

**MOLECULAR-LEVEL KINETIC MODELING OF CARBON
FEEDSTOCKS UPGRADING THROUGH HYDROTREATMENT ON
BIFUNCTIONAL CATALYSTS**

by

Nicholas Evenepoel

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NOMENCLATURE

a_{ad}, b_{ad}, c_{ad}	Site-dependent constants relating the structural elements to adsorption constants
A_j	Arrhenius constant for reaction family j
E	Activation energy [$kcal/mol$]
F_j	Molar flowrate of species j [mol/s]
ΔG_{rxn}	Gibbs free energy of reaction [kJ/mol]
ΔH_i	enthalpy of reaction for reaction i [kJ/mol]
k_{sr}	Surface reaction rate coefficient
K_{ad}	Adsorption equilibrium constant
K_{eq}	Overall reaction equilibrium constant
m	Exponent of adsorption group
n	Reaction rank
N	Entrainment speed of the fluid [m/s]
N_C	Number of carbon atoms
N_O	Number of oxygen atoms
P_i	Partial pressure of species i [MPa]
r_i	Reaction rate of species i per volume bed [$mol/(s \cdot m^3)$]
R	Ideal gas constant [$kcal/(mol \cdot K)$]
T	Reaction temperature [K]
V	Packed bed volume [m^3]
X	Reactant conversion
y_{cat}	Catalyst site distribution [$kg \text{ cat}/m^3 \text{ bed}$]

y_{obs}	Experimental property value from experiment
y_{pred}	Experimental property value from simulation
Y	Molar yield
α	Bell-Evans-Polanyi linear free energy relationship factor
β	Hydrogen pressure dependence of acid or metal catalyst site
μ	Dynamic viscosity [$N \cdot s/m^2$]
ν_{ij}	Stoichiometric coefficient of species j in reaction i
ρ_B	Packed bed density [kg/m^3]
σ	Normal load [N/m]
σ_y	Experimental property weight

ABSTRACT

The primary objective of this thesis is to develop molecular-level kinetic models for hydrotreating processes of conventional and non-conventional hydrocarbon feedstocks on bifunctional catalysts. A comprehensive comparison of the kinetics of the most important industrial hydroprocessing operations is obtained by developing a model for the green diesel and petroleum-derived lube base oil production. An overview is given of the different steps required for constructing the models. These are developed using the in-house Kinetic Modeling Toolbox software by reconstructing the molecular feed composition, building a reaction network and using an optimization algorithm to develop the reaction kinetics. Experimental data is used throughout this process to optimize and evaluate the obtained kinetics. Both hydrotreating processes are modeled assuming the Langmuir-Hinshelwood-Hougen-Watson kinetics formalism and using the Bell-Evans-Polanyi linear free energy relationship to reduce the number of tunable kinetic parameters.

To model the hydroprocessing for green diesel production, a fatty acid methyl ester is used as model compound to represent whole vegetable oil feeds. Experimental data of a coconut oil hydroprocessing operation is subsequently used to verify the accuracy of the obtained kinetics. This model consisted of 150 molecular species and 309 reactions, grouped into 8 reaction families. The hydroprocessing of a pretreated deasphalted oil is more complex and represented by a network containing 1 690 species and 24 754 individual reactions grouped in 11 reaction families. The model results for both processes show good agreement with the experimental results for a range of process conditions. While both models comprise the same reaction types, a significant difference in kinetics is witnessed based on operation conditions, feed properties and catalyst type. The biomass hydrotreatment is performed at mild conditions with a

mildly acidic catalyst resulting in fast saturation reactions and removal of heteroatoms. A quantitative relation between the Ni and Mo content of the Ni-Mo/Al₂O₃ catalysts and the reaction rate constants for the hydrotreatment is developed. On the other hand, the heavier feed for the lube base oil production undergoes primarily hydrocracking and -isomerization reactions favored by the high hydrogen pressure and strong acidic catalyst.

The molecular-level kinetic modeling approach appeared feasible to model all hydrotreating processes and has great potential modeling the co-treatment of a petroleum-derived and biomass feedstock and enabling the accurate prediction of important product properties.

Chapter 1

INTRODUCTION AND BACKGROUND

1.1 Importance of Molecular-level Kinetic Modeling

In today’s (petro)chemical industry, molecular-level kinetic modeling is motivated by meeting governmental, environmental, and efficiency optimization requirements. Especially for complex chemistries, there is a need to model product properties as function of chemical process conditions. Despite the corresponding high computational load and long solution time, the molecular composition is an ideal starting point to predict mixture properties. While lumped kinetic models are still common practice, molecular-level kinetic models have large potential due to the ability to link atomic and process levels of chemistry. Reactivity information from empirical or semi-empirical quantum mechanical calculations are used as input to get global rates and selectivities and finally perform a full process simulation. In the lube oil and green diesel case, an important property which depends on both molecule type and even specific isomer is the cloud/pour point [1]. Figure 1.1 shows the variation of fusion temperature of isoparaffins with the same carbon number, but different branching positions. The pour point varies significantly, with differences of more than 30 kelvin. This proves that it is necessary to explicitly model these isomers to get accurate property estimations.

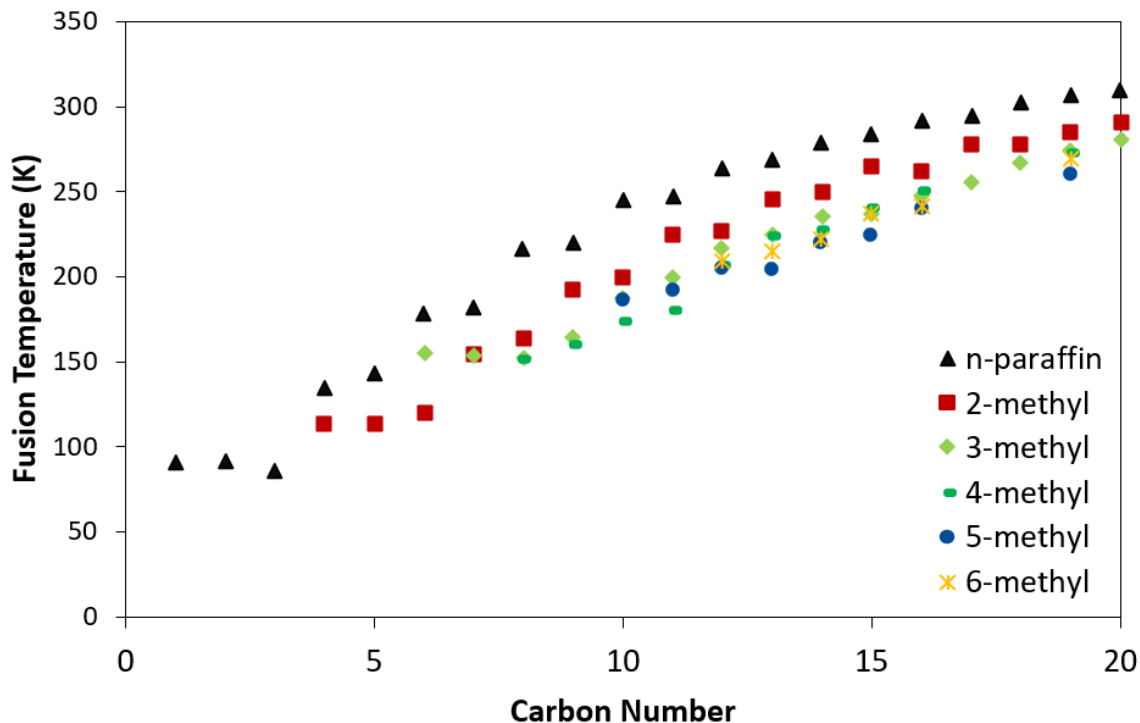


Figure 1.1: Fusion temperatures of n-paraffins and 1-branch isoparaffins [2].

1.2 Hydrotreating Processes

Hydroprocessing is a crucial catalytic process as part of oil refining [3]. It is used for challenging applications such as processing heavier petroleum feeds, producing high-performance lubricants and using biomass as a sustainable fuel source. This refinery process can be used with various product properties in mind as several classes of reactions occur simultaneously. Functionalities of hydroprocessing include cracking, saturation, purification and isomerization reactions [4]. Hydroconversion processes are carried out on bifunctional catalysts with acid and metal active sites. Based on the reaction conditions and catalyst choice, hydroconversion processes are classified in two groups, hydrocracking and hydrorefining.

Hydrocracking focuses on converting heavy oil fractions into lighter, more valuable products via destructive hydrogenation. An example is the production of diesel

and jet fuel from gas oil [5]. It involves mainly cracking and isomerization reactions. The increase in branching by isomerization is also beneficial for the cloud point of green diesel products as will be discussed in section 1.3. Hydrocracking and -isomerization reactions take place on the acid active sites of the catalyst and are favored by a high reaction temperature and hydrogen pressure. These severe reaction conditions are necessary to minimize the condensative chain polymerization reactions that lead to coke formation [6].

On the other hand, in hydrorefining operations, the emphasis lies on the removal of contaminants, such as sulfur and nitrogen, from distilled crude oil fractions and intermediate process streams. This is important as products of petroleum refining must meet tight specifications and as the process is used for the production of green diesel from oxygen-rich biomass. During the hydrotreatment also saturation reactions occur to convert olefins into paraffins and aromatics into naphthenes. This is desired to improve product properties such as the viscosity index of lube oils [7]. The non-destructive hydrogenation is achieved by using a mild temperature and hydrogen pressure so that only the more unstable compounds are converted to more stable compounds [6]. The saturation and purification reactions occur on the metal sites of the catalyst.

1.3 Green Diesel

With the declining availability of petroleum resources and the increased demand for fuels by emerging economies, there is a big interest in finding sustainable alternatives for fossil fuels. The conversion of biomass into valuable fuel products and chemicals has potential to provide such an alternative [8]. Vegetable oils consist mainly of triglycerides and can be directly used as engine fuels. However, the high viscosity and cloud point of plant oils makes this technically unfeasible. Problems that can occur are poor fuel atomization and incomplete combustion in a diesel engine, high engine wear and a significant increase in particulate and CO emissions [9], [10], [11].

