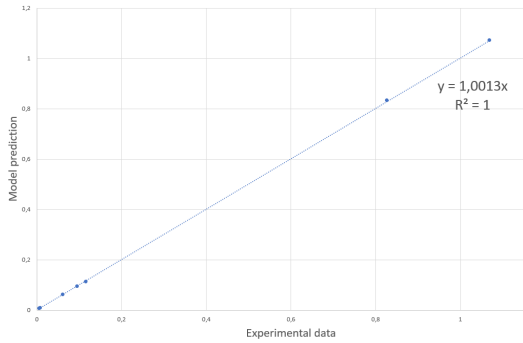
6.2.1 Residual Oil

Figure 6.5 shows the comparison between the experimental data found in [14] and the model prediction. The numerical values are shown together with their graphical representation in a parity plot. Two parity plots are constructed because the numerical values of the WSimDis properties are large compared to the other properties.

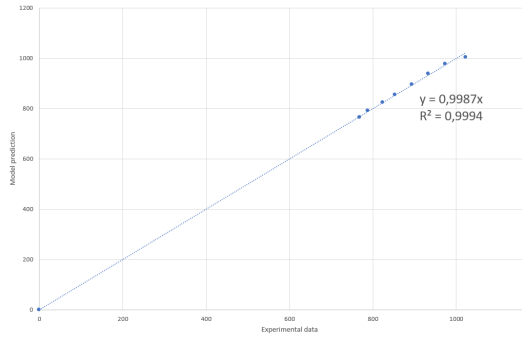
F = 482.87

Current Best Results		
ExpName	Value	PredictedValue
Density	1.07	1.0707
WSimDis5	768	764.15
WSimDis10	788	791.28
WSimDis20	823	824.15
WSimDis30	853	855.48
WSimDis40	893	895.7
WSimDis50	933	938.66
WSimDis60	973	975.52
WSimDis70	1023	1002.9
WSimDis80	0	1017.6
WSimDis90	0	1030.6
WSimDis95	0	1040.8
Carbon	0.827	0.83124
Hydrogen	0.0963	0.093413
Oxygen	0.0084	0.0083621
Nitrogen	0.006	0.0060005
Sulfur	0.0618	0.061173
nParaffins	0	0.012519
iParaffins	0	0.012533
Olefins	0	0.0099219
Naphthenics	0	0.012533
Aromatics	0	0.95249
WA_MW	0	851.85
MA_MW	0	745.92

(a) Numerical values



(b) Parity plot 1



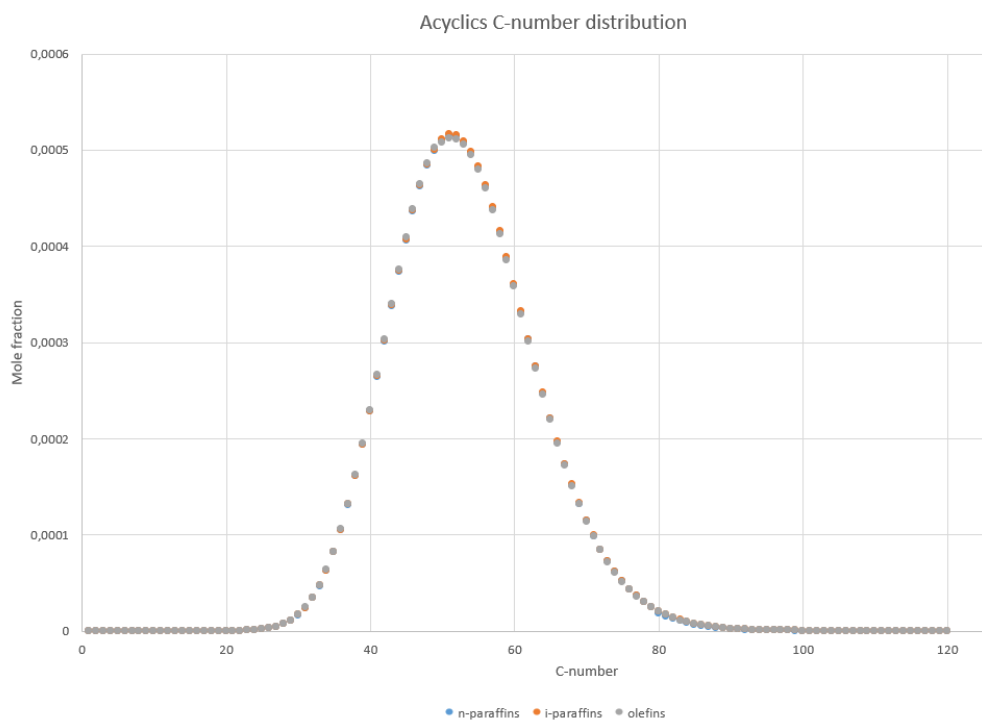
(c) Parity plot 2

Figure 6.5: ICG results residual oil

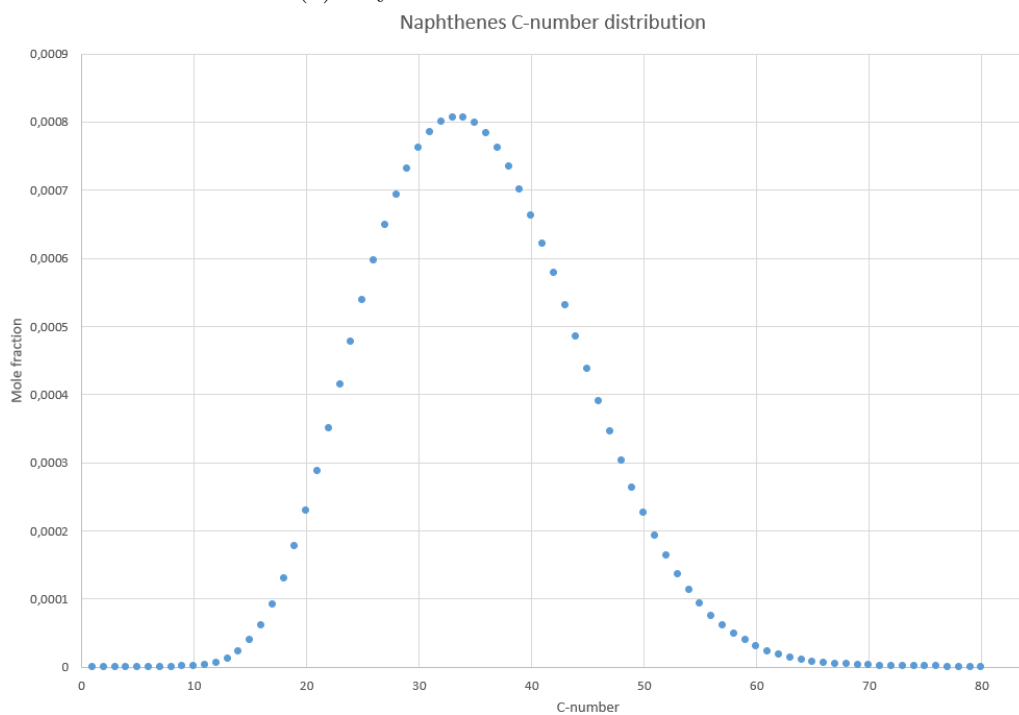
The match between the experimental data and the simulated properties is very good. There are a few properties that could have been matched better. The biggest relative error between the predicted and the experimental value is 0.0382 and corresponds to the H/C ratio. The prediction for the H/C is a little too low. This means that the simulated composition is slightly too aromatic. The value for the WSimDis70 has a substantial absolute error. The experimental value for this property is very high, which will also have consequences for the carbon number distributions. There was no data point available for the properties which have a 'Value' equal to zero. They are shown because the predicted values give valuable information about the simulated composition.

The parity plots confirm the excellent match. The curves are well fitted by a straight line through the origin that has a slope close to 1.

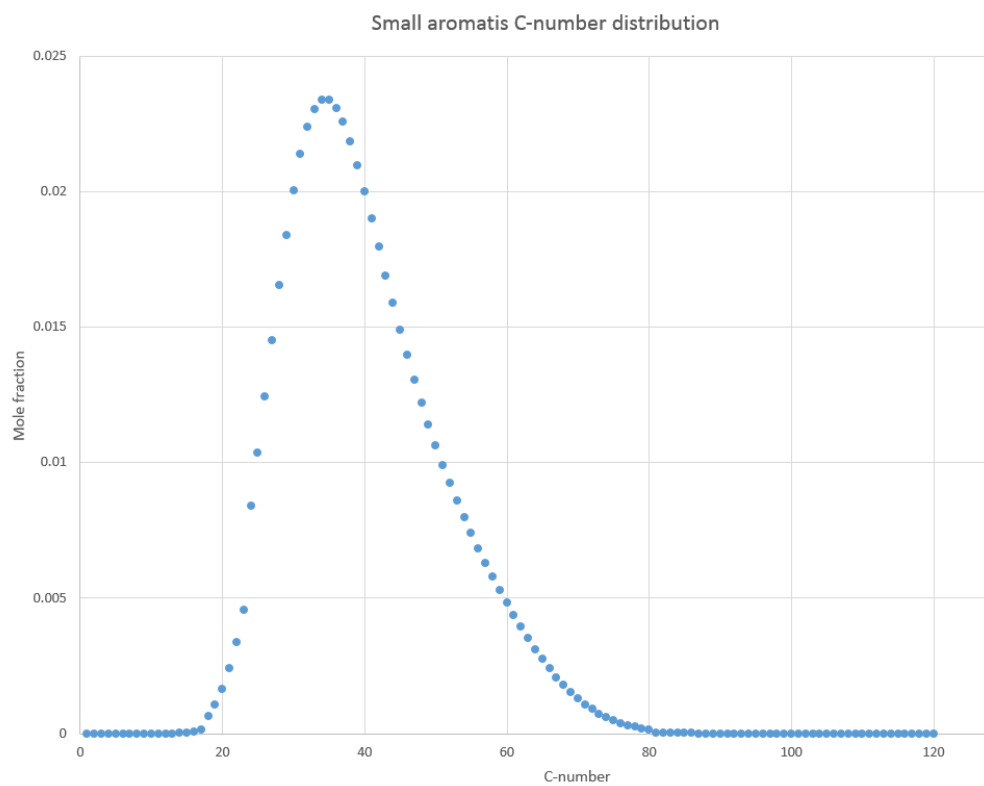
Besides having a good match between experimental-and simulated properties, it is also important to have smooth carbon number distributions. The carbon number distributions for different fractions of residual oil are plotted in figure 6.6.