Green diesel is an isoparaffin-rich fuel produced by hydroprocessing vegetable oil feedstocks. It has a smaller ecological footprint and has a higher energy-density compared to petroleum-derived diesel fuels [12]. Unlike biofuels produced by transesterifications with methanol, it is fully compatible with petroleum-derived diesel fuels [11]. Its excellent cold flow properties, high cetane number, high oxidation stability and low impurity content makes it a high quality fuel compatible with current diesel engines. Green diesel is primarily composed of paraffins with a carbon number in the range of 15 to 20. As green diesel doesn't contain any sulfur or nitrogen impurities, no harmful NO_x or SO_x compounds are emitted during its combustion.

Two key properties of green diesel are the cetane number and cloud point. The cetane number is a measure for the ignition quality of a fuel. The cloud point is the temperature at which cloudiness in a fluid appears due to wax forming. It is an important property for the cold flow properties of the fuel, especially in colder climates. Without hydroisomerization, green diesel has a very high cetane number due to the high normal paraffin content [1]. On the other hand, more branching of the paraffins is beneficial for a low cloud point. By hydroisomerizing some of the normal paraffins into isoparaffins, an optimal trade-off can be found between a high cetane number and low cloud point [13].

In practice, green diesel is still mostly used as an additive to petroleum-derived diesel to improve the cetane number. However, once it becomes economically feasible, it is expected it will be used as standalone fuel as well [12]. The biomass feed for the green diesel production can be from algal, plant or animal sources. Figure 1.2 shows a simplified process flow diagram of the UOP-Ecofining process for green diesel production [14]. In the first reactor, hydrodeoxygenation of the triglycerides and fatty acids happens. This is a hydrotreatment process at relatively low hydrogen pressure. The second hydroisomerization reactor focuses on increasing the amount of branched paraffins in the product and operates at more severe reaction conditions.

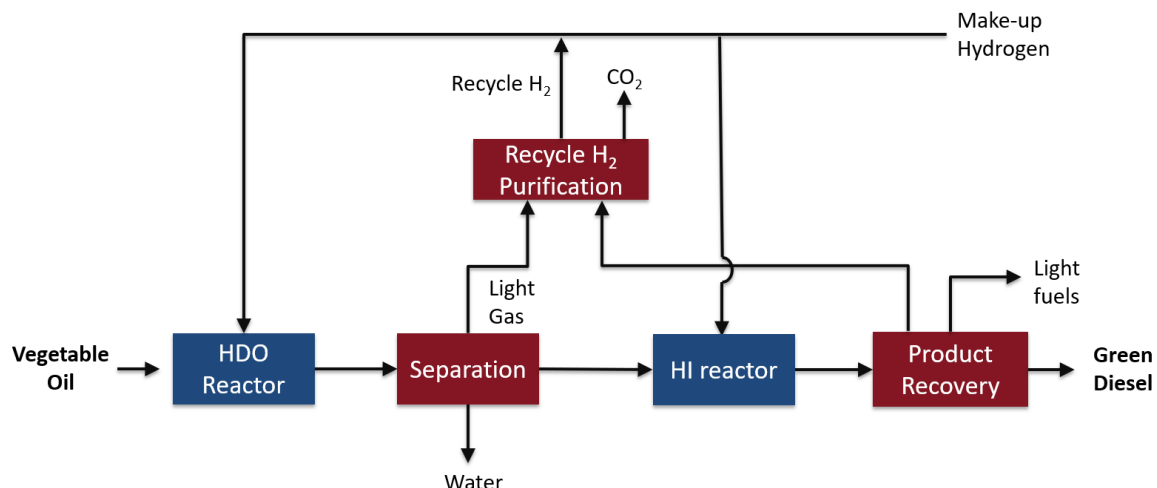


Figure 1.2: Process flow diagram of the green diesel production based on the UOP-Ecofining process [14].

Several experimental studies have been performed studying the hydroconversion of triglycerides and its derivatives such as fatty acid and fatty acids methyl esters for green diesel production, but very few attempts have been made to model triglyceride hydroprocessing. Studies have been published modeling the process via thermodynamic equilibrium [15] or component lumps [16], [17], but these failed to fully characterize and predict carbon-number based experimental data.

1.4 Lubricant Oil

Lubricants play an important role in several industrial applications. Common applications are automotive engine oils, gear oils, hydraulic fluids and marine oils. Lubricant oils are used to reduce friction between moving surfaces in contact. Reducing friction is necessary to reduce heat generation, surface fatigue, operation noise and vibrations [18], [19]. Additionally, lubricant oils also perform several other functions such as transmission of forces, transfer of heat, corrosion prevention, dispersion of use-generated contaminants etc. In order to fulfill all these functions, lubricants have some specific chemical and physical properties. The most important characteristics are the

pour point, viscosity, viscosity index, and oxidative and thermal stability [7]. It is crucial that a lubricant keeps his functionality over a broad range of temperatures. A low pour point is important to avoid the lubricant losing its flow characteristics at low temperatures, e.g. when starting up a car engine at winter conditions. The viscosity index (VI) is a measure for the sensitivity of the viscosity to changing temperature. High quality lubricants have a high viscosity index which means a small viscosity change with temperature. The viscosity itself should be sufficiently high and is essential as it greatly influences the reduction of friction between the parts. Figure 1.3 shows how the dynamic viscosity μ has a big influence on the friction coefficient [20].

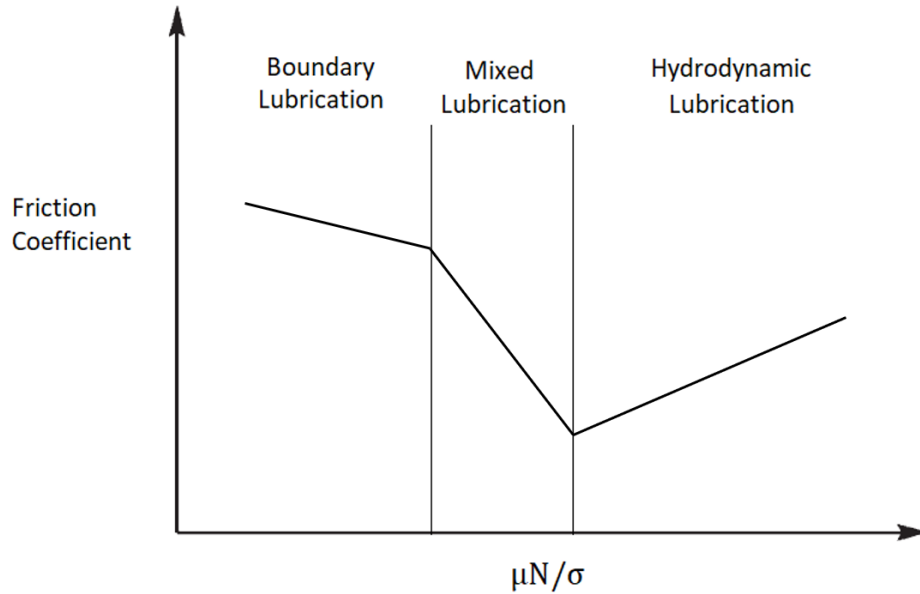


Figure 1.3: Dependence of friction coefficient on the Hersey number [20].

Lubricants consist of a base oil and a small percentage of additives to further improve the characteristics or provide additional functionalities. The lube base oils can be classified in three classes based on their sources: mineral oils, synthetic oils and plant oils. Mineral oils are lube base oils derived from crude oil feedstocks. They typically consist of a wide selection of C_{20} - C_{50} hydrocarbon species including normal paraffins, isoparaffins, aromatics, naphthenes and olefins supplemented with heteroatoms sulfur

and nitrogen. In the past, only specific crude fractions from Pennsylvania crudes were considered for the manufacture of lubricant base oils due to required viscosity and viscosity index for automobile engines [18]. Nowadays, the use of less desirable crude oils and crude oil fractions is common due to the development of hydrogenation processes to upgrade these heavier fractions into suitable base oils. Lube base oils are typically produced through upgrading processes of deasphalted oil (DAO) or vacuum gas oil (VGO) which have relatively low value. These crude oil fractions have been recuperated from a distillation column and are deasphalted using an extractive precipitation process to remove undesirable asphalts and resins [18].

Different hydrogenation processes are used to improve various properties of the base oils. Figure 1.4 shows a simplified process flow diagram of a lubricants base oil hydrocracking unit [21]. The goal of this unit is to improve the pour point and viscosity index. Additionally, the lube distillate is often send through a hydrorefining unit to removes heteroatomic contaminants. This improves the thermal and oxidative stability of the product. An intermediate catalytic dewaxing step is used to remove wax from the oils [22], [23].

Table 1.1 shows the influence of hydrocarbon type on the most important lubricant properties. It is clear that naphthenes and aromatics degrade the quality of the lube oil due to their low viscosity index. The severe hydrocracking process is used to convert these compounds into more favorable isoparaffins and fewer-ring naphthenes. Although normal paraffins have a positive impact on the viscosity index, the very high pour point is problematic. Hydroisomerization reactions in the hydrocracking unit will increase the branching of the product. Also the catalytic dewaxing helps in removing normal paraffins from the product. All these processes are crucial as it makes mineral oils the most cheap, stable and readily available type of base oil.