(a) Acyclics C-number distribution

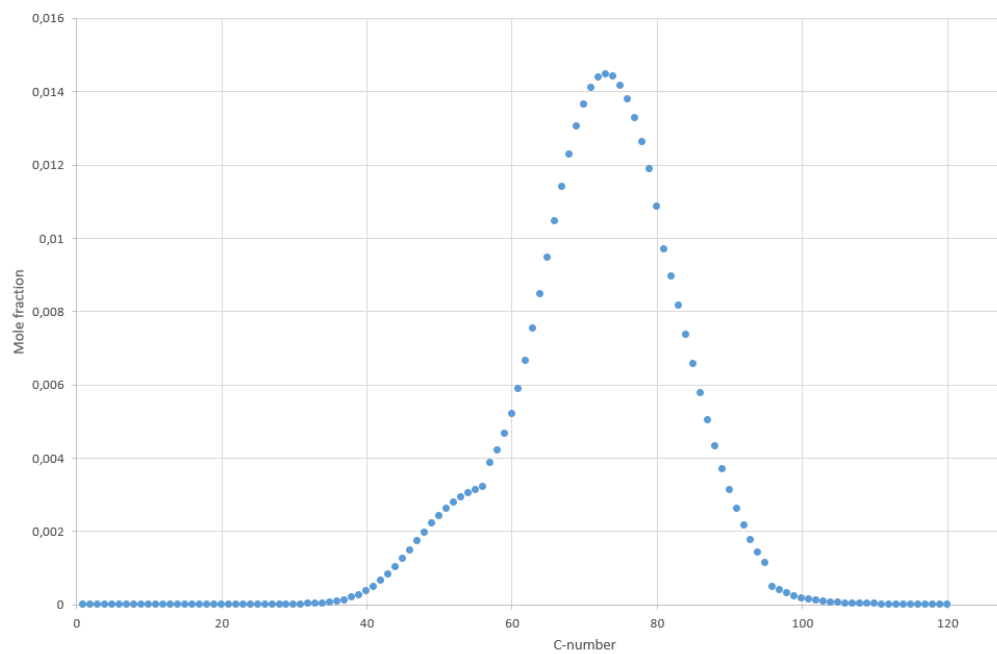


(b) Naphthenes C-number distribution

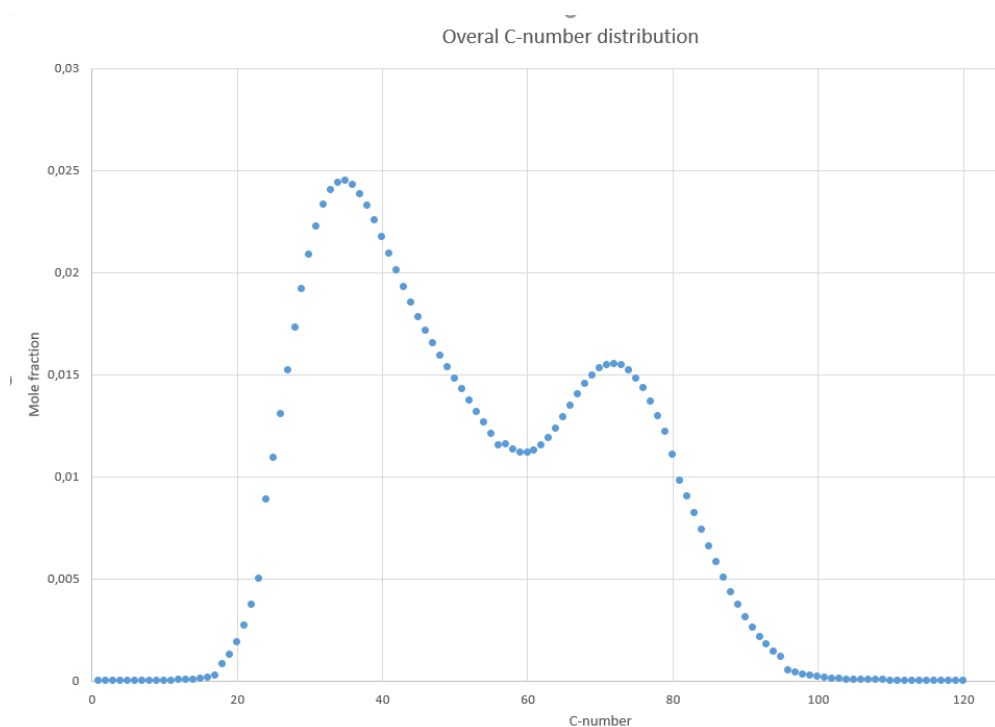


(c) Small aromatics C-number distribution

Asphaltenes C-number distribution



(d) Asphaltenes C-number distribution



(e) Overall C-number distribution

Figure 6.6: C-number distributions residual oil

The carbon number distributions for the different fractions of residual oil all have smooth distributions with one local maximum. The overall carbon number distribution also has a smooth distribution, but there are two local maxima. It is a bimodal distribution. During the development of the ICG model, it was tried to avoid this bimodal distribution. The second mode is caused by the asphaltene molecules. These molecules are the ones that have the highest carbon numbers. The fact that the mole fractions of the asphaltene molecules is high causes the second mode. The reason why the mole fractions of the asphaltene molecules are so high is because of the experimental value for WSimDis70. A large part (30 percent) of the components must have a boiling point higher than this value. In order to obtain this boiling point, carbon numbers must be very high. Besides increasing the carbon number, high boiling points can also be obtained by increasing the aromaticity of the components. This was done in an attempt to move the second mode to smaller carbon numbers, to

get a curve with one mode. However, the other experimental data points put limitations to this. The simulated H/C ratio is a little smaller than the experimental one. Which indicates that the simulated system is already slightly to aromatic. Component categories in table 6.2 like QuinDBT, QDBT, PCC, and Triple Carbazole were added to the model in an attempt to eliminate the second mode. The addition of these components made the two modes approach, but complete elimination was not possible.

6.2.2 VGO

Figure 6.7 shows the comparison between the model results for VGO and the experimental data found in [15]. The numerical values are shown together with their graphical representation in a parity plot.

Current Best Results			F = 190.8
ExpName	Value	PredictedValue	
Density	0.993	1.0004	
WSimDis5	610	613.57	
WSimDis10	637	640.98	
WSimDis20	668	668.24	
WSimDis30	683	683.28	
WSimDis40	698	695.71	
WSimDis50	708	706.64	
WSimDis60	715	715.95	
WSimDis70	723	729.47	
WSimDis80	734	744.59	
WSimDis90	0	776.3	
WSimDis95	0	802.8	
Carbon	0.8597	0.8519	
Hydrogen	0.1057	0.10867	
Oxygen	0	0.0046677	
Nitrogen	0.01136	0.011415	
Sulfur	0.0233	0.023428	
H/C	0.1234	0.12756	
WA_MW	0	352.39	
MA_MW	0	336.84	
nParaffins	0	0.020002	
iParaffins	0	0.019999	
Olefins	0	0.023003	
Naphthenics	0	0.16613	
Aromatics	0	0.77086	

(a) Numerical values

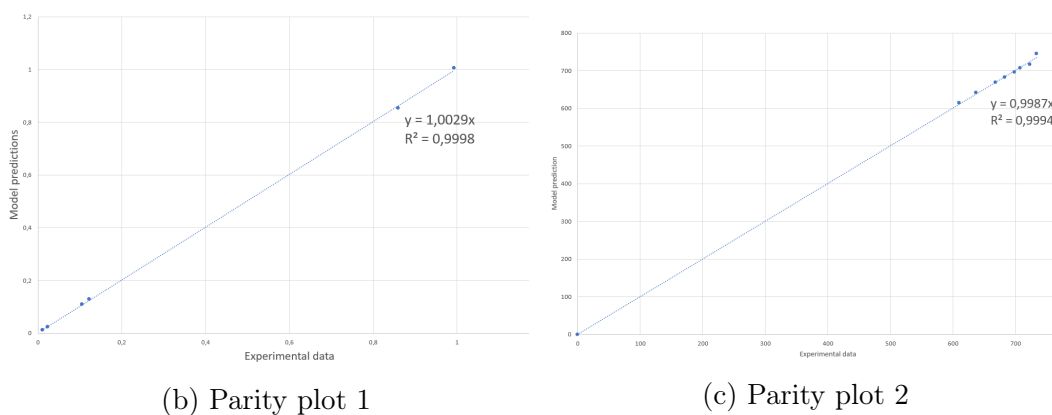


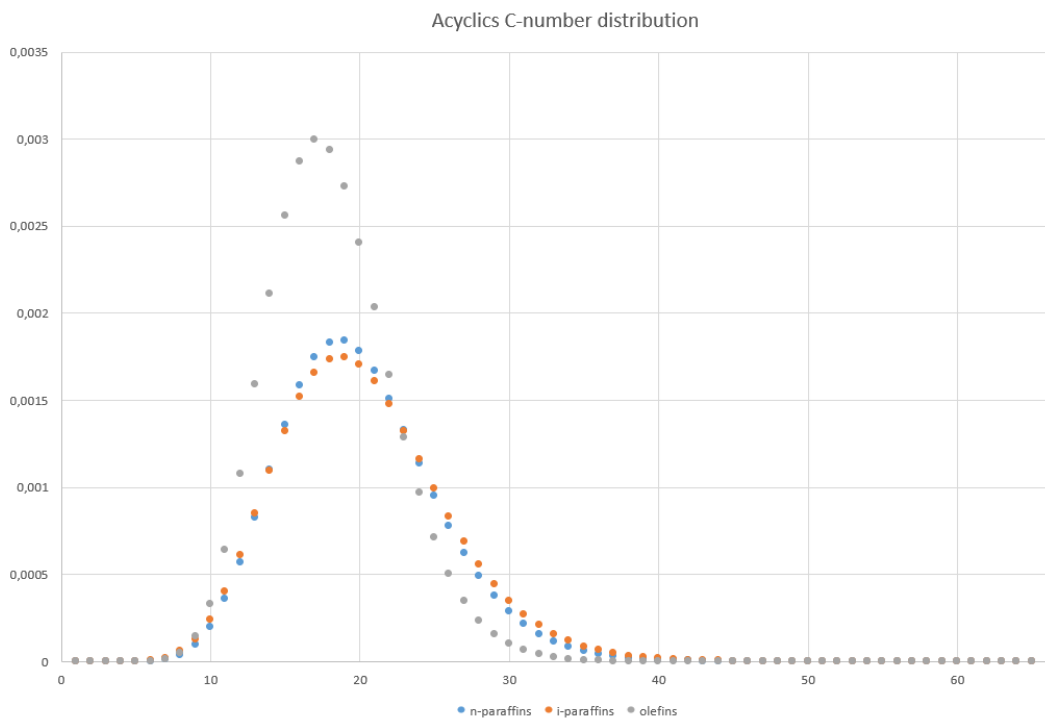
Figure 6.7: ICG results VGO

There is a good match between the simulated properties and the experimental values for all experimental data points. The biggest relative error is 0.0337 for the value of H/C. This means the molecular representation is a little too aliphatic. There was no data point available for the properties which have a 'Value' equal to zero. They are shown because the predicted values give valuable information about the simulated composition.

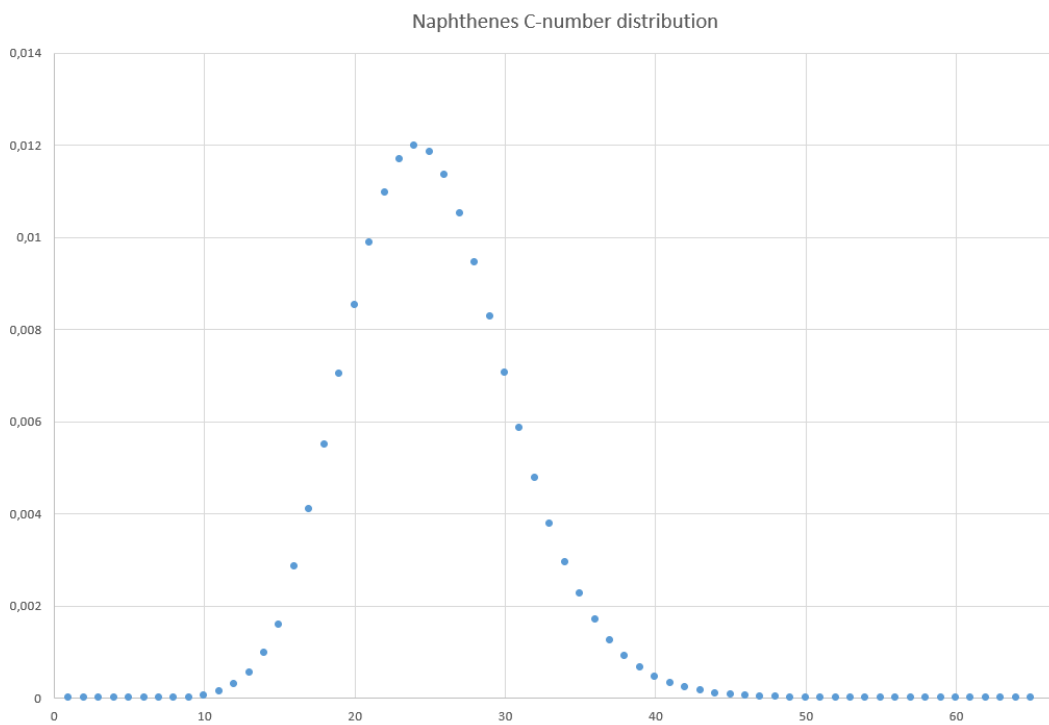
The parity plots confirm the excellent match. The curves are well fitted by a straight line through the origin that has a slope close to 1.

In order to get a good match between simulated-and experimental properties, a large part of the mole fraction are zero. All heavy, highly aromatic components, that are necessary to model residual oil correctly, are not present in VGO. All acyclic-and naphthenic components in table 6.2 are included in the VGO model. Only aromatic components in table 6.2 that have five or fewer aromatic rings are included in the VGO model. The other aromatic components have a mole fraction that is equal to zero.

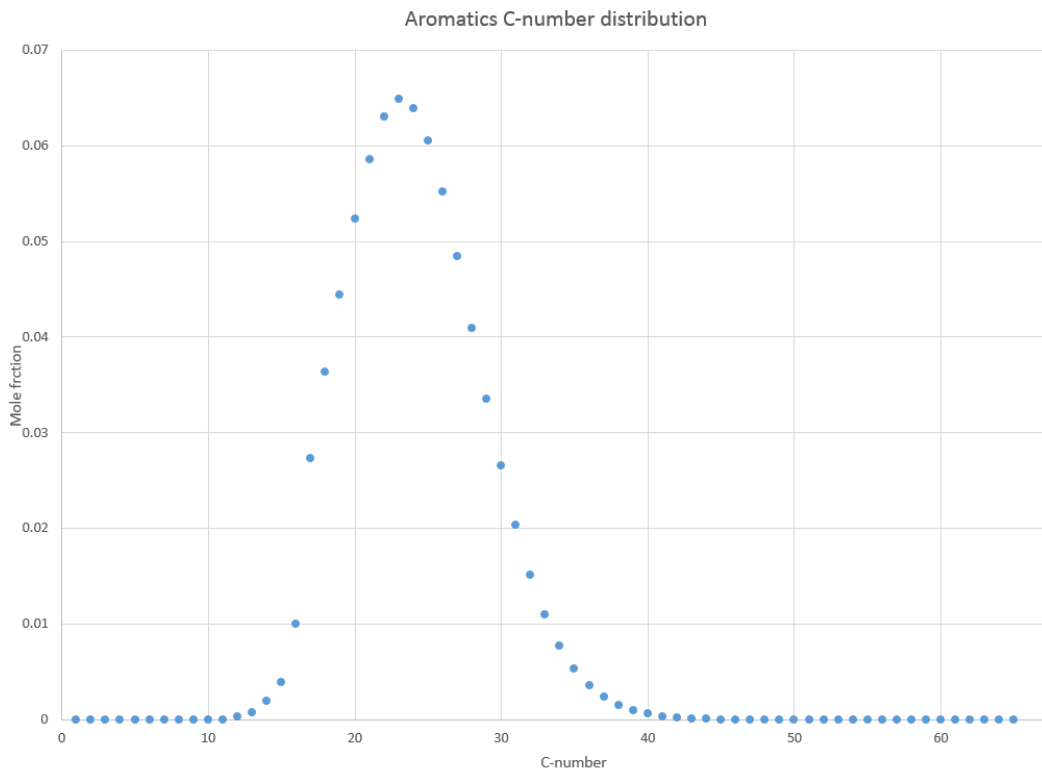
The carbon number distributions for different fractions of the VGO are plotted in figure 6.8.



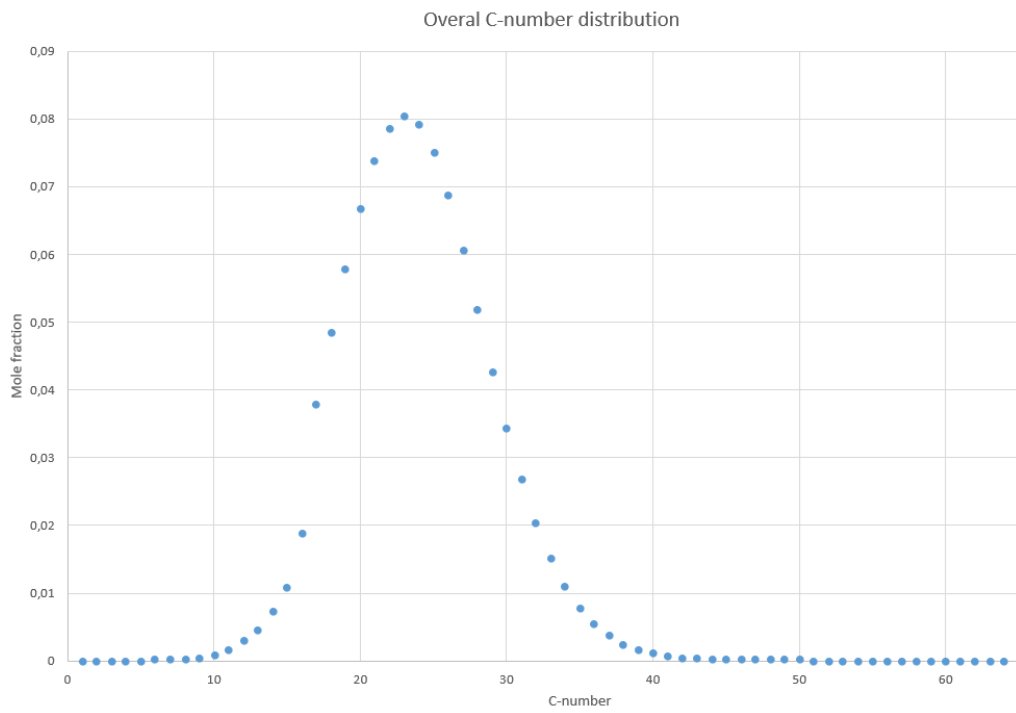
(a) Acyclics C-number distribution



(b) Naphthenes C-number distribution



(c) Aromatics C-number distribution



(d) Overall C-number distribution

Figure 6.8: C-number distributions VGO

All carbon number distributions for VGO are smooth curves with a single maximum. The problem regarding the asphaltenes, that is explained in subsection 6.2.1 is not present.

6.3 Kinetic Model Evaluation

The reaction network, the molecular composition of the feed stream and the format of the rate laws are modeled. The final part of the kinetic model development is the tuning of the kinetic parameters. In order to do so, a data set that contains product data and the corresponding reactor conditions is required. As indicated earlier, such a data set could not be found for SCW upgrading of residual oil. Tuning of the kinetic parameters of the rate laws will not be done in this thesis. However, KME is used in order to indicate that the developed reaction network contains the right chemical pathways to match experimental data. Data regarding SCW upgrading of VGO is available in [15]. The next section shows the match between the experimental data and the tuned model predictions.

6.3.1 VGO

In [15], an extended data set is available for one set of reactor conditions. The developed reaction network, the molecular composition of the feed stream, the reaction rate laws and the molecular properties of the model compounds are loaded in KME together with the product experimental data and the reactor conditions. Table 6.4 show the reactor conditions. In order to match the experimental data, the tunable parameters, described in section 5.2, are given numerical values. A simulation is done, and the product properties are analyzed and compared with the experimental data. Changes are made to the numerical values of the kinetic parameters, and a new simulation is done. This process is repeated until the match of the simulated-and the experimental properties is good enough. As indicated earlier, there are 10025 different chemical reactions occurring. Therefore, the tuning of the kinetic parameters is not done for each individual reaction, but for each reaction family. Note

that in table 6.1 there are 11 reaction families. In KME the kinetic parameters of 54 reactions families can be tuned. This is partly because of the reactions that are manually added, and partially because KME also takes the kind of reactant into account when it creates the reaction family. The 'MidChainCracking' reaction family in table 6.1 can, for example, be applied to a normal paraffin or an alcohol. This creates two reaction families 'MidChainCracking Nparaffin' and 'MidChainCracking Alcohol'. The kinetic parameters of both reactions can be tuned independently. The parameters K and κ in equations 5.6 and 5.13 are taken the same for all reactions. For a more detailed explanation on how to use the KME software to do simulations for this specific kinetic model, see appendix D.

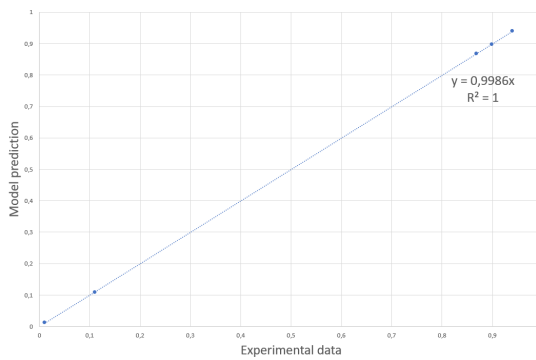
Table 6.5 shows the experimental data points and the corresponding model predictions. The graphical representation of this data is shown in figure 6.9. Two parity plots are made because the numerical values for the 'WSimDis' values are a lot larger than the other numerical values.

Table 6.4: Reactor conditions experimental data

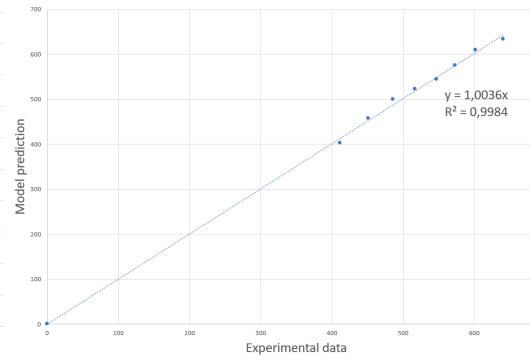
T [K]	693.15
P [MPa]	25
ρ_{water} [$\frac{g}{cm^3}$]	0.15
<i>water-oil mass ratio</i>	2
<i>reaction time</i> [h]	1

Table 6.5: Comparison model results KME

Property	Experimental value	Model prediction
ρ [$\frac{g}{cm^3}$]	0.8993	0.8973
C [wt%]	86.86	86.70
H [wt%]	11.11	10.78
N [wt%]	1.09	1.09
S [wt%]	0.94	0.94
$WSimDis10$ [K]	412	402
$WSimDis20$ [K]	451	458
$WSimDis30$ [K]	486	500
$WSimDis40$ [K]	517	523
$WSimDis50$ [K]	547	544
$WSimDis60$ [K]	573	575
$WSimDis70$ [K]	602	609
$WSimDis80$ [K]	641	634



(a) Parity plot 1



(b) Parity plot 2

Figure 6.9: Parity plots product properties

The match between the experimental data and the model predictions is good for all available data points. This is confirmed by the slope of the parity plot curves being close to one. The biggest relative error is 0.0297 and corresponds to the weight

fraction of hydrogen. This is partly because the experimental data doesn't report a weight fraction for oxygen, while oxygen is present in VGO and in the kinetic model. The oxygen takes up a small part of the weight fraction, that is missing for hydrogen. The computational time for doing this simulation is 19 seconds. A simulation, with the molecular representation of the residual oil feed, is made with the same numerical values for the kinetic parameters. The computational time for this simulation is 19 seconds too. As indicated earlier, the goal is to keep this time limited to one minute. This objective is clearly met.

The purpose of this section is not to determine the numerical values of the kinetic parameters, but to prove that the developed kinetic model represents the reactions occurring in SCW upgrading. The determination of the kinetic parameters will be done in future work. The numerical values of the kinetic constants, used to get the model predictions in table 6.5, will not be discussed. They can be found in appendix E.

Table 6.6 shows the simulated properties for the VGO feed-and product stream.