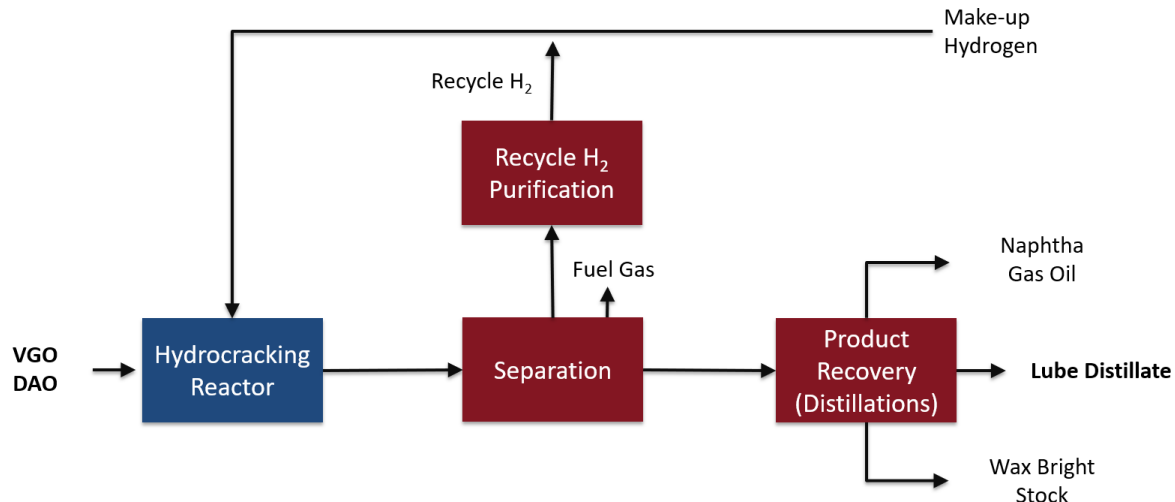


Figure 1.4: Simplified lube base oil hydroprocessing flow diagram [21].

Table 1.1: Influence of hydrocarbon structure type on pour point and viscosity index of lube base oils [7].

Hydrocarbon type	Effect on pour point (pp)	Effect on viscosity index (VI)
n-Paraffin	Very high pp	Very high VI
i-Paraffin	Medium to low pp	High VI
Monoring Naphthene	Low pp	high to medium VI
Multiring Naphthene	Very low pp	Very low VI
Monoring Aromatic	Low pp	Medium to low VI
Multiring Aromatic	Very low pp	Very low VI

The two other lube base oils types are synthetic oils and plant oils. Synthetic oils consist of petroleum-derived synthetic hydrocarbons such as polyalphaolefins and alkylbenzenes [24]. They are used for applications where performance requirements can't be met by mineral oils. However, as they are more expensive and incompatible

with other lubricants and standard additives, they are restricted in use. The triglycerides esters in plant oils can be used as biolubricants. Direct usage of these oils as lubricant is rarely done however. Plant oils have poor oxidative and thermal stability, which is due to the presence of acyl groups. Additional chemical modifications are necessary before usage. Biolubricants represent only a small, but growing percentage of the total lubricant sales [19], [25].

The API (American Petroleum Institute) classified lube base oils in different base stock categories based on their source, weight percentage of sulfur and saturates, the viscosity index, and processing method. Table 1.2 shows the five categories. A high sulfur and low saturates concentration have a negative impact on the oxidative stability of the lubricants.

Table 1.2: Lube base oil categories given by the API [26].

Group	Sulfur wt %	Saturates wt %	VI	Manufacturing Method
I	>0.03	<90	80-119	Solvent Refined
II	<0.03	>90	80-119	Hydroprocessed
III	>0.03	>90	>120	Severely Hydroprocessed
IV	Polyalphaolefins			
V	All Others			

While some kinetic models have been developed for the hydrocracking of vacuum gas oil feeds [27], [28], the molecular-level kinetic modeling of hydrocracking processes designed for the lube base oil production is rather novel.

1.5 Thesis Objectives and Outline

As explained in section 1.2, hydroprocessing is a common treatment in industry to improve properties of valuable chemicals and fuels. Besides the desired functionality, also the hydrocarbon feedstock may vary, ranging from petroleum-derived feeds to biomass from algal, plant, or animal sources. To reduce the fossil fuel consumption,

there is even a growing interest in hydrotreating vegetable oil and petroleum-derived products together in conventional oil refineries for the production of diesel [8].

In this thesis, the Kinetic Modelers Toolbox, an in-house software of the Kleins research group, is used and customized to build kinetic models for the hydroprocessing of conventional and unconventional feedstocks on bifunctional catalysts. The main objective of this study, is to show how molecular-level kinetic modeling can be used as an industrial tool in the control and optimization of a broad range of hydrotreating processes and related product properties. Based on the experimental data found in four scientific papers [29], [30], [31], [32], two different, but interrelated, kinetic models are developed for hydrotreating processes promoted by bifunctional catalysts. The two processes are the hydroconversion of a pure methyl laurate feed for green diesel applications and the hydroprocessing of the gas oil fraction of a petroleum-derived deasphalted vacuum residue to a high-quality lube base oil. Methyl laurate serves as a model compound for whole vegetable oil feeds and the obtained kinetics are tested by applying them on the hydrotreating process of coconut oil. The goal of this thesis is to optimize self-developed molecular reaction networks based on the available experimental data and investigate the influence of feed, reactor conditions and catalyst on the reaction kinetics and dominating reaction families. This work is a comprehensive overview of the modeling of the universal kinetics of hydrotreatment of carbon feedstocks on bifunctional catalysts. By providing accurate models for the hydrotreatment of biomass and petroleum-derived products separately, this may form the basis of modeling a blend of both in future studies.

Chapter 2 of this manuscript discusses the in-house software used to build the process kinetics models, the Kinetic Modelers Toolbox (KMT). An overview is given of the four submodels included for building a reaction network, modeling the feed conditions and tuning the reaction kinetics. A kinetic model is a set of mathematical equations that describes the dependence of the rate of chemical reactions on process variables such as temperature, pressure and feed composition. This requires defining material balances and rate laws based on the kinetics of bifunctional catalysis. The

model equations and kinetics are explained in chapter 3. The development of the kinetic model for the hydrotreating processes consists of different steps. First, the reaction networks are generated based on experimental data and literature. Secondly, the experimental data of the feed properties has to be converted into mole fractions of the individual molecules. Finally, the network kinetics are optimized by matching experimentally available reaction data and product properties. The results of these three modeling steps are discussed in chapter 4.¹ This section also includes a comparison of the kinetics of the two hydrotreating processes. Finally, the main conclusions and ideas for future work are summarized in chapters 5 and 6.

¹ In chapter 4, section 4.1.1 and section 4.3.1 are partially based on a paper co-authored by the author of this thesis: P. Agarwal, N. Evenepoel, S. S Al-Khattaf, and M. T. Klein. Molecular-Level Kinetic Modeling of Methyl Laurate: The Intrinsic Kinetics of Triglyceride Hydroprocessing. *Energy & Fuels*.

Chapter 2

KINETIC MODELER’S TOOLBOX

The Kinetic Modeler’s Toolbox (KMT) is an in-house software of the Klein Research Group developed for molecular-level kinetic modeling of complex reaction systems. KMT combines three interrelated models. Firstly, the Interactive Network Generator (INGen) is used to create a molecular reaction network and to include the required molecule species in the model. Secondly, the Initial Condition Generator (ICG) models the initial molecular flow rates of the feedstock based on experimentally measured feed properties and the molecule species included in the ICG submodel. Thirdly, the Kinetic Model Editor (KME) is used to construct the kinetic rate laws. It relies for this on the reaction network developed in INGen and the molecular composition from ICG. Local and global optimization methods are used to optimize the reaction kinetics based on experimental data. Finally, a fourth modeling tool, the Property Generator (PropGen), is used to obtain molecule and bulk properties based on thermodynamics and molecular composition of feed and product. Figure 2.1 gives an overview of the structure of the Kinetic Modeler’s Toolbox. The toolbox can be used for molecule-based modeling to do once-through calculations, tuning/parameter estimations and goal seeking scenarios [33].

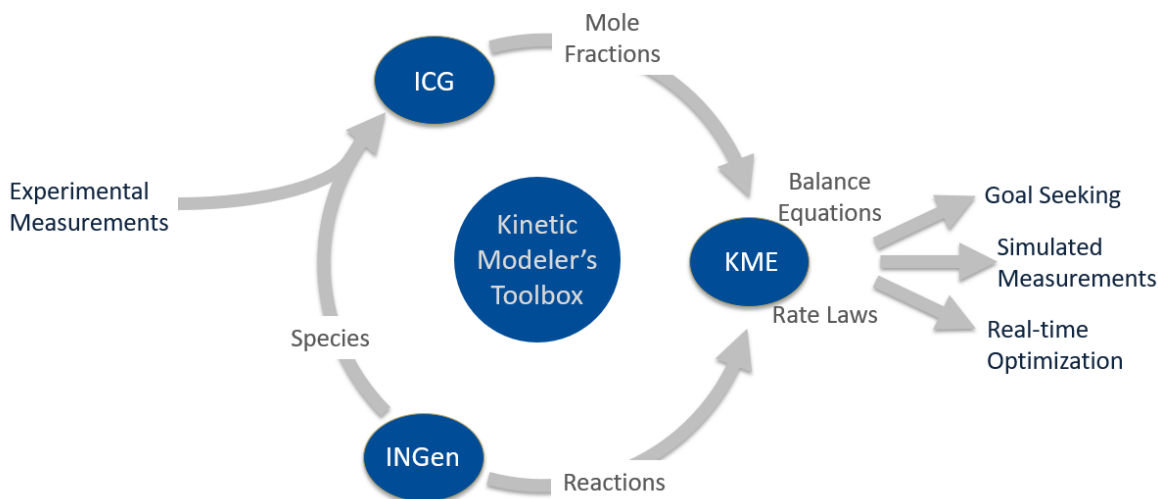


Figure 2.1: Overview of the Kinetic Modeler's Toolbox.

2.1 Interactive Network Generator

Molecular-level kinetic models for the complex chemistries in the petroleum refinery industry can comprise tens of thousand of measurable molecules and reactions. Therefore, a tool that can construct these models automatically is needed. The Interactive Network generator (INGen) tool is designed exactly for this purpose. By representing chemical reactions as bond-making and bond-breaking reactions, INGen implements the reaction network as reaction matrices. For every reaction family, e.g. ring saturation, paraffin cracking etc., there is one reaction matrix. Every molecular species also has a computational representation in the form of a bond electron matrix. This computational structure makes it possible to transform reactant into products via simple matrix operations. Figures 2.2 shows a simplified computational representation of an olefin hydrogenation.