Table 6.6: Comparison between VGO feed-and product properties

Property	Value feed stream	Value product stream
ρ [$\frac{g}{cm^3}$]	0.9991	0.8973
C [wt%]	85.14	86.70
H [wt%]	10.91	10.78
N [wt%]	1.14	1.09
S [wt%]	2.34	0.94
$WSimDis10$ [K]	641	402
$WSimDis20$ [K]	669	458
$WSimDis30$ [K]	683	500
$WSimDis40$ [K]	696	523
$WSimDis50$ [K]	707	544
$WSimDis60$ [K]	717	575
$WSimDis70$ [K]	731	609
$WSimDis80$ [K]	748	634
MW [$\frac{g}{mol}$]	339.28	190.85
H/C ratio [$\frac{mol}{mol}$]	1.470	1.493
Normal paraffins [wt%]	2	26.8
Iso paraffins [wt%]	2	1.1
Olefins [wt%]	2.3	27.4
Naphthenes [wt%]	16.6	0.008
Aromatics [wt%]	77.1	44.5

Table 6.6 shows what the effect is of SCW upgrading of VGO. All the observed trends are as expected. The density is reduced due to an increase of smaller, more linear molecules. The heteroatom content decreases, mainly as a result of the hydrolysis reactions. The nitrogen content only slightly decreases because most nitrogen is present in pyrrole or pyridine-like structures. These structures don't take part in

hydrolysis reactions. The boiling point distribution decreases on average with 168 *K*. This is mainly due to the cracking reactions. The molecular weight decreases due to cracking. The H/C ratio increases because the product contains fewer aromatic structures. The PIONA distribution of both streams shows the overall pathways. The number of aromatics decreases heavily, causing an increase in normal paraffins and olefins. Naphthenic components get aromatized and iso-paraffins are partially converted to normal paraffins.

Chapter 7

CONCLUSIONS

This thesis showed how a molecular-level kinetic model for SCW upgrading of residual oil can be developed. The KMT was a very useful software package to develop this model with. It also became clear how complex molecular-level kinetic modeling of mixtures with a large variety in molecular structures and large carbon numbers can be.

In order to develop a reaction network that contains the necessary chemical pathways, but has a limited number of components, limitations had to be added to the INGen software. This resulted in the creation of a rank zero network. In this rank zero network, parallel reaction pathways that represent the same chemistry are avoided. Based on literature and the reaction pathways that are included in the model, a set of model compounds is chosen. This set of model compounds changed during the modeling process until one was found that modeled the feed accurately, allowed all reaction pathways to occur and is not too extensive to limit the computational times. Some reaction pathways are too complicated for INGen or are modeled in a certain way (to limit the number of components) that InGen cannot do. Therefore, these reaction pathways are added manually. In total this resulted in a reaction network that contains 10025 reactions between 2894 species.

While developing the reaction network in InGen, a molecular representation of the feed was made in ICG. Mole fractions for the chosen model compounds are determined by developing a PDF structure. The initial set of model compounds was not able to fit the experimental data for VGO and residual oil. Different model compounds were chosen, and the reaction network was adapted. These iterations occurred a couple of times until an accurate molecular representation of both feeds

was obtained. All available experimental data points of both mixtures are matched well. The molecular representation of the VGO stream has smooth, unimodal carbon number distributions. The overall carbon number distribution of the molecular representation of residual oil is bimodal. This is due to the high amount of asphaltene molecules, necessary to match the boiling point distribution.

Rate laws for the different kinds of reactions are chosen. Because the system can be approximated as a single (supercritical) phase without the presence of a catalyst, the underlying principle behind the rate laws is microkinetics. Due to the solvent effects of SCW, the reaction rate is influenced in various ways. The three types of solvent effects that are incorporated in the rate laws are the solvent cage effect, the effect of the dielectric constant and the water-oil phase behavior. Four different types of reactions are present, which all have a different format for their rate law. The four types are pyrolysis reactions, hydrolysis reactions, aromatization reactions, and coking reactions. The number of tunable parameters for each reaction type is equal to two or three. A small kinetic model was developed in Matlab to visualize how the solvent effects of SCW are incorporated in the format of the rate laws.

Finally, the reaction network, the molecular composition of the feed and the format of the rate laws are combined in the KME software. No data set for residual oil upgrading in SCW was available. Therefore, a VGO model was made in ICG, using the same model compounds. For VGO upgrading in SCW, there is some data available in literature. The kinetic parameters are tuned in KME to generate a product stream that matches the experimental product data for VGO. The computational time for simulating the VGO or the residual oil system is 19 seconds. The goal was to keep this time, below one minute. The match between experimental and simulated properties is good. This indicates that the developed reaction network, the molecular representation, and the chosen rate laws can simulate the SCW upgrading of VGO and by extension of residual oil within the allowed computational time.

Chapter 8

FUTURE WORK

This molecular-level kinetic model is a big step forward compared to the earlier developed kinetic models for SCW upgrading of residual oil. A large step is taken, but there is still work that needs to be done. In general, this can be divided into model development work and model usage work.

8.1 Model Development

First, the tuning of the kinetic parameters should be done. In order to do so a data set that contains reactant-and product data for SCW upgrading of residual oil is required. In order to do a complete tuning of all parameters, multiple data sets are needed. One data set can be used as a reference. The other data sets should correspond to different reactor temperatures and different water densities. Measurements that should be included in these data sets are density, molecular weight, boiling point distribution, heteroatom content. In order to make the model more accurate, the following measurements should be included: PIONA data (instead of the frequently reported SARA data), specification of the structures in which heteroatoms are present (e.g. N in pyrrole structure), carbon number/molecular weight distribution data. Another important part of the data set, that usually is not mentioned in literature, is the analysis of the SCW after the reaction. Most data sets report how the organic phase is separated from the SCW, but none of them do an analysis of what product molecules are still present in the SCW phase.

Besides the tuning of the kinetic parameters, there are other improvements that can be made to the model. Right now, there is no mechanism that allows naphthenic

rings to open. This was not included because it would add a large number of components to the system and because it is not one of the main chemical pathways. Because the computational time is still small enough with the currently used components, the reaction network could be expanded with naphthene ring opening reactions.

In general, more detail could be added to the reaction network. What changes should be made depends on three things: the more detailed chemistry that modeler wants to add to the model, the computational time that is allowed for the model to solve and the kind experimental that is available to tune the parameters of the more detailed chemistry. Examples of the addition of more detail to the reaction network are the addition of more dealkylation pathways besides the one that has the most stable intermediates, addition of cracking reactions beside MidChainCracking for small carbon number, the inclusion of partially aromatized naphthenic compounds.

In the current model, the tunable parameters κ and K are taken constant for all reactions. An improvement of the model could be made by giving each reaction family a separate value for these parameters.

8.2 Model Usage

After determining the kinetic parameters, the model can be used to simulate situations that differ from the ones that correspond to the experimental data. Simulations with different temperatures, different water densities, different water-oil ratios or different reaction times can be done. Analysis of the yield of certain products for these different operating conditions or reaction times can be used to optimize reactor conditions or to find the optimal reaction time to maximize the yield of a certain product. Besides looking for better reactor conditions, analysis of these simulations can result in a better understanding of the phenomena that are occurring on the molecular scale. This should be focused on coke production. By looking at what parts the rate equations cause the coke production to go down, the underlying cause behind the promising experimental data can be found.

BIBLIOGRAPHY

- [1] US Energy Information Administration. International energy outlook 2017, 2017.
- [2] Murray R. Gray. *Upgrading petroleum residues and heavy oils*, chapter 1, pages 1–40. Marcel Dekker Inc, 1994.
- [3] Zhenyu Liu Tao Xu, Qingya Liu and Junfei Wu. The role of supercritical water in pyrolysis of carbonaceous compounds. *Energy and fuels*, 2013.
- [4] Martin A. Abraham and Michael T. Klein. Pyrolysis of benzylphenylamine neat and with tetralin, methanol, and water solvents, 1985.
- [5] YSusan H. Townsend and Michael T. Klein. Dibenzyl ether as a probe into the supercritical fluid solvent extraction of volatiles from coal with water. *FUEL*, 1984.
- [6] Zhanlong Song Xiqiang Zhao Chunyuan Maa Guifang Chen, Shouyan Chen. Lignite sulfur transformation during the supercritical water gasification process. *Journal of Analytical and Applied Pyrolysis*, 2015.
- [7] Ayhan Demirbas. Sulfur removal from crude oil using supercritical water. *Petroleum Science and Technology*, 2016.
- [8] J. DiNaro J.W. Tester R. Lachance, J. Paschkewitz. Thiodiglycol hydrolysis and oxidation in suband supercritical water. *Journal of Supercritical Fluids*, 1999.
- [9] Murray R. Gray. *Upgrading petroleum residues and heavy oils*, chapter 3, pages 83–115. Marcel Dekker Inc, 1994.
- [10] l Gilbert L. Huppert l Michael T. Klein Susan H. Townsend, Martin A. Abraham and Stephen C. Paspekt. Solvent effects during reactions in supercritical water, 1988.
- [11] Phillip E. Savage. Organic chemical reactions in supercritical water. *Chem Rev*, 1999.
- [12] Abd El-Aal M. Gaber and M.M. Aly. Thermolysis of some thioether derivatives. *Journal of Analytical and Applied Pyrolysis*, 1992.

- [13] JEAN L. BOIVIN and RODERICK MACDONAID. Pyrolysis of ethyl mercaptan. *Canadian Journal of Chemistry*, 1955.
- [14] Jinwen Chen Anton Alvarez-Majmutov, Rafal Gieleciak. Modeling the molecular composition of vacuum residue from oil sand bitumen. *Fuel*, 2019.
- [15] Li-Qun Zhao Pei-Qing Yuan Zhen-Min Cheng, Yong Ding and Wei-Kang Yuan. Effects of supercritical water in vacuum residue upgrading. *Energy Fuels*, 2009.
- [16] Dwijen K Banerjee. *Oil Sands, Heavy Oil, Bitumen : From Recovery to Refinery*, chapter 7, pages 83–100. PennWell Corp., 2012.
- [17] M. A. PARFENOVA R. KH. STARTSEVA N. V. DAVIDENKO G. A. GLEBOV R. N. FAKRN TD OV, N. K. LYAPINA and L. N. GAGARINA. Composition of alkanes in residual oils. *Petrol. Chem. U. S.*, 1990.
- [18] V. I. Titov V. S. Aksenov and V. F. Kam'yanov. Nitrogen compounds of petroleum oil. *Plenum Publishing Corporation*, 1979.
- [19] Lloyd R. Snyder. Petroleum nitrogen compounds and oxygen compounds. *accounts of chemical research*, 1970.
- [20] Yin Liu Pei-Qing Yuan Zhen-Min Cheng Wei-Kang Yuan Fan Bai, Chun-Chun Zhu. Co-pyrolysis of residual oil and polyethylene in sub- and supercritical water. *FUEL PROCESSING TECHNOLOGY*, 2013.
- [21] Yong Ding-Pei-Qing Yuan-Shan-Xiang Lu Li-Qun Zhao, Zhen-Min Cheng and Wei-Kang Yuan. Experimental study on vacuum residuum upgrading through pyrolysis in supercritical water. *Energy Fuels*, 2006.
- [22] Jicheng Bia Lina Han, Rong Zhang. Experimental investigation of high-temperature coal tar upgrading in supercritical water. *Fuel processing and technology*, 2009.
- [23] Can Erkey Ramazan Oğuz Canıaz. Process intensification for heavy oil upgrading using supercritical water. *Chemical Engineering Research and Design*, 2014.
- [24] Lawrence Lai-Yuko Kida Tamba Monroe-William H. Green Adam G. Carr, Caleb A. Class2. Supercritical water treatment of crude oil and hexylbenzene: An experimental and mechanistic study on alkylbenzene decomposition. *Energy Fuels*, 2015.
- [25] Benjamin C. Wu Michael T. Klein, Lori A. Torry and Susan H. Townsend. Hydrolysis in supercritical water: Solvent effects as a probe of the reaction mechanism. *The Journal of Supercritical Fluids*, 1990.

- [26] Michael T. Klein Benjamin C. Wu and Stanley I. Sandler. Solvent effects on reactions in supercritical fluids. *Industrial Engineering Chemistry Research*, 1991.
- [27] Chun-Chun Zhu Pei-Qing Yuan Zhen-Min Cheng Wei-Kang Yuan Ying Liu, Fan Bai. Upgrading of residual oil in sub- and supercritical water: An experimental study. *Fuel Processing Technology*, 2013.
- [28] Michael T. Klein Gang Hou Ralph J. Bertolacini Linda J. Broadbelt Ankush Kumar. *Molecular Modeling in Heavy Hydrocarbon Conversions*, chapter 1, pages 2–4. CRC Press Taylor Francis Group ., 2006.
- [29] Satoshi Ishizeki Hiroshi Inomata Richard Lee Smith Jr Masaru Watanabe, Shinosuke Kato. Heavy oil upgrading in the presence of high density water: Basic study. *Journal of supercritical fluids*, 2010.
- [30] Die Wang Dongxiang Zhang, Zhong Ren and Kun Lu. Upgrading of crude oil in supercritical water: A five-lumped kinetic model. *Journal of Analytical and Applied Pyrolysis*, 2017.
- [31] Ahmed F. Ghoniem Michael T. Timko and William H. Green. Upgrading and desulfurization of heavy oils by supercritical water. *Journal of supercritical fluids*, 2015.
- [32] Martin A. Abraham and Michael T. Klein. Solvent effects during the reaction of coal model compounds. *ACS*, 1987.
- [33] Ryuzo Tanaka Gang Hou Michael T. Klein Jr. Michael T. Klein Wei Wei, Craig A. Bennett. Computer aided kinetic modeling with kmt and kme. *FUEL PROCESSING TECHNOLOGY*, 2008.
- [34] MORENO Brian M. BENNETT Craig A. KLEIN Michael T. HORTON Scott R., HOU Zhen. Molecule-based modeling of heavy oil. *Science China*, 2013.
- [35] J. Marrero and R. Gani. Group-contribution based estimation of pure component properties. *Fluid Phase Equilib*, 2001.
- [36] D. M. Golden G. R. Haugen H. E. O’Neal A. S. Rodgers R. Shaw S. W. Benson, F. R. Cruickshank and R. Walsh. Additivity rules for estimation of thermochemical properties. *Chem. Rev.*, 1969.
- [37] Stanley I. Sandler. *Chemical, Biochemical, and Engineering Thermodynamics*, chapter 6, page 241. john wiley sons inc, 2006.
- [38] Kelly Louie. Eyring equation, 2017.

- [39] Stephan Kraft and Frédéric Vogel. Estimation of binary diffusion coefficients in supercritical water: Mini review. *Industrial Engineering Chemistry Research*, 2017.
- [40] R. S. Basu B. Kamgar-Parsi J. V. Sengers, J. T. R. Watson and R. C. Hendricks. Representative equations for the thermal conductivity of water substance. *Journal of physical and chemical reference data*, 2009.
- [41] Eric W. Lemmon J. M. H. Levelt Sengers D. P. Fernández, A. R. H. Goodwin and R. C. Williams. A formulation for the static permittivity of water and steam at temperatures from 238 K to 873 K at pressures up to 1200 MPa, including derivatives and Debye-Hückel coefficients. *Journal of physical and chemical reference data*, 2009.
- [42] A. K. Dalai M. Mapiour, V. Sundaramurthy and J. Adjaye. Effects of hydrogen partial pressure on hydrotreating of heavy gas oil derived from oil-sands bitumen: Experimental and kinetics. *Energy Fuels*, 2010.
- [43] G.B. Marin S. Wauters. Computer generation of a network of elementary steps for coke formation during the thermal cracking of hydrocarbons. *Chemical Engineering Journal*, 2001.
- [44] Litao Wang Yindong Liu Chun Yangc Ting Yan, Jie Xu and Tao Fang. A review of the upgrading of heavy oils with supercritical fluids. *Royal Society of Chemistry*, 2015.
- [45] Harold H Schobert. *Chemistry of Fossil Fuels and Biofuels*, chapter 23, pages 415–426. Cambridge, 2013.
- [46] Howard Freund Prasanna V. Joshi and Michael T. Klein. Directed kinetic model building: Seeding as a model reduction tool. *Energy Fuels*, 1999.
- [47] Michael T. Klein Gang Hou Ralph J. Bertolacini Linda J. Broadbelt Ankush Kumar. *Molecular Modeling in Heavy Hydrocarbon Conversions*, chapter 12, pages 205–220. CRC Press Taylor Francis Group ., 2006.
- [48] Anthony Andrews and Richard K. Lattanzio. Petroleum coke: Industry and environmental issues. *Congressional Research Service*, 2013.
- [49] Stanley I. Sandler. *Chemical, Biochemical, and Engineering Thermodynamics*, chapter 13, pages 703–720. John Wiley Sons Inc, 2006.
- [50] Stanley I. Sandler. *Chemical, Biochemical, and Engineering Thermodynamics*, chapter Appendices, pages 912–929. John Wiley Sons Inc, 2006.
- [51] wired chemist. Standard heats and free energies of formation and absolute entropies of organic compounds, 2019.

Appendix A

EXAMPLE OF A PDF TREE STRUCTURE

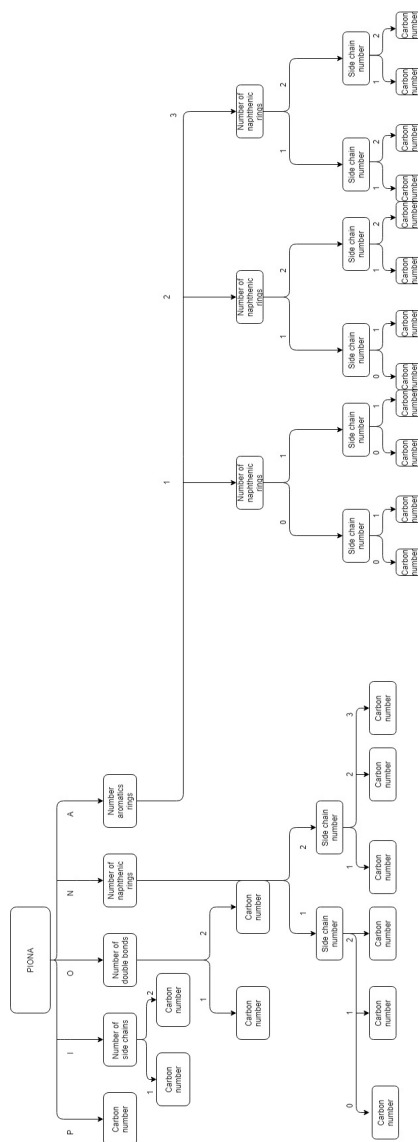


Figure A.1: Example of a simple PDF tree structure

Appendix B
**DERIVATION EQUILIBRIUM CONSTANT HYDROLYSIS
 REACTION**

Figure B.1 shows the hydrolysis reaction for which the equilibrium constant is calculated.

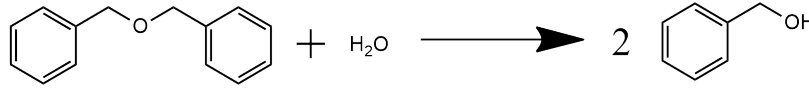


Figure B.1: Hydrolysis reaction for the calculation of the equilibrium constant

The formulas on which the calculations are based were found in [49].

$$K_{eq}(T) = \exp\left(\frac{-\Delta_{rxn}G^0}{RT}\right) \quad (\text{B.1})$$

$$\Delta_{rxn}G^0(298.15K) = \sum_i \nu_i \Delta_f G_i^0(298.15K) \quad (\text{B.2})$$

Combining both formulas results in the calculation of K_{eq} at a temperature of $298.15K$. In order to calculate the equilibrium constant at a different temperature the following equation is required.

$$\left(\frac{d\ln(K_{eq})}{dT}\right)_P = \frac{\Delta_{rxn}H^0(T)}{RT^2} \quad (\text{B.3})$$

Integration of this equation from $T = 298.15K$ to T , results in an expression for the equilibrium constant as a function of temperature.

$$\ln\left(\frac{K_{eq}(T)}{K_{eq}(298.15K)}\right) = \int_{298.15}^T \frac{\Delta_{rxn}H^0(T')}{RT'^2} dT' \quad (\text{B.4})$$

In order to calculate the integral, an expression for $\Delta_{rxn}H^0(T)$ is needed.

$$\Delta_{rxn}H^0(T) = \Delta_{rxn}H^0(298.15K) + \int_{298.15}^T \Delta_{rxn}C_p^0(T) \quad (B.5)$$

With:

$$\Delta_{rxn}H^0(298.15K) = \sum_i \nu_i \Delta_f H_i^0(298.15K) \quad (B.6)$$

And:

$$\Delta_{rxn}C_p^0(T) = \sum_i \nu_i C_{p,i}^0(T) \quad (B.7)$$

The following expression is used to compute $C_{p,i}^0(T)$.

$$C_{p,i}^0(T) = a + bT + cT^2 \quad (B.8)$$

Table B.1 contains all the constants, required to calculate the equilibrium constant.

Table B.1: Thermodynamic data to calculate the equilibrium constant

/	Water	Dibenzyl ether	Benzyl alcohol
ν	-1	-1	2
$\Delta_f G_i^0(298.15K) [\frac{kJ}{mol}]$	-237.1 [50]	277.5751	-27.5 [51]
$\Delta_f H_i^0(298.15K) [\frac{kJ}{mol}]$	-285.8 [50]	177.1933	-161.0 [51]
$a [\frac{kJ}{Kmol}]$	29.163 [50]	-52.148	-32.089
$b [\frac{kJ}{K^2mol}]$	$1.449 \cdot 10^{-2}$ [50]	1.1128	0.6239
$c [\frac{kJ}{K^3mol}]$	$-0.202 \cdot 10^{-5}$ [50]	-0.000689	-0.000419

The values in table B.1 that do not have a reference, are calculated with the Gani and Benson group contribution methods [35, 36] in the PropGen software.

Inserting the numerical values gives the following equations:

$$\Delta_{rxn}C_p^0(T) = -101.37 + 1.58721T - 1.4698 \cdot 10^{-4}T^2 \quad (B.9)$$

$$\Delta_{rxn}H^0(298.15K) = -213.3933 \frac{kJ}{mol} \quad (B.10)$$

$$\Delta_{rxn}H^0(T) = -39237.7 - 101.37T + 0.793605T^2 - 0.000048993T^3 \quad (\text{B.11})$$

$$K_a(298.15K) = 1.0393 \quad (\text{B.12})$$

$$K_a(T) = K_a(298.15K) \cdot \exp(0.09544831319T - 12.19195382 \cdot \ln(T) + \frac{4719.188638}{T} - 0.000002946258544T^2 + 25.4405394) \quad (\text{B.13})$$

For a temperature of $650K$ the equilibrium constant is:

$$K_a(T) = 2.124 \cdot 10^7 \quad (\text{B.14})$$

Appendix C

RATE OF HYDROLYSIS VS RATE OF PYROLYSIS

This calculation is based on experimental data from [32]. This paper contains first order rate constants for the pyrolysis reaction of benzyl-phenyl-amine (BPA) and second order rate constant for the hydrolysis reaction of BPA. In SCW upgrading, the water concentration is so high compared to the other reactant concentrations, that it can be approximately taken constant. The second order rate constant for hydrolysis is converted into a pseudo first order rate constant for hydrolysis. This value is compared to the first order rate constant for pyrolysis. The paper only contains one data point for water in the supercritical phase. This data point is given in table C.1.

Table C.1: Data hydrolysis-and pyrolysis rate constants

$T[K]$	$P[atm]$	ρ_r	$k_{pyrolysis}[min^{-1}]$	$k_{hydrolysis}[\frac{l}{mol \cdot min}]$
659	264	1.2	$18 \cdot 10^{-3}$	$1.8 \cdot 10^{-3}$

The relative density can be converted to the water concentration.

$$C_{water} = \frac{\rho_r \cdot \rho_{crit}}{M_{water}} \quad (C.1)$$

$$C_{water} = 21.45 \frac{mol}{l} \quad (C.2)$$

$$k_{hydrolysis,1st,order} = k_{hydrolysis} \cdot C_{water} \quad (C.3)$$

$$k_{hydrolysis,1st,order} = 38.61 \cdot 10^{-3} min^{-1} \quad (C.4)$$

$$\frac{k_{hydrolysis,1st,order}}{k_{pyrolysis}} = 2.145 \quad (C.5)$$

Based on this value, it is estimated that the rate of hydrolysis of BPA is more than twice as fast as the rate of pyrolysis. The reactor conditions that correspond to this data are similar to the ones that are encountered in SCW upgrading.