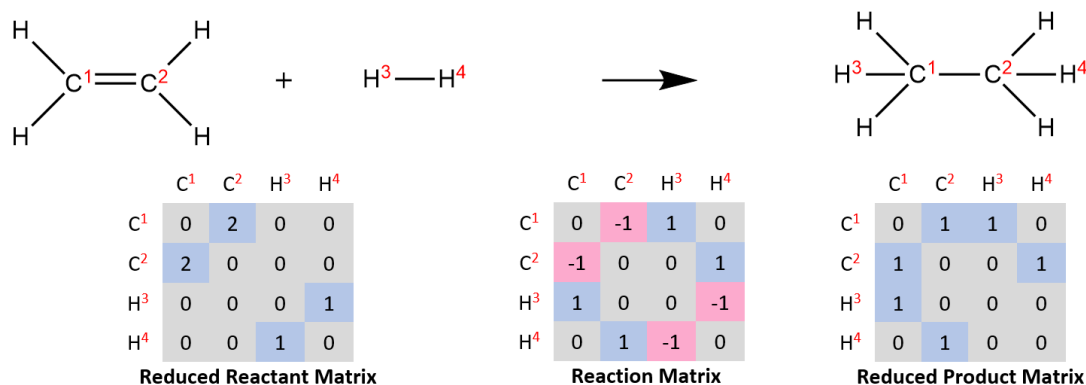


Figure 2.2: Matrix representation: olefin hydrogenation [34].

The INGen tool is unique as it uses the reaction matrices on each structural sub-unit of the feed molecules and intermediates to carry out and write chemical reactions. Due to this, one reaction family may generate thousands of reactions. In case of a network consisting of several reaction families, this can result in an exponential increase of the number of reactions and species. However, this will in many cases conflict with the main principle of building a model as simple as necessary for a specific application. To minimize the computational workload while obtaining the desired molecular detail, the INGen tool uses seeding as a model reduction tool as described by Joshi *et al.* [35]. Seed molecules are added manually to the model and serve as starting point for the reaction network. For each reaction family, it is possible to limit the termination rank. The termination rank of a reaction is equal to the maximum number of reaction steps from the seed molecule. The goal of seeding is to prune the reaction network to its essential building blocks without losing pathways to important products. Figure 2.3 shows an example of how the number of species increases dramatically with increasing termination rank. Other ways of limiting the number of reactions of each reaction family is adding restrictions on the reactant and products such as the reactant species type, number of carbon-rings, double bonds etc.

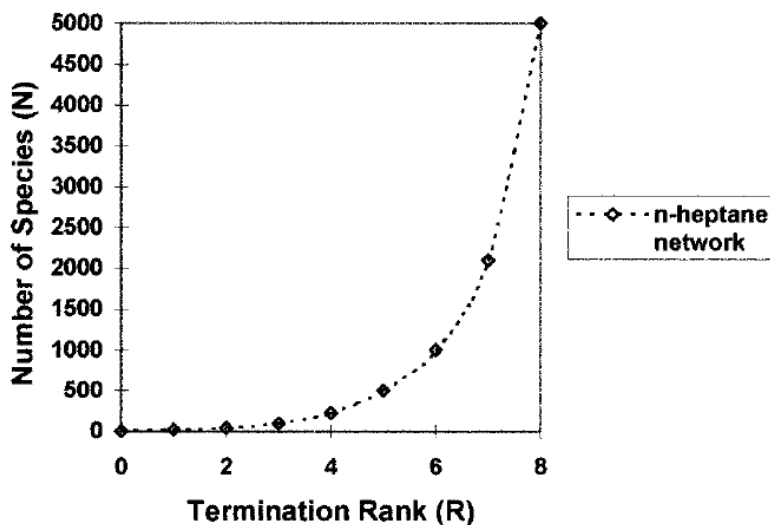


Figure 2.3: Increase in number of species (N) as a function of the termination rank (R) for n-heptane mechanistic reaction network by acid chemistry.¹

2.2 Initial Condition Generator

In industry, in most cases only bulk property measurements of the feedstock are available. The ICG tool is developed by the Klein Research Group to convert these bulk properties into a molecular representation of the feed. This molecular representation consists of the mole or weight fraction of each molecular species in the molecule set, obtained by the INGen tool. Figure 2.4 shows the flowsheet of ICG. Firstly, based on the available data, the full molecule set is represented as an attribute probability density function (PDF) tree. This PDF tree represents the numerical probability of each structure moiety, like naphthenic rings, aromatic rings, heteroatoms, present in the molecular set, as a branch. For all molecules satisfying some user-defined conditions, the average carbon number and standard deviation can also be defined if a Gaussian distribution for the carbon numbers is expected. Next, the software converts the attribute PDF tree and histogram parameters into a simulated molecular

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composition. Thirdly, the Property Generator of the KMT software is used to obtain simulated bulk properties of the simulated composition. By comparing and minimizing the difference between the experimental and simulated properties, the attribute PDF tree, and subsequently molecular composition, is iteratively optimized to match the experiments. The use of PDF trees and histograms reduces the computational load significantly as the fractions of every single molecule type don't have to be optimized individually while still obtaining a trustworthy composition. The power of ICG is that there is not a minimum amount of required data, but that all available experimental measurements can be used to further improve the optimization.

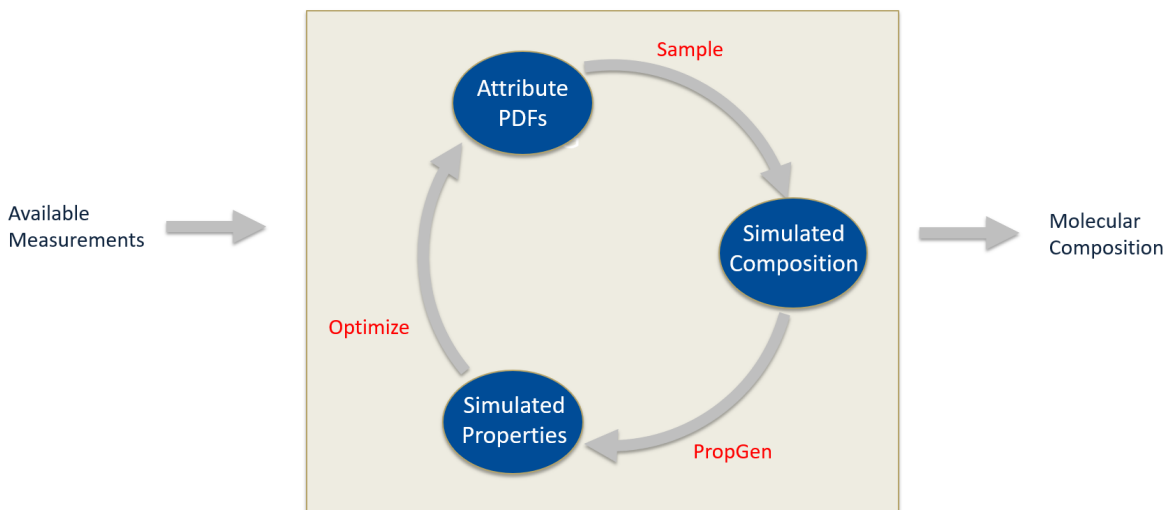


Figure 2.4: Flowsheet of the Initial Condition Generator (ICG).

2.3 Kinetic Model Editor

The Kinetic Model Editor (KME) is responsible for the development of the reaction kinetics based on the reactor specifications. It is the final step of the modeling process and brings together the composition from ICG and reaction network from INGen. The main focus of KME is to determine the reaction kinetics by fitting experimental reaction and product properties. The software is capable of handling different kinds of reactors, both homogeneous and heterogeneous reactions and different catalyst types.

For the green diesel and lubricant oil case, only the plug-flow reactor option is be used and all reactions are assumed to be heterogeneous reactions with a bifunctional catalyst following the Langmuir-Hinshelwood-Hougen-Watson kinetics (LHHW). To reduce the amount of tunable kinetic parameters, the linear free energy relationship formalism is used. A complete in debt overview of the mathematical and scientific principles used in KME is given in chapter 3. The reaction kinetics can be tuned manually or using the global optimization methods Simulated Annealing (SA). If the agreement between the experimental and simulated data is insufficient, it can be feasible going back to the INGen and ICG models to adjust the included molecular species and reactions.

2.4 Property Generator

The Property Generator (PropGen) transforms the molecular set of the product into chemical and physical properties. The pure component thermodynamical properties such as critical pressure, temperature, volume, boiling point and melting point are calculated using group contribution methods [36], [37]. This gives a sufficiently accurate result with only exception the small components such as hydrogen and water for which the online NIST database is consulted instead [2]. Pure component structural properties such as molecular weight, total carbon atoms, number of side chains etc., are derived from the bond electron matrices used in the INGen tool. To provide an estimation for bulk properties like density and molecular weight, mixing rules are used. PropGen is an additional tool in KMT which delivers the necessary molecular and bulk properties needed during the ICG and KME modeling phases.

Chapter 3

MODEL EQUATIONS AND KINETICS

This chapter gives an overview of the theoretical background necessary to build a molecular-level kinetic model and how this is implemented in the methyl laurate, coconut oil and lube base oil models. A kinetic model is build based on the specifications of the reactor system. This is discussed in section 3.1. Besides the reactor specifications, also the reaction kinetics are crucial to develop a comprehensive model. Section 3.2.1 gives an overview of the Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetics of heterogeneous catalytic reactions, typical for hydrotreatment processes. The Bell-Evans-Polanyi linear free energy Relationship (LFER) is explained in section 3.2.2 as a way of reducing the number of tunable kinetic parameters.

3.1 Material Balances and Reactor Specifications

The KME tool is capable of modeling different type of reactors such as plug-flow reactors, continuous stir-tank reactors, batch reactor, packed bed reactors etc. For the hydroprocessing applications, the experimental data is obtained from experiments in packed bed reactors with a bifunctional metal/acid catalyst under plug flow conditions. Equation 3.1 gives the material balance for a packed bed plug flow reactor in steady state [38].

$$\frac{dF_j}{dV} = \sum_i^n \nu_{ij} r_i \rho_B \quad (3.1)$$

With F_j the molar flowrate of species j, V the reactor volume, ν_{ij} the stoichiometric coefficient of species j in reaction i, r_i the reaction rate of reaction i per kilogram catalyst and ρ_B the packed bed density. In KME, a slightly adjusted equation is used

with the reaction rate defined per volume unit by the LHHW formalism and without a ρ_B -term. A complete molecular-level kinetic model consists of one material balance per molecular species and an overall energy balance. The three hydrotreating processes discussed in this paper are performed at approximately isothermal conditions, so no energy balances are implemented. The energy balances could be easily added using the KME tool if necessary. The material balances, along with the initial conditions of the reactor and the feed, define the initial value problem solved by the kinetic model.

3.2 Kinetics of Bifunctional Catalysis

Hydroprocessing of conventional and unconventional feedstocks is an heterogeneous catalytic process. Hydrogen is passed through a bifunctional catalyst containing both acid and metal (Lewis base) active sites [4]. The destructive hydrocracking and hydroisomerization reactions take place on the acid sites. Common industrially commercialized catalysts have an acidic support in the form of amorphous aluminosilicates, silicoaluminophosphates (SAPO) or crystalline zeolites. Hydrotreating involves non-destructive hydrogenation and happens at mild reactor conditions. These processes take place on the metallic active sites. Examples are CoMo and NiMo in sulfide state and noble metals. Ni-Mo/Al₂O₃ is one of the most commonly used catalysts in the petroleum refining industry. To incorporate the dual dual-site mechanism, the Langmuir-Hinshelwood-Hougen-Watson (LHHW) formalism is implemented in the kinetic model. This is discussed in section 3.2.1. Section 3.2.2 explains how the Bell-Evans-Polanyi linear free energy relationship (LFER) is used to simplify the kinetics optimization process.

3.2.1 Langmuir-Hinshelwood-Hougen-Watson Kinetics

To be able to derive the change in molar flowrates of the species from the material balances, an expression for the reaction rates has to be formulated. The hydrotreatment reactions happen either on the metal or acid sites of the catalyst.

These reactions on the catalyst surface can be modeled using the LHHW rate law formalism [39]. Equation 3.2 gives the general form of a LHHW rate law.

$$r = \frac{(kinetic\ factor)(driving - force\ group)}{(adsorption\ group)^m} \quad (3.2)$$

The reaction determining step of a heterogeneous catalytic reaction can either be the adsorption of the reactants on the surface, the surface reaction or the desorption of the reaction products. For the commercial hydrotreatment processes, surface reaction control is assumed. An explicit hydrogen partial pressure dependence is added to the adsorption denominator. Equation 3.3 gives the modified LHHW kinetic rate law for reversible reactions, used by the KME tool. The reaction rate is defined per volume unit of the reactor by assuming a uniform distribution of active sites over the bed. Catalyst deactivation can be added to model less active catalysts.

$$r = \frac{k_{sr} \cdot \prod_i^{reactants} K_{ad,i} \cdot y_{cat} (\prod_i^{reactants} P_i - \frac{\prod_j^{products} P_j}{K_{eq}})}{P_{H_2}^\beta \cdot (1 + \sum_l^{species} K_{ad,l} P_l)^m} \quad (3.3)$$

In this equation, r is the reaction rate, k_{sr} is the surface reaction rate coefficient, y_{cat} is the concentration of free catalyst sites, K_{eq} is the overall reaction equilibrium constant, β is the hydrogen pressure dependence factor of the acid or metal catalyst sites and K_{ad} is the adsorption equilibrium constant, also depending on the catalyst site. The adsorption constant K_{ad} and equilibrium constant K_{eq} are calculated based on theoretical and empirical correlations. For K_{eq} the standard thermodynamic formulation is given by equation 3.4. The Gibbs free energy and other thermodynamic properties of each molecular species are calculated from group contribution methods and corresponding state functions. More specifically, Marrero [36] and Benson [37] group contribution methods are used to calculate the properties at a reference temperature of 298K.

$$\ln K_{eq} = -\frac{\Delta G_{rxn}}{RT} \quad (3.4)$$

Korre and Klein [40] developed a quantitative structure/reactivity relationship (QSRR) to calculate the adsorption equilibrium constant K_{ad} of each reaction. Equation 3.5 gives a modified version of this relationship used in this study. The adsorption constant of a molecule is defined as a function of its structure and the type of site (acid/metal) the species is adsorbed on. Both a carbon and oxygen number dependency are included. The parameters a_{ad} , b_{ad} and c_{ad} have different values depending on which type of site, acid or metal, the adsorption happens on.

$$\ln K_{ad} = a_{ad} + \frac{b_{ad}N_C + c_{ad}N_O}{RT} \quad (3.5)$$

3.2.2 Bell-Evans-Polanyi Linear Free Energy Relationship

The tunable parameters in the model are the surface reaction rate coefficient k_{sr} for every reaction i and the hydrogen pressure dependence β depending on the type of catalyst site. The surface reaction rate coefficients are modeled using the Arrhenius equation with the Arrhenius constant or pre-exponential factor A and activation energy E as variables. This is given by equation 3.6. This results in two tunable parameters per reaction and the two overall hydrogen pressure dependencies. However, as in most hydrotreatment processes ten thousands of reactions can occur, an additional method to reduce the number of tunable parameters in the model is desired. The Bell-Evans-Polanyi linear free energy relationship (LFER) exploits the similarity and reaction enthalpy dependency of the activation energy of reactions of the same reaction family [41], [42]. Each reaction family j consists of a homologous set of reactants subject to the same type of reactions. The activation energy for each reaction i is defined by equation 3.7. Every reaction family now only requires three tunable parameters in total, rather than two per individual reaction. As a hydrotreatment process consists of $O(10)$ reaction families, this is a significant parameter reduction.

$$\ln k_{sr,i} = \ln A_j - \frac{E_{j,i}}{RT} \quad (3.6)$$

$$E_{j,i} = E_{0,j} + \alpha_j \Delta H_i \quad (3.7)$$

Chapter 4

RESULTS AND DISCUSSION

As discussed in chapter 2, the development of a molecular-level kinetic model consists of three interrelated steps. Firstly, a reaction network is generated based on experimental data and literature studies with the INGen tool. The results of this process are shown in section 4.1. In case the feedstock of the hydrotreating process consists of a mixture with unknown composition, this molecular composition is reconstructed based on experimental data. Section 4.2 discusses the results of the initial condition generation for the lube base oil hydroprocessing. Next, the kinetics of the networks are optimized by matching product data at different reaction temperature, pressure and catalyst metal composition with the model results. The evaluation of the obtained kinetics is done in section 4.3. An objective function of the form given by equation 4.1 was minimized to reduce the difference in value between each observed and predicted experimental property y for all sets of data. σ_y is an user defined weight function. Finally, section 4.4 consist of a qualitative comparison of the kinetics of the discussed hydroprocessing operations.

$$obj = \sum_{set} \sum_{exp} \left(\frac{y_{obs} - y_{pred}}{\sigma_y} \right)^2 \quad (4.1)$$

4.1 Reaction Network Generation

4.1.1 Methyl Laurate Hydroconversion

Imai *et al.* [29] investigated the effect of differences in metal composition of the bifunctional Ni-Mo/Al₂O₃ catalyst on the methyl laurate hydroconversion process. This fatty acid methyl ester (FAME) is used as model compound to easily develop the kinetics of vegetable oil hydroprocessing. The data of methyl laurate conversion

and yields of various products for different Ni and Mo content of the catalyst are used to generate reaction pathways for the hydrotreatment. As it is reasonable to anticipate that the metal composition of the catalyst only influences the activity and not the occurrence of the reaction pathways, a delplot method is used on this data. This method makes it possible to determine the rank of the products [43]. The rank of a product is equal to the order of appearance in a reaction network. A first-rank delplot plots the ratio of the molar yields (Y) over the reactant conversion (X) versus the reactant conversion. Products with a finite intercept are predicted to be primary products. Products with a higher rank have a zero intercept. To predict the exact rank of the higher rank products, higher rank delplots are generated. In this case, the ratio X/Y^n is plotted against X with n the current reaction rank. The current rank (n) products have finite intercepts, higher rank products have zero intercept, and lower rank products diverge for zero conversion.

Figure 4.1 shows the delplots for the methyl laurate case. The conversion and yields used for this analysis are tabulated in appendix A. The first rank deplot indicates that methane, undecane and paraffin cracking products with carbon number between 2 and 10 are primary products as their extrapolated curves have a finite intercept. On the other hand, dodecane appears to be formed further down the reaction chain. Figure b, the second rank delplot, shows methane, C_{11} and C_2 to C_{10} diverging for zero conversion. This confirms the conclusions of the first rank deplot. The C_{12} -curve has still a zero intercept which means that the product rank is higher than 2. Looking at the third-rank deplot, C_{12} has a finite intercept. The fourth delplot shows that the curves of all products, including C_{12} , diverge towards the zero conversion limit. This proves that dodecane is primarily a third rank product in the network. For all delplots, the carbon monoxide formation was difficult to interpret. This is caused by the high methanation activity of the nickel-molybdenum catalyst resulting in a non-detectable concentration of CO in some of the experiments.