Appendix D

MANUAL ON HOW TO USE THE KINETIC MODEL

This appendix is meant for people who have access to the KMT software and the kinetic model that is described in this thesis. It describes how the files are used to do simulations. All necessary files are in the folder 'Thesis_Roel_Upgrading_Of_Residual_Oil_In_SCW'. Within this folder, there are folders that correspond to the different software packages in KMT. The following sections describe how to use the files in the different software packages.

D.1 InGen_Model

This folder contains three subfolders. 'Molecules_SCW_Upgrading_Resid' contains the .dat files for all the model compounds in the reaction network except the coke (precursor) molecules. 'Molecules_SCW_Upgrading_Resid_Coking' contains the .dat files for the coke precursor molecules. 'SCW_Upgrading_Resid' is the actual INGen model folder. The use of the INGen model is straight forward for people who are familiar with the software.

D.2 Manually_added_reactions

This folder contains the excel files that are used to write the reactions that couldn't be generated by INGen.

D.3 ICG_models

This folder contains three subfolders. 'SCW_Upgrading_Resid' and 'SCW_Upgrading_VGO' are respectively the ICG model folders for the residual oil-and VGO reactant streams. The use of the ICG models is straight forward for people who are

familiar with the software. The 'result_file' folder contains two excel files which are used to generate the carbon number distributions for the reactant streams. These plots can be generated by pasting the mole fractions of the components (generated by ICG) in column D in the 'raw data' sheet.

D.4 KME_model

This folder contains two subfolders and six other files that help with the use of the KME model. The SCW_Upgrading_Resid_ingen_reactions_and_coking.eqn file is the list of reactions that is loaded in the KME model. It is the combination of the reactions generated by INGen and the manually added reactions. The 'SCW_Upgrading_Resid' folder is the actual KME model folder. In order to open the KME model, go to Computer/OS(C:)/KME6.0_ChenTest/ Codegen/ KME6.61p.xlsm and open the model 'SCW_Upgrading_Resid'. The basic use of KME will not be explained, only the specific aspects of working with the 'SCW_Upgrading_Resid' model.

D.4.1 Generating input stream

Open the 'Stream_Generator.xlsx' file. Go to one of the 'input stream generator' sheets. Paste the mole fractions generated by ICG in column E. Specify the water density, reactor volume, mass ratio between water and oil and the molar mass of the oil stream in cells F2 to J2. Column M contains the molar flow rates that must be pasted in the 'input' sheet in the KME model.

D.4.2 Include cage effect and the influence of the dielectric constant

Open the 'Solvent_Effect_Rate_Laws' file. Copy cells B2 until B64 of the 'Dielectric' sheet. Paste these cells in cell E57 of the 'REACTIONS' sheet in the KME model. In the 'Solvent_Effect_Rate_Laws' file it is indicated which parameter of the correlations is in which cell. Important is that the cell that corresponds to 'correction factor k' in the 'Solvent_Effect_Rate_Laws' file is in cell E118 in the 'REACTIONS' sheet in the KME model.

Copy cells B2 until E7376 from the 'Cage' sheet in the 'Solvent_Effect_Rate_Laws' file. Paste these cells in cell D400 of the 'REACTIONS' sheet in the KME model. Replace the content in cells D400 until D458 with random numbers. This is required to be able to save the parameters. Press 'Save RTK' on top of the sheet. After doing this together with the general KME modeling procedure, press 'run model'.

D.4.3 Get product properties

Open the 'Product_Stream_Property_Calculator.xlsx' file and the 'Stream_Generator.xlsx' file. Go to the 'WSimDis_SHEET' sheet of the 'Product_Stream_Property_Calculator.xlsx' file and copy cells A1 to E2896. Paste these cells in cell F1. Keep the cells selected and go to 'Sort & Filter' and select custom sort. Press 'OK'. This sorts the molecules from low to high boiling point. Go to the 'Result_SHEET' sheet and see the model results. For the density value, one more thing must be done. Go to Computer/OS(C:)/KME6.0_ChenTest/Codegen/KME6.61p-Copy.xlsm and open the model 'SCW_Upgrading_Resid_Property_Simulator'. Go to the 'Stream_Generator.xlsx' file and go to the Output stream generator sheet corresponding to VGO or residual oil. Copy the 'liquid output [mol/s]' column. Paste this column in the 'input' sheet of the 'SCW_Upgrading_Resid_Property_Simulator' KME model. Run this KME model. Now also the density value in the 'Result_SHEET' sheet of the 'Product_Stream_Property_Calculator.xlsx' file is shown.

What components are included and excluded from the liquid stream depends on the conditions of the product stream and how it is recovered from the reactor. Therefore, modification to the columns liquid output [mol/s], gas output [g/s] and solid output [g/s] may have to be made by the future user of the model.

Appendix E

KINETIC CONSTANTS

This table contains the kinetic constants used to generate the model results shown in table 6.5. Because the experimental data is isothermal, only the pre exponential factor is determined. E , ΔS and ΔH are zero. The values for κ and K are $-5 \cdot 10^{-30}$ and 10^{17} .

Table E.1: Kinetic constants KME model

reaction family number	$\log(A)_{[s \cdot atm^{(\nu-1)}]}$
1	1.5
2	1.5
3	1.5
4	1.5
5	2
6	1.5
7	4
8	2.15
9	4
10	2.8
11	1.5
12	1.5
13	1.5
14	1.5
15	1.5

16	1.5
17	2
18	2
19	2
20	-0.5
21	0.75
22	0.75
23	0.75
24	0.75
25	0.75
26	0.75
27	0.75
28	-0.5
29	-0.5
30	0.8
31	0.8
32	0.8
33	0.8
34	0.8
35	1.05
36	-10
37	-10
38	1.32
39	-10
40	2
41	2
42	1.08

43	2
44	1.32
45	2
46	2
47	-10
48	1
49	1
50	2.5
51	2
52	2
53	2.5
54	2.5

Appendix F
REPRINT PERMISSION DOCUMENTS

**ELSEVIER LICENSE
TERMS AND CONDITIONS**

Apr 12, 2019

This Agreement between University of Delaware -- Roel Smits ("You") and Elsevier ("Elsevier") consists of your license details and the terms and conditions provided by Elsevier and Copyright Clearance Center.

License Number	4566561236038
License date	Apr 12, 2019
Licensed Content Publisher	Elsevier
Licensed Content Publication	Chemical Engineering Research and Design
Licensed Content Title	Process intensification for heavy oil upgrading using supercritical water
Licensed Content Author	Ramazan Oğuz Canıaz,Can Erkey
Licensed Content Date	Oct 1, 2014
Licensed Content Volume	92
Licensed Content Issue	10
Licensed Content Pages	19
Start Page	1845
End Page	1863
Type of Use	reuse in a thesis/dissertation
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1
Format	both print and electronic
Are you the author of this Elsevier article?	No
Will you be translating?	No
Original figure numbers	Figure 3
Title of your thesis/dissertation	Molecular-level kinetic modeling of the upgrading of residual oil in supercritical water
Expected completion date	Apr 2019
Estimated size (number of pages)	100
Requestor Location	University of Delaware 210 South College Ave NEWARK, DE 19716 United States Attn: University of Delaware
Publisher Tax ID	98-0397604
Total	0.00 USD
Terms and Conditions	

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions

established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at <http://myaccount.copyright.com>).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.
3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:
"Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit - "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."
4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.
5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com). No modifications can be made to any Lancet figures/tables and they must be reproduced in full.
6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.
7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.
8. License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.
9. Warranties: Publisher makes no representations or warranties with respect to the licensed material.
10. Indemnity: You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.
11. No Transfer of License: This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.
12. No Amendment Except in Writing: This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).
13. Objection to Contrary Terms: Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of

any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.

14. **Revocation:** Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:

15. **Translation:** This permission is granted for non-exclusive world **English** rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article.

16. **Posting licensed content on any Website:** The following terms and conditions apply as follows: Licensing material from an Elsevier journal: All content posted to the web site must maintain the copyright information line on the bottom of each image; A hyper-text must be included to the Homepage of the journal from which you are licensing at <http://www.sciencedirect.com/science/journal/xxxxx> or the Elsevier homepage for books at <http://www.elsevier.com>; Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

Licensing material from an Elsevier book: A hyper-text link must be included to the Elsevier homepage at <http://www.elsevier.com>. All content posted to the web site must maintain the copyright information line on the bottom of each image.

Posting licensed content on Electronic reserve: In addition to the above the following clauses are applicable: The web site must be password-protected and made available only to bona fide students registered on a relevant course. This permission is granted for 1 year only. You may obtain a new license for future website posting.

17. **For journal authors:** the following clauses are applicable in addition to the above:

Preprints:

A preprint is an author's own write-up of research results and analysis, it has not been peer-reviewed, nor has it had any other value added to it by a publisher (such as formatting, copyright, technical enhancement etc.).

Authors can share their preprints anywhere at any time. Preprints should not be added to or enhanced in any way in order to appear more like, or to substitute for, the final versions of articles however authors can update their preprints on arXiv or RePEc with their Accepted Author Manuscript (see below).

If accepted for publication, we encourage authors to link from the preprint to their formal publication via its DOI. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help users to find, access, cite and use the best available version. Please note that Cell Press, The Lancet and some society-owned have different preprint policies. Information on these policies is available on the journal homepage.

Accepted Author Manuscripts: An accepted author manuscript is the manuscript of an article that has been accepted for publication and which typically includes author-incorporated changes suggested during submission, peer review and editor-author communications.

Authors can share their accepted author manuscript:

- immediately
 - via their non-commercial person homepage or blog
 - by updating a preprint in arXiv or RePEc with the accepted manuscript

- via their research institute or institutional repository for internal institutional uses or as part of an invitation-only research collaboration work-group
- directly by providing copies to their students or to research collaborators for their personal use
- for private scholarly sharing as part of an invitation-only work group on commercial sites with which Elsevier has an agreement
- After the embargo period
 - via non-commercial hosting platforms such as their institutional repository
 - via commercial sites with which Elsevier has an agreement

In all cases accepted manuscripts should:

- link to the formal publication via its DOI
- bear a CC-BY-NC-ND license - this is easy to do
- if aggregated with other manuscripts, for example in a repository or other site, be shared in alignment with our hosting policy not be added to or enhanced in any way to appear more like, or to substitute for, the published journal article.

Published journal article (JPA): A published journal article (PJA) is the definitive final record of published research that appears or will appear in the journal and embodies all value-adding publishing activities including peer review co-ordination, copy-editing, formatting, (if relevant) pagination and online enrichment.

Policies for sharing publishing journal articles differ for subscription and gold open access articles:

Subscription Articles: If you are an author, please share a link to your article rather than the full-text. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help your users to find, access, cite, and use the best available version. Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

If you are affiliated with a library that subscribes to ScienceDirect you have additional private sharing rights for others' research accessed under that agreement. This includes use for classroom teaching and internal training at the institution (including use in course packs and courseware programs), and inclusion of the article for grant funding purposes.

Gold Open Access Articles: May be shared according to the author-selected end-user license and should contain a [CrossMark logo](#), the end user license, and a DOI link to the formal publication on ScienceDirect.

Please refer to Elsevier's [posting policy](#) for further information.

18. **For book authors** the following clauses are applicable in addition to the above: Authors are permitted to place a brief summary of their work online only. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version. **Posting to a repository:** Authors are permitted to post a summary of their chapter only in their institution's repository.

19. **Thesis/Dissertation:** If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for Proquest/UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission. Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

Elsevier Open Access Terms and Conditions

You can publish open access with Elsevier in hundreds of open access journals or in nearly 2000 established subscription journals that support open access publishing. Permitted third party re-use of these open access articles is defined by the author's choice of Creative Commons user license. See our [open access license policy](#) for more information.

Terms & Conditions applicable to all Open Access articles published with Elsevier:

Any reuse of the article must not represent the author as endorsing the adaptation of the article nor should the article be modified in such a way as to damage the author's honour or reputation. If any changes have been made, such changes must be clearly indicated.

The author(s) must be appropriately credited and we ask that you include the end user license and a DOI link to the formal publication on ScienceDirect.

If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder.