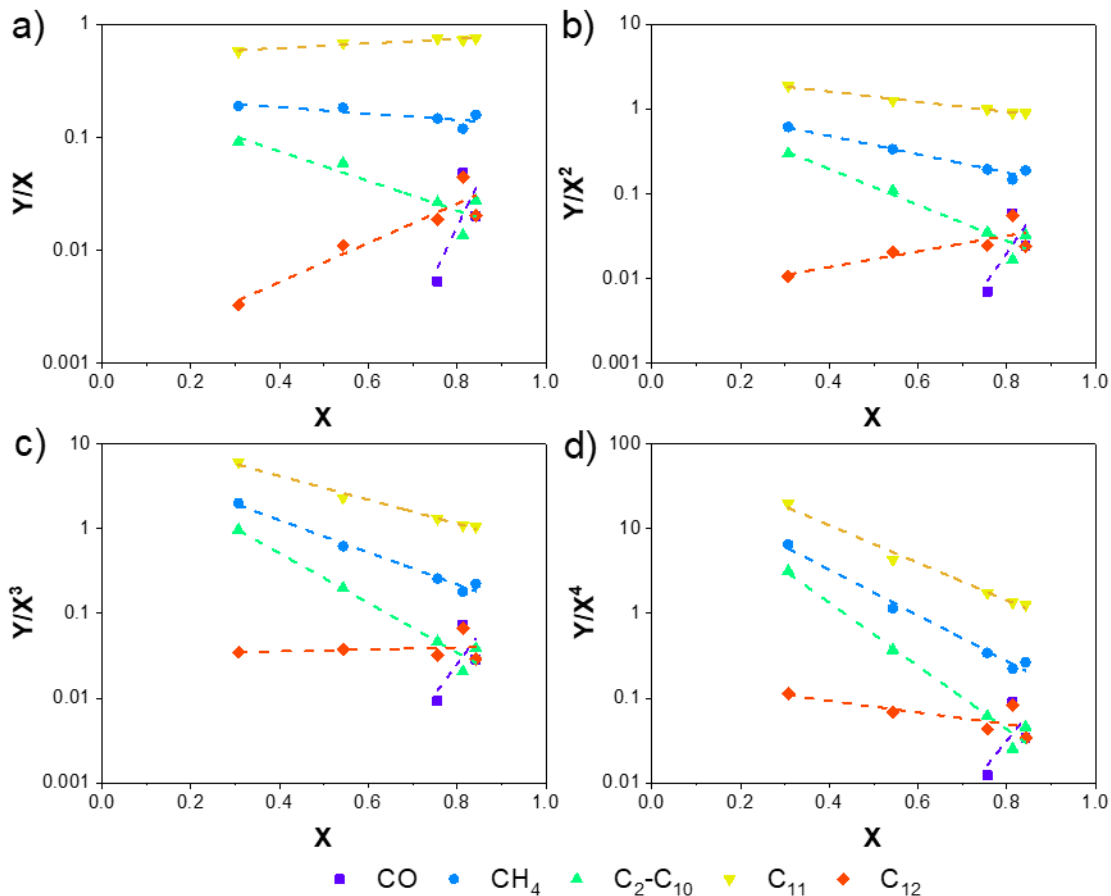


Figure 4.1: a) First-rank, b) second-rank, c) third-rank, and d) fourth-rank delplots for methyl laurate conversion from experimental data by Imai *et al.* [29], where Y is the yield and X is the conversion of methyl laurate.¹

Findings from earlier studies in literature experimentally investigating the reaction pathways of fatty acid hydroprocessing are combined with the results of the delplot analysis to build a complete reaction network for the kinetic model [45], [46], [47], [48]. A candidate reaction families list is generated based on this information. These reaction families are tabulated in table 4.1. The complete reaction network is shown in figure 4.2. The decarbonylation reaction results in an immediate conversion

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of methyl laurate in undecane, like the delplot predicted. Methane is formed as primary product by a CO cleavage reaction on the methyl laurate ester group, with a carboxylic acid as co-product, or by a CC hydrogenolysis at the end of the carbon chain in methyl laurate. As CC hydrogenolysis reactions are in general much slower than CO cleavage reactions, they were ignored in the final network. While the C_2 to C_{10} cracking products were predicted to be first rank products, only paraffin cracking of undecane and dodecane is added to the network. C_2 - C_{10} could be directly formed from cracking methyl laurate (first-rank) or any other intermediate, but as the cracking activity of the reactor is low, this is left out of the model to reduce the overall network complexity. Dodecane is a third rank product as predicted, formed by a CO hydrogenolysis in series with a hydrogenation and hydrodeoxygenation reaction, with dodecanal and dodecanol as consecutive intermediates. The aldehyde dodecanal was not experimentally observed in significant quantities due to its high reactivity which makes it difficult to determine its rank [47]. An alternative reaction pathway consists of forming a carboxylic acid by a CO hydrogenolysis reaction followed by two hydrodeoxygenation reactions. An additional methanation reaction models the conversion of carbon monoxide to methane on the metal sites as a way to match the experimentally observed lack of carbon monoxide formation on the catalyst [49], [50]. Finally, paraffin isomerization and the hydrodeoxygenation of the carboxylic acid to the aldehyde are added to complete the reaction network. All paraffin cracking is preceded by a paraffin isomerization to introduce branching in the paraffin as this increases the stability of the intermediate carbenium ion.

Table 4.1: Reaction families for methyl laurate hydroprocessing.¹

Reaction Family	Sample Reaction	Reaction site
Decarbonylation		Metal
CO Hydrogenolysis		Metal
Hydrodeoxygenation		Metal
CC Hydrogenolysis		Metal
Aldehyde Hydrogenation		Metal
Paraffin Isomerization		Acid
Paraffin Cracking		Acid

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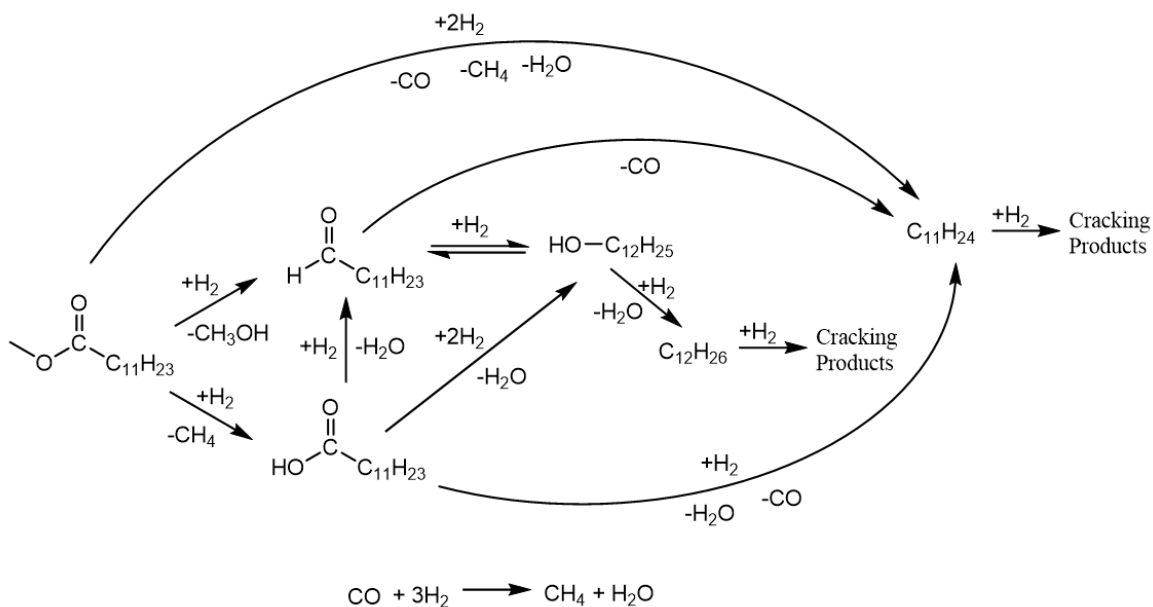


Figure 4.2: Reaction network for methyl laurate hydroprocessing.¹

Table 4.2 gives an overview of the species and reaction types added to the Interactive Network Generator (INGen). By using the reaction family concept, 83 individual chemical reactions are grouped into only 8 reaction types.

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Table 4.2: Network statistics of methyl laurate hydroconversion, generated using the Interactive Network Generator (INGen).¹

Species Type	Number	Reaction Type	Count
FAME	1	CO Hydrogenolysis	2
Carboxylic Acid	1	Hydrodeoxygenation	3
Aldehyde	1	Decarbonylation	3
Alcohol	2	Aldehyde Hydrogenation	1
n-Paraffin	12	Paraffin Isomerization	25
i-Paraffin	25	Paraffin Cracking	28
CO, H ₂ O, H ₂	3	CC Hydrogenolysis	19
		Methanation	1
Total Species	45	Total Reactions	83

4.1.2 Coconut Oil Hydroconversion

As methyl laurate is assumed to be a model compound for a whole vegetable oil feed, the same type of reactions should occur when hydroprocessing coconut oil. Coconut oil is a mixture of various triglycerides with up to 18 carbon atoms in the fatty acid chain. More specifically, Kimura *et al.* [31] determined experimentally that the coconut oil triglycerides consist of C_8 , C_{10} , C_{12} , C_{14} , C_{16} , C_{18} fatty acid chains. Table 4.3 gives an overview of the species and reaction types included in the reaction network. The assumption is made that every glycerol backbone has three identical fatty acid chains attached to it. Additionally to the methyl laurate reaction pathways, the fatty acid chains have to be removed from the glycerol backbone. This is considered to be done in one sequence to reduce the combinatorial load of multiple routes. To limit the number of individual species without getting rid of any important species types,

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only the isoparaffin isomers with one methyl sidechain on the penultimate carbon atom are included in the model.

Table 4.3: Network statistics of coconut oil hydroconversion, generated using the Interactive Network Generator (INGen) [51].

Species Type	Number	Reaction Type	Count
Triglyceride	6	CO Hydrogenolysis	36
Diglyceride	12	Hydrodeoxygenation	49
Monoglyceride	24	Decarbonylation	30
Fatty Acid	6	Aldehyde Hydrogenation	6
Aldehyde	6	Paraffin Isomerization	64
Alcohol	11	Paraffin Cracking	91
n-Paraffin	18	CC Hydrogenolysis	32
i-Paraffin	64	Methanation	1
CO, H ₂ O, H ₂	3		
Total Species	150	Total Reactions	309

4.1.3 Lube Base Oil Hydroprocessing

For the lube base oil hydroprocessing a general reaction network is developed based on experimental studies described in literature [3], [7], [18]. In contrast to the methyl laurate and coconut oil hydroconversion, the lube base oil hydroprocessing operation has a complex mixture of organic compounds as feed. Wang *et al.* [32] found experimentally that the deasphalted oil feed and lube base oil product consisted of organic compounds with carbon numbers up to 46. To make sure the reaction network is suited for all hydrotreating processes for lube base oil production, organic compounds with a carbon number between 1 and 50 are included. Pure hydrocarbons included are normal paraffins, isoparaffins, olefines, naphthenes and aromatics. Also sulfur and nitrogen compounds are common, but undesired, in lube oils. Table 4.4 gives an overview of all molecules included in the model. In total 1 690 species are added. These species

can undergo various reactions typical for both hydroisomerization, hydrocracking and hydrorefining processes. Table 4.5 shows how 24 739 unique reactions are grouped into 11 reaction types. Again this significantly reduces the complexity of the kinetic model optimization using the Kinetic Model Editor (KME).

Table 4.4: Species in lube base oil hydrotreating process.

Species type	Count
n-Paraffin	50
i-Paraffin	205
Olefin	49
Naphthene	223
Mononring Naphthene	50
Diring Naphthene	95
Triring Naphthene	45
Tetraring Naphthene	33
Aromatic	513
Monoring Aromatic	251
Diring Aromatic	159
Triring Aromatic	70
Tetraring Aromatic	33
Sulfide & Mercaptan	100
Thiophene Derivative	125
Pyridine Derivative	213
Pyrrole Derivative	209
H ₂ , H ₂ S, NH ₃	3
Total Species	1690

Table 4.5: Network statistics of lube base oil hydroprocessing, generated using the Interactive Network Generator (INGen).

Reaction Type	Catalyst site	Count
1. Denitrogenation	Metal	256
2. Desulfurization	Metal	280
3. Heterocyclic Saturation	Metal	166
4. Hydrodealkylation	Acid	1342
5. Hydrogenation	Metal	49
6. Paraffin Isomerization	Acid	205
7. Paraffin Cracking	Acid	297
8. Ring Isomerization	Acid	40
9. Ring Opening	Acid	119
10. Ring Saturation	Metal	542
11. Sidechain Cracking	Acid	21458
Total reactions		24754

Figure 4.3 shows all reaction pathways for the pure hydrocarbon compounds. Between brackets the number of the reaction type is added for every reaction as tabulated in table 4.5. R stands for the sidechain which can have a various lengths such that for each hydrocarbon type, molecules with carbon numbers up to 50 are included in the model. Ring saturations are necessary to convert aromatics into naphthenes with the same number of rings. Ring opening reactions bring down the number of rings in aromatics with a single cycloalkane ring. As it is impossible to include all different isomers of each molecule type, a reasonable choice is made to at least match the level of detail reported by the experimental studies. Ring isomerization converts cyclohexanes into cyclopentanes, but is limited to di- and monoring naphthenes and carbon numbers below 20 for complexity reasons. The sidechain cracking, paraffin cracking and hydrodealkylation reactions are crucial for hydrocracking processes as they all break

long molecules in shorter fractions. Sidechain cracking and hydrodealkylation is shown solely for a monoaromatic species in figure 4.3 , but will occur on any naphthenic, aromatic and sulfur or nitrogen containing organic compound with a sidechain. Paraffin isomerization converts normal paraffins into isoparaffins which can be cracked into smaller chains. Finally, hydrogenation is added to saturate the double bond of olefins.

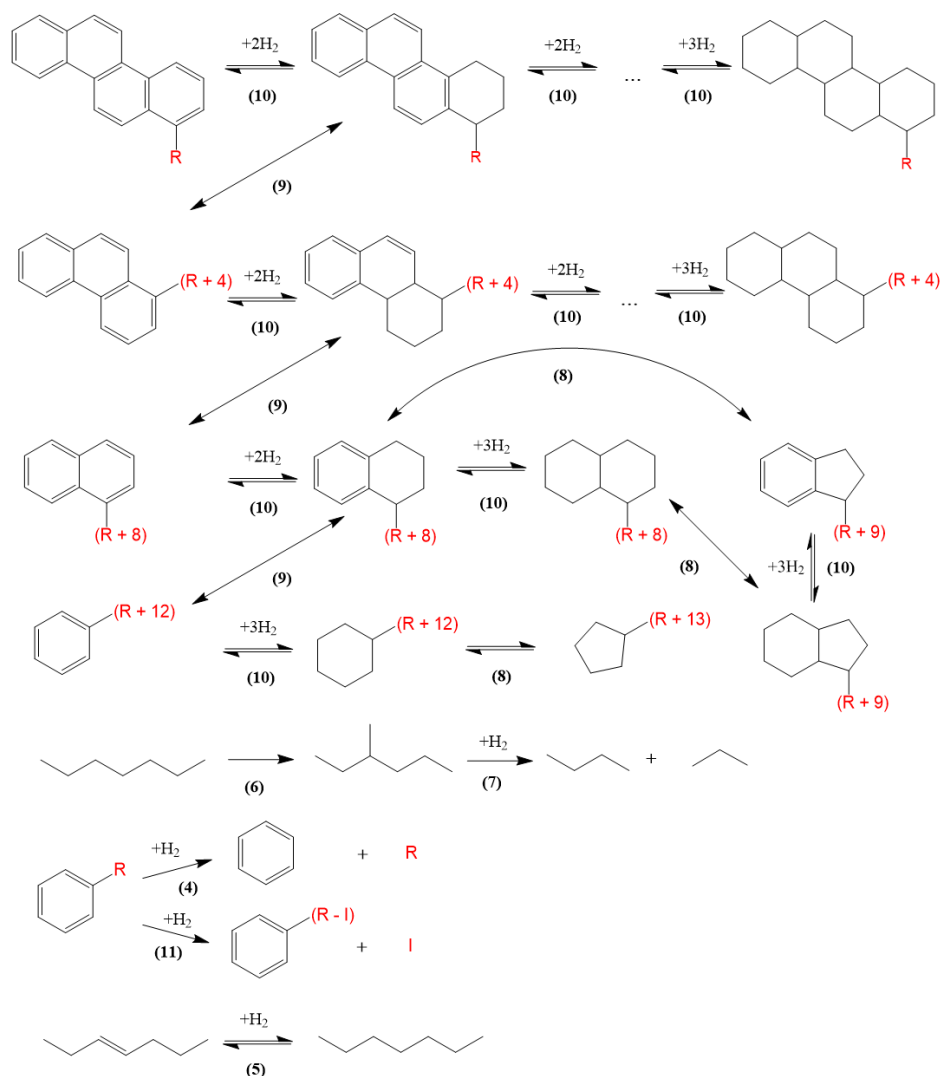


Figure 4.3: Reaction pathways of pure hydrocarbon compounds for lube base oil hydroprocessing

Figure 4.4 and 4.5 display the thermodynamically favored reaction pathways

for hydrocarbons containing a sulfur or nitrogen atom [3]. The nitrogen containing compounds are carbazoles, indoles, quinolines, indolines and their derivatives. The pyrrole and pyridine heteroatomic-rings are saturated first before the denitrogenation cleaves the carbon-nitrogen bonds [52]. On the other hand, desulfurization reactions are more likely to happen directly on the unsaturated thiophene ring. Finally, also thiols, sulfides, disulfides and their derivatives are part of the network. Desulfurization of these compounds will cleave either sulfur-sulfur or carbon-sulfur bonds.

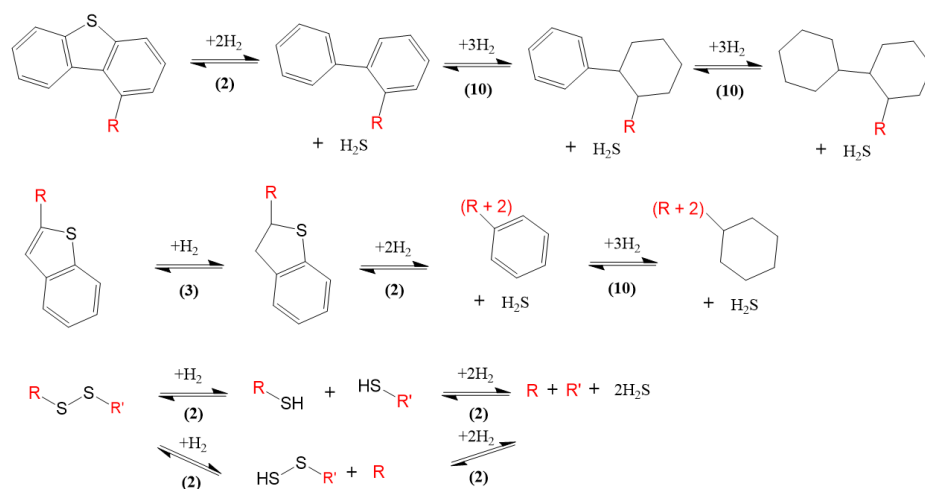


Figure 4.4: Reaction network of sulfur containing species for lube base oil hydroprocessing.

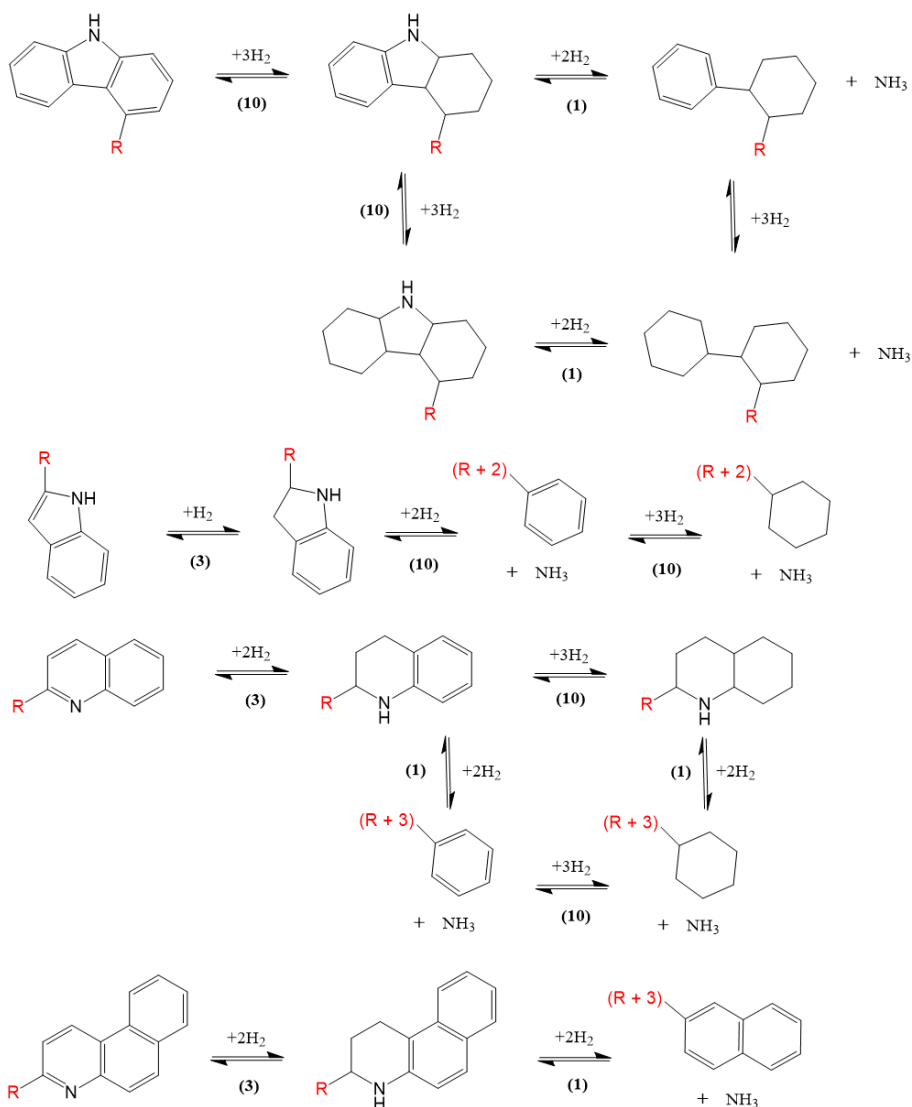


Figure 4.5: Reaction network of nitrogen containing species for lube base oil hydroprocessing.