Additional Terms & Conditions applicable to each Creative Commons user license:

CC BY: The CC-BY license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article and to make commercial use of the Article (including reuse and/or resale of the Article by commercial entities), provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. The full details of the license are available at <http://creativecommons.org/licenses/by/4.0>.

CC BY NC SA: The CC BY-NC-SA license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article, provided this is not done for commercial purposes, and that the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. Further, any new works must be made available on the same conditions. The full details of the license are available at <http://creativecommons.org/licenses/by-nc-sa/4.0>.

CC BY NC ND: The CC BY-NC-ND license allows users to copy and distribute the Article, provided this is not done for commercial purposes and further does not permit distribution of the Article if it is changed or edited in any way, and provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, and that the licensor is not represented as endorsing the use made of the work. The full details of the license are available at <http://creativecommons.org/licenses/by-nc-nd/4.0>.

Any commercial reuse of Open Access articles published with a CC BY NC SA or CC BY NC ND license requires permission from Elsevier and will be subject to a fee.

Commercial reuse includes:

- Associating advertising with the full text of the Article
- Charging fees for document delivery or access
- Article aggregation
- Systematic distribution via e-mail lists or share buttons

Posting or linking by commercial companies for use by customers of those companies.

20. Other Conditions:

v1.9

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

**ELSEVIER LICENSE
TERMS AND CONDITIONS**

Apr 12, 2019

This Agreement between University of Delaware -- Roel Smits ("You") and Elsevier ("Elsevier") consists of your license details and the terms and conditions provided by Elsevier and Copyright Clearance Center.

License Number	4566570210497
License date	Apr 12, 2019
Licensed Content Publisher	Elsevier
Licensed Content Publication	Fuel Processing Technology
Licensed Content Title	Upgrading of residual oil in sub- and supercritical water: An experimental study
Licensed Content Author	Ying Liu,Fan Bai,Chun-Chun Zhu,Pei-Qing Yuan,Zhen-Min Cheng,Wei-Kang Yuan
Licensed Content Date	Feb 1, 2013
Licensed Content Volume	106
Licensed Content Issue	n/a
Licensed Content Pages	8
Start Page	281
End Page	288
Type of Use	reuse in a thesis/dissertation
Intended publisher of new work	other
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	2
Format	both print and electronic
Are you the author of this Elsevier article?	No
Will you be translating?	No
Original figure numbers	Figures 8 and 9
Title of your thesis/dissertation	Molecular-level kinetic modeling of the upgrading of residual oil in supercritical water
Expected completion date	Apr 2019
Estimated size (number of pages)	100
Requestor Location	University of Delaware 210 South College Ave NEWARK, DE 19716 United States Attn: University of Delaware
Publisher Tax ID	98-0397604
Total	0.00 USD
Terms and Conditions	

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at <http://myaccount.copyright.com>).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.

3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:

"Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit - "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."

4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.

5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com). No modifications can be made to any Lancet figures/tables and they must be reproduced in full.

6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.

7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.

8. License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.

9. Warranties: Publisher makes no representations or warranties with respect to the licensed material.

10. Indemnity: You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.

11. No Transfer of License: This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.

12. No Amendment Except in Writing: This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).

13. Objection to Contrary Terms: Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment

terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.

14. **Revocation:** Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:

15. **Translation:** This permission is granted for non-exclusive world **English** rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article.

16. **Posting licensed content on any Website:** The following terms and conditions apply as follows: Licensing material from an Elsevier journal: All content posted to the web site must maintain the copyright information line on the bottom of each image; A hyper-text must be included to the Homepage of the journal from which you are licensing at <http://www.sciencedirect.com/science/journal/xxxxx> or the Elsevier homepage for books at <http://www.elsevier.com>; Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

Licensing material from an Elsevier book: A hyper-text link must be included to the Elsevier homepage at <http://www.elsevier.com>. All content posted to the web site must maintain the copyright information line on the bottom of each image.

Posting licensed content on Electronic reserve: In addition to the above the following clauses are applicable: The web site must be password-protected and made available only to bona fide students registered on a relevant course. This permission is granted for 1 year only. You may obtain a new license for future website posting.

17. **For journal authors:** the following clauses are applicable in addition to the above:

Preprints:

A preprint is an author's own write-up of research results and analysis, it has not been peer-reviewed, nor has it had any other value added to it by a publisher (such as formatting, copyright, technical enhancement etc.).

Authors can share their preprints anywhere at any time. Preprints should not be added to or enhanced in any way in order to appear more like, or to substitute for, the final versions of articles however authors can update their preprints on arXiv or RePEc with their Accepted Author Manuscript (see below).

If accepted for publication, we encourage authors to link from the preprint to their formal publication via its DOI. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help users to find, access, cite and use the best available version. Please note that Cell Press, The Lancet and some society-owned have different preprint policies. Information on these policies is available on the journal homepage.

Accepted Author Manuscripts: An accepted author manuscript is the manuscript of an article that has been accepted for publication and which typically includes author-incorporated changes suggested during submission, peer review and editor-author communications.

Authors can share their accepted author manuscript:

- immediately

- via their non-commercial person homepage or blog
- by updating a preprint in arXiv or RePEc with the accepted manuscript
- via their research institute or institutional repository for internal institutional uses or as part of an invitation-only research collaboration work-group
- directly by providing copies to their students or to research collaborators for their personal use
- for private scholarly sharing as part of an invitation-only work group on commercial sites with which Elsevier has an agreement
- After the embargo period
 - via non-commercial hosting platforms such as their institutional repository
 - via commercial sites with which Elsevier has an agreement

In all cases accepted manuscripts should:

- link to the formal publication via its DOI
- bear a CC-BY-NC-ND license - this is easy to do
- if aggregated with other manuscripts, for example in a repository or other site, be shared in alignment with our hosting policy not be added to or enhanced in any way to appear more like, or to substitute for, the published journal article.

Published journal article (JPA): A published journal article (PJA) is the definitive final record of published research that appears or will appear in the journal and embodies all value-adding publishing activities including peer review co-ordination, copy-editing, formatting, (if relevant) pagination and online enrichment.

Policies for sharing publishing journal articles differ for subscription and gold open access articles:

Subscription Articles: If you are an author, please share a link to your article rather than the full-text. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help your users to find, access, cite, and use the best available version. Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

If you are affiliated with a library that subscribes to ScienceDirect you have additional private sharing rights for others' research accessed under that agreement. This includes use for classroom teaching and internal training at the institution (including use in course packs and courseware programs), and inclusion of the article for grant funding purposes.

Gold Open Access Articles: May be shared according to the author-selected end-user license and should contain a [CrossMark logo](#), the end user license, and a DOI link to the formal publication on ScienceDirect.

Please refer to Elsevier's [posting policy](#) for further information.

18. **For book authors** the following clauses are applicable in addition to the above: Authors are permitted to place a brief summary of their work online only. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version. **Posting to a repository:** Authors are permitted to post a summary of their chapter only in their institution's repository.

19. **Thesis/Dissertation:** If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for Proquest/UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission. Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

Elsevier Open Access Terms and Conditions

You can publish open access with Elsevier in hundreds of open access journals or in nearly 2000 established subscription journals that support open access publishing. Permitted third

party re-use of these open access articles is defined by the author's choice of Creative Commons user license. See our [open access license policy](#) for more information.

Terms & Conditions applicable to all Open Access articles published with Elsevier:

Any reuse of the article must not represent the author as endorsing the adaptation of the article nor should the article be modified in such a way as to damage the author's honour or reputation. If any changes have been made, such changes must be clearly indicated.

The author(s) must be appropriately credited and we ask that you include the end user license and a DOI link to the formal publication on ScienceDirect.

If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder.

Additional Terms & Conditions applicable to each Creative Commons user license:

CC BY: The CC-BY license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article and to make commercial use of the Article (including reuse and/or resale of the Article by commercial entities), provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. The full details of the license are available at <http://creativecommons.org/licenses/by/4.0>.

CC BY NC SA: The CC BY-NC-SA license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article, provided this is not done for commercial purposes, and that the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. Further, any new works must be made available on the same conditions. The full details of the license are available at <http://creativecommons.org/licenses/by-nc-sa/4.0>.

CC BY NC ND: The CC BY-NC-ND license allows users to copy and distribute the Article, provided this is not done for commercial purposes and further does not permit distribution of the Article if it is changed or edited in any way, and provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, and that the licensor is not represented as endorsing the use made of the work. The full details of the license are available at <http://creativecommons.org/licenses/by-nc-nd/4.0>.

Any commercial reuse of Open Access articles published with a CC BY NC SA or CC BY NC ND license requires permission from Elsevier and will be subject to a fee.

Commercial reuse includes:

- Associating advertising with the full text of the Article
- Charging fees for document delivery or access
- Article aggregation
- Systematic distribution via e-mail lists or share buttons

Posting or linking by commercial companies for use by customers of those companies.

20. Other Conditions:

v1.9

Questions? customer care@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

ELSEVIER LICENSE TERMS AND CONDITIONS

Apr 12, 2019

This Agreement between University of Delaware -- Roel Smits ("You") and Elsevier ("Elsevier") consists of your license details and the terms and conditions provided by Elsevier and Copyright Clearance Center.

License Number	4566570897105
License date	Apr 12, 2019
Licensed Content Publisher	Elsevier
Licensed Content Publication	Fuel Processing Technology
Licensed Content Title	Computer aided kinetic modeling with KMT and KME
Licensed Content Author	Wei Wei,Craig A. Bennett,Ryuzo Tanaka,Gang Hou,Michael T. Klein,Michael T. Klein
Licensed Content Date	Apr 1, 2008
Licensed Content Volume	89
Licensed Content Issue	4
Licensed Content Pages	14
Start Page	350
End Page	363
Type of Use	reuse in a thesis/dissertation
Intended publisher of new work	other
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	6
Format	both print and electronic
Are you the author of this Elsevier article?	No
Will you be translating?	No
Original figure numbers	Figures 7, 10, 11, 12, 13 and 14
Title of your thesis/dissertation	Molecular-level kinetic modeling of the upgrading of residual oil in supercritical water
Expected completion date	Apr 2019
Estimated size (number of pages)	100
Requestor Location	University of Delaware 210 South College Ave NEWARK, DE 19716 United States Attn: University of Delaware
Publisher Tax ID	98-0397604
Total	0.00 USD
Terms and Conditions	

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at <http://myaccount.copyright.com>).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.

3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:

"Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit - "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."

4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.

5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com). No modifications can be made to any Lancet figures/tables and they must be reproduced in full.

6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.

7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.

8. License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.

9. Warranties: Publisher makes no representations or warranties with respect to the licensed material.

10. Indemnity: You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.

11. No Transfer of License: This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.

12. No Amendment Except in Writing: This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).

13. Objection to Contrary Terms: Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment

terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.

14. **Revocation:** Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:

15. **Translation:** This permission is granted for non-exclusive world **English** rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article.

16. **Posting licensed content on any Website:** The following terms and conditions apply as follows: Licensing material from an Elsevier journal: All content posted to the web site must maintain the copyright information line on the bottom of each image; A hyper-text must be included to the Homepage of the journal from which you are licensing at <http://www.sciencedirect.com/science/journal/xxxxx> or the Elsevier homepage for books at <http://www.elsevier.com>; Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

Licensing material from an Elsevier book: A hyper-text link must be included to the Elsevier homepage at <http://www.elsevier.com>. All content posted to the web site must maintain the copyright information line on the bottom of each image.

Posting licensed content on Electronic reserve: In addition to the above the following clauses are applicable: The web site must be password-protected and made available only to bona fide students registered on a relevant course. This permission is granted for 1 year only. You may obtain a new license for future website posting.

17. **For journal authors:** the following clauses are applicable in addition to the above:

Preprints:

A preprint is an author's own write-up of research results and analysis, it has not been peer-reviewed, nor has it had any other value added to it by a publisher (such as formatting, copyright, technical enhancement etc.).

Authors can share their preprints anywhere at any time. Preprints should not be added to or enhanced in any way in order to appear more like, or to substitute for, the final versions of articles however authors can update their preprints on arXiv or RePEc with their Accepted Author Manuscript (see below).

If accepted for publication, we encourage authors to link from the preprint to their formal publication via its DOI. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help users to find, access, cite and use the best available version. Please note that Cell Press, The Lancet and some society-owned have different preprint policies. Information on these policies is available on the journal homepage.

Accepted Author Manuscripts: An accepted author manuscript is the manuscript of an article that has been accepted for publication and which typically includes author-incorporated changes suggested during submission, peer review and editor-author communications.

Authors can share their accepted author manuscript:

- immediately

- via their non-commercial person homepage or blog
- by updating a preprint in arXiv or RePEc with the accepted manuscript
- via their research institute or institutional repository for internal institutional uses or as part of an invitation-only research collaboration work-group
- directly by providing copies to their students or to research collaborators for their personal use
- for private scholarly sharing as part of an invitation-only work group on commercial sites with which Elsevier has an agreement
- After the embargo period
 - via non-commercial hosting platforms such as their institutional repository
 - via commercial sites with which Elsevier has an agreement

In all cases accepted manuscripts should:

- link to the formal publication via its DOI
- bear a CC-BY-NC-ND license - this is easy to do
- if aggregated with other manuscripts, for example in a repository or other site, be shared in alignment with our hosting policy not be added to or enhanced in any way to appear more like, or to substitute for, the published journal article.

Published journal article (JPA): A published journal article (PJA) is the definitive final record of published research that appears or will appear in the journal and embodies all value-adding publishing activities including peer review co-ordination, copy-editing, formatting, (if relevant) pagination and online enrichment.

Policies for sharing publishing journal articles differ for subscription and gold open access articles:

Subscription Articles: If you are an author, please share a link to your article rather than the full-text. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help your users to find, access, cite, and use the best available version. Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

If you are affiliated with a library that subscribes to ScienceDirect you have additional private sharing rights for others' research accessed under that agreement. This includes use for classroom teaching and internal training at the institution (including use in course packs and courseware programs), and inclusion of the article for grant funding purposes.

Gold Open Access Articles: May be shared according to the author-selected end-user license and should contain a [CrossMark logo](#), the end user license, and a DOI link to the formal publication on ScienceDirect.

Please refer to Elsevier's [posting policy](#) for further information.

18. **For book authors** the following clauses are applicable in addition to the above: Authors are permitted to place a brief summary of their work online only. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version. **Posting to a repository:** Authors are permitted to post a summary of their chapter only in their institution's repository.

19. **Thesis/Dissertation:** If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for Proquest/UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission. Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

Elsevier Open Access Terms and Conditions

You can publish open access with Elsevier in hundreds of open access journals or in nearly 2000 established subscription journals that support open access publishing. Permitted third

party re-use of these open access articles is defined by the author's choice of Creative Commons user license. See our [open access license policy](#) for more information.

Terms & Conditions applicable to all Open Access articles published with Elsevier:

Any reuse of the article must not represent the author as endorsing the adaptation of the article nor should the article be modified in such a way as to damage the author's honour or reputation. If any changes have been made, such changes must be clearly indicated.

The author(s) must be appropriately credited and we ask that you include the end user license and a DOI link to the formal publication on ScienceDirect.

If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder.

Additional Terms & Conditions applicable to each Creative Commons user license:

CC BY: The CC-BY license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article and to make commercial use of the Article (including reuse and/or resale of the Article by commercial entities), provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. The full details of the license are available at <http://creativecommons.org/licenses/by/4.0>.

CC BY NC SA: The CC BY-NC-SA license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article, provided this is not done for commercial purposes, and that the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. Further, any new works must be made available on the same conditions. The full details of the license are available at <http://creativecommons.org/licenses/by-nc-sa/4.0>.

CC BY NC ND: The CC BY-NC-ND license allows users to copy and distribute the Article, provided this is not done for commercial purposes and further does not permit distribution of the Article if it is changed or edited in any way, and provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, and that the licensor is not represented as endorsing the use made of the work. The full details of the license are available at <http://creativecommons.org/licenses/by-nc-nd/4.0>.

Any commercial reuse of Open Access articles published with a CC BY NC SA or CC BY NC ND license requires permission from Elsevier and will be subject to a fee.

Commercial reuse includes:

- Associating advertising with the full text of the Article
- Charging fees for document delivery or access
- Article aggregation
- Systematic distribution via e-mail lists or share buttons

Posting or linking by commercial companies for use by customers of those companies.

20. Other Conditions:

v1.9

Questions? customer care@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

AIP PUBLISHING LICENSE TERMS AND CONDITIONS

Apr 12, 2019

This Agreement between University of Delaware -- Roel Smits ("You") and AIP Publishing ("AIP Publishing") consists of your license details and the terms and conditions provided by AIP Publishing and Copyright Clearance Center.

License Number	4566580041641
License date	Apr 12, 2019
Licensed Content Publisher	AIP Publishing
Licensed Content Publication	Journal of Physical & Chemical Reference Data
Licensed Content Title	Representative Equations for the Thermal Conductivity of Water Substance
Licensed Content Author	J. V. Sengers, J. T. R. Watson, R. S. Basu, et al
Licensed Content Date	Jul 1, 1984
Licensed Content Volume	13
Licensed Content Issue	3
Type of Use	Thesis/Dissertation
Requestor type	Student
Format	Print and electronic
Portion	Figure/Table
Number of figures/tables	2
Title of your thesis / dissertation	Molecular-level kinetic modeling of the upgrading of residual oil in supercritical water
Expected completion date	Apr 2019
Estimated size (number of pages)	100
Requestor Location	University of Delaware 210 South College Ave NEWARK, DE 19716 United States Attn: University of Delaware
Total	0.00 USD

Terms and Conditions

AIP Publishing -- Terms and Conditions: Permissions Uses

AIP Publishing hereby grants to you the non-exclusive right and license to use and/or distribute the Material according to the use specified in your order, on a one-time basis, for the specified term, with a maximum distribution equal to the number that you have ordered. Any links or other content accompanying the Material are not the subject of this license.

1. You agree to include the following copyright and permission notice with the reproduction of the Material: "Reprinted from [FULL CITATION], with the permission of AIP Publishing." For an article, the credit line and permission notice must be printed on the first page of the article or book chapter. For photographs, covers, or tables, the notice may appear with the Material, in a footnote, or in the reference list.
2. If you have licensed reuse of a figure, photograph, cover, or table, it is your responsibility to ensure that the material is original to AIP Publishing and does not contain the copyright of another entity, and that the copyright notice of the figure, photograph, cover, or table does not indicate that it was reprinted by AIP Publishing, with permission, from another

source. Under no circumstances does AIP Publishing purport or intend to grant permission to reuse material to which it does not hold appropriate rights.

You may not alter or modify the Material in any manner. You may translate the Material into another language only if you have licensed translation rights. You may not use the Material for promotional purposes.

3. The foregoing license shall not take effect unless and until AIP Publishing or its agent, Copyright Clearance Center, receives the Payment in accordance with Copyright Clearance Center Billing and Payment Terms and Conditions, which are incorporated herein by reference.
4. AIP Publishing or Copyright Clearance Center may, within two business days of granting this license, revoke the license for any reason whatsoever, with a full refund payable to you. Should you violate the terms of this license at any time, AIP Publishing, or Copyright Clearance Center may revoke the license with no refund to you. Notice of such revocation will be made using the contact information provided by you. Failure to receive such notice will not nullify the revocation.
5. AIP Publishing makes no representations or warranties with respect to the Material. You agree to indemnify and hold harmless AIP Publishing, and their officers, directors, employees or agents from and against any and all claims arising out of your use of the Material other than as specifically authorized herein.
6. The permission granted herein is personal to you and is not transferable or assignable without the prior written permission of AIP Publishing. This license may not be amended except in a writing signed by the party to be charged.
7. If purchase orders, acknowledgments or check endorsements are issued on any forms containing terms and conditions which are inconsistent with these provisions, such inconsistent terms and conditions shall be of no force and effect. This document, including the CCC Billing and Payment Terms and Conditions, shall be the entire agreement between the parties relating to the subject matter hereof.

This Agreement shall be governed by and construed in accordance with the laws of the State of New York. Both parties hereby submit to the jurisdiction of the courts of New York County for purposes of resolving any disputes that may arise hereunder.

V1.2

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

AIP PUBLISHING LICENSE TERMS AND CONDITIONS

Apr 12, 2019

This Agreement between University of Delaware -- Roel Smits ("You") and AIP Publishing ("AIP Publishing") consists of your license details and the terms and conditions provided by AIP Publishing and Copyright Clearance Center.

License Number	4566580351746
License date	Apr 12, 2019
Licensed Content Publisher	AIP Publishing
Licensed Content Publication	Journal of Physical & Chemical Reference Data
Licensed Content Title	A Formulation for the Static Permittivity of Water and Steam at Temperatures from 238 K to 873 K at Pressures up to 1200 MPa, Including Derivatives and Debye-Hückel Coefficients
Licensed Content Author	D. P. Fernández, A. R. H. Goodwin, Eric W. Lemmon, et al
Licensed Content Date	Jul 1, 1997
Licensed Content Volume	26
Licensed Content Issue	4
Type of Use	Thesis/Dissertation
Requestor type	Student
Format	Print and electronic
Portion	Figure/Table
Number of figures/tables	1
Title of your thesis / dissertation	Molecular-level kinetic modeling of the upgrading of residual oil in supercritical water
Expected completion date	Apr 2019
Estimated size (number of pages)	100
Requestor Location	University of Delaware 210 South College Ave NEWARK, DE 19716 United States Attn: University of Delaware
Total	0.00 USD

Terms and Conditions

AIP Publishing -- Terms and Conditions: Permissions Uses

AIP Publishing hereby grants to you the non-exclusive right and license to use and/or distribute the Material according to the use specified in your order, on a one-time basis, for the specified term, with a maximum distribution equal to the number that you have ordered. Any links or other content accompanying the Material are not the subject of this license.

1. You agree to include the following copyright and permission notice with the reproduction of the Material: "Reprinted from [FULL CITATION], with the permission of AIP Publishing." For an article, the credit line and permission notice must be printed on the first page of the article or book chapter. For photographs, covers, or tables, the notice may appear with the Material, in a footnote, or in the reference list.
2. If you have licensed reuse of a figure, photograph, cover, or table, it is your responsibility to ensure that the material is original to AIP Publishing and does not contain the copyright of another entity, and that the copyright notice of the figure, photograph, cover, or table

does not indicate that it was reprinted by AIP Publishing, with permission, from another source. Under no circumstances does AIP Publishing purport or intend to grant permission to reuse material to which it does not hold appropriate rights.

You may not alter or modify the Material in any manner. You may translate the Material into another language only if you have licensed translation rights. You may not use the Material for promotional purposes.

3. The foregoing license shall not take effect unless and until AIP Publishing or its agent, Copyright Clearance Center, receives the Payment in accordance with Copyright Clearance Center Billing and Payment Terms and Conditions, which are incorporated herein by reference.
4. AIP Publishing or Copyright Clearance Center may, within two business days of granting this license, revoke the license for any reason whatsoever, with a full refund payable to you. Should you violate the terms of this license at any time, AIP Publishing, or Copyright Clearance Center may revoke the license with no refund to you. Notice of such revocation will be made using the contact information provided by you. Failure to receive such notice will not nullify the revocation.
5. AIP Publishing makes no representations or warranties with respect to the Material. You agree to indemnify and hold harmless AIP Publishing, and their officers, directors, employees or agents from and against any and all claims arising out of your use of the Material other than as specifically authorized herein.
6. The permission granted herein is personal to you and is not transferable or assignable without the prior written permission of AIP Publishing. This license may not be amended except in a writing signed by the party to be charged.
7. If purchase orders, acknowledgments or check endorsements are issued on any forms containing terms and conditions which are inconsistent with these provisions, such inconsistent terms and conditions shall be of no force and effect. This document, including the CCC Billing and Payment Terms and Conditions, shall be the entire agreement between the parties relating to the subject matter hereof.

This Agreement shall be governed by and construed in accordance with the laws of the State of New York. Both parties hereby submit to the jurisdiction of the courts of New York County for purposes of resolving any disputes that may arise hereunder.

V1.2

Questions? customer care@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.