4.2 Feed Composition Modeling

4.2.1 Lube Base Oil Hydroprocessing

While for the methyl laurate and coconut oil models the feed composition was completely determined on a molecular level, the lube base oil feedstocks consist of a complex mixture of organic compounds. Wang *et al.* [32] experimentally measured

feed properties including density, simulated distillation data, hydrocarbon type analysis, carbon number distribution, and sulfur and nitrogen level. As described in section 2.4, the Initial Condition Generator is used to simulate the molecular composition by matching the mixture properties. The probability density function tree developed for this case, is shown in figure 4.6. The experimental study mentions that no olefins were found in the feed which excludes any hydrogenation reactions happening in the process. As the feed is pre-hydrotreated to remove heteroatoms, the small amount of sulfur-containing compounds consist mainly of thiophenes and (di)benzothiophenes. In general however, the vacuum gas oil or deasphalted oil feedstocks can contain a significant sulfur and nitrogen fraction. An additional branch that is added to the model, but not used for the optimization due to a lack of data is the distribution of aromatic compounds containing nitrogen into mono-, di- and triring aromatic compounds.

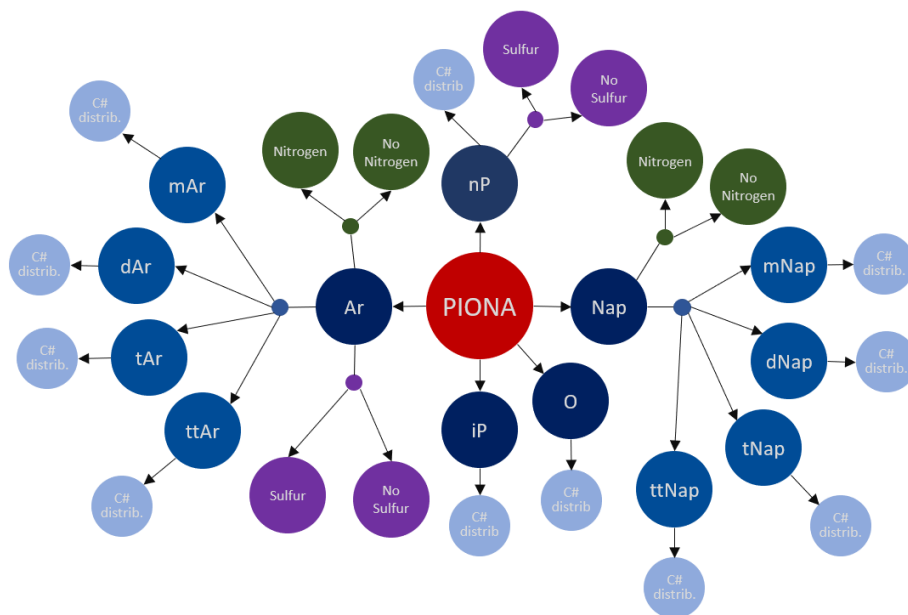


Figure 4.6: Probability density function tree for feed reconstruction of lube base oil hydroprocessing.

Figure 4.7 compares the experimental mixture data and the simulated data of

the reconstructed molecular composition. All composition data can be matched very accurately. To get an optimal accuracy of the kinetic model discussed in section 4.3.3 and to match the simulated distillation and density data as good as possible, small adjustments were made, but the deviation in molecular composition stays within the experimental error margin. Also the simulated density is in good agreement with the experimental data with a error of only 2.1 %. Only the simulated true boiling points differ slightly from the experimentally obtained simulated distillation data. A first cause could be experimental errors and the simulated distillation method used in the experimental study. Simulated distillation experiments are only an approximation of the boiling point ranges for a mixture, especially in this case as a vacuum distillation method, ASTM D 1160, is used to avoid preliminary degrading of long carbon chains before boiling at atmospheric conditions. A second reason is the incapability of the group contribution methods to simulate the boiling point of some of the heavier molecular species. Manually, boiling point data from literature is used to improve the boiling point estimation for chrysene and naphthalene compounds. As the relative errors are less than 6 % between the simulated boiling points and the experimental simulated distillation temperatures in kelvin, the differences are within an acceptable error margin.

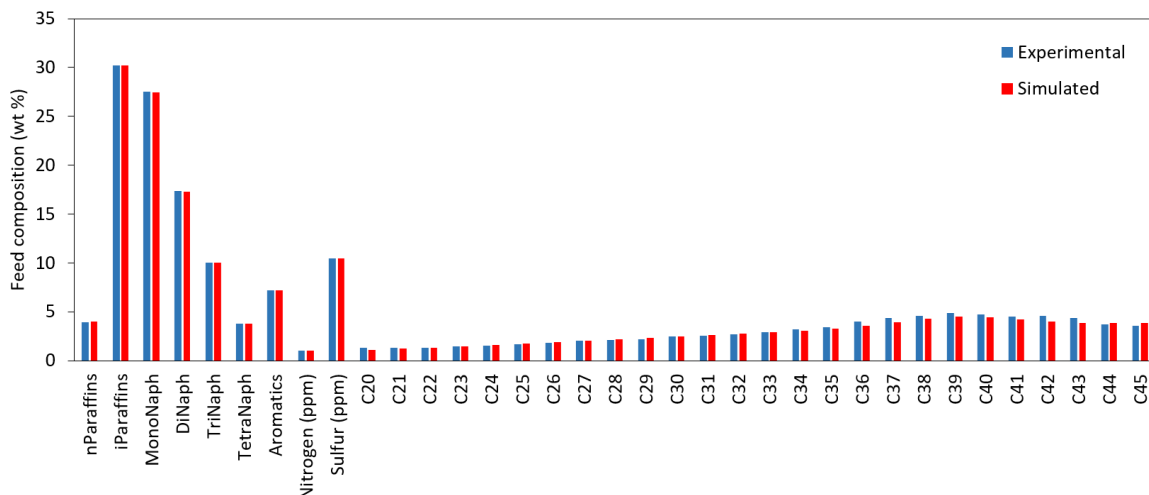


Figure 4.7: Evaluation of feed reconstruction for lube base oil hydroprocessing.

4.3 Kinetic Model Evaluation

4.3.1 Methyl Laurate Hydroconversion

With the feed and reaction network completely defined, the KME tool is used to determine the reaction kinetics based on the product composition reported in literature. All the experiments were done at similar reaction conditions as can be seen in table 4.6. Here LHSV stands for the liquid hourly space velocity. Imai *et al.* [29] built nine experimental set-ups with varying nickel and molybdenum content in the catalyst while Kimura *et al.* [30] repeated the process for four different hydrogen pressures. The later data is used to include hydrogen pressure dependencies of in the kinetics, represented by β in equation 3.3. The former makes it possible to determine the changes in kinetics with varying metal composition of the catalyst and to develop a catalyst family concept.

Table 4.6: Reaction conditions of the methyl laurate hydroprocessing [29], [30].

	Imai <i>et al.</i> [29] 20 wt % Ni	Imai <i>et al.</i> [29] 10 wt % Ni	Kimura <i>et al.</i> [30]
Temperature (°C)		300	
H ₂ pressure (MPa)	0.4	0.4	0.1-0.8
H ₂ /ML (molar ratio)		15	
LHSV (h ⁻¹)		40	
Catalyst Type		Ni-Mo/Al ₂ O ₃	
Ni content (wt %)	20	10	20
Mo conten (wt %)	0-8	0-4	8
Cat. volume (mL)	0.15	0.5	0.25

As all experiments were done at the same reaction temperature, the temperature dependency of the reaction families can't be optimized. However, the KME tool requires for each catalyst family j to define the Arrhenius constant constants A , the activation energy $E_{j,0}$ and the coefficient of the linear free energy relationship α_j . Because of the lack of temperature dependent data, these last 2 parameters have been given constant values of 20 kcal/mol and 0.1 respectively. These values don't stroke with the kinetic reality, but can be adjusted with experimental data at different reaction temperatures in future studies. However, the overall surface reaction coefficient k_{sr} , calculated with equations 3.6 and 3.7, will stay the same. For now, the logarithms of the Arrhenius constants A are optimized using a simulated annealing method with the objective function given by equation 4.1. For every reaction set-up, the available experimental data for the kinetics optimization are the methyl laurate conversion and CO , CH_4 , C_2 to C_{10} , C_{11} , and C_{12} selectivities. Since only the metal site activity was changed by changing the nickel and molybdenum content of the catalysts, the activity of the acid site cracking and isomerization reaction families was kept constant. Figure 4.8 shows the result of the optimization as a parity plot of all the experimental data

versus the simulated process output. As an example a more detailed comparison is shown in figure 4.9 for a hydrogen pressure of 0.8 MPa and catalyst with 20 wt % Ni and 8 wt % Mo. Both figures show the excellent agreement between experimental and simulated product data.

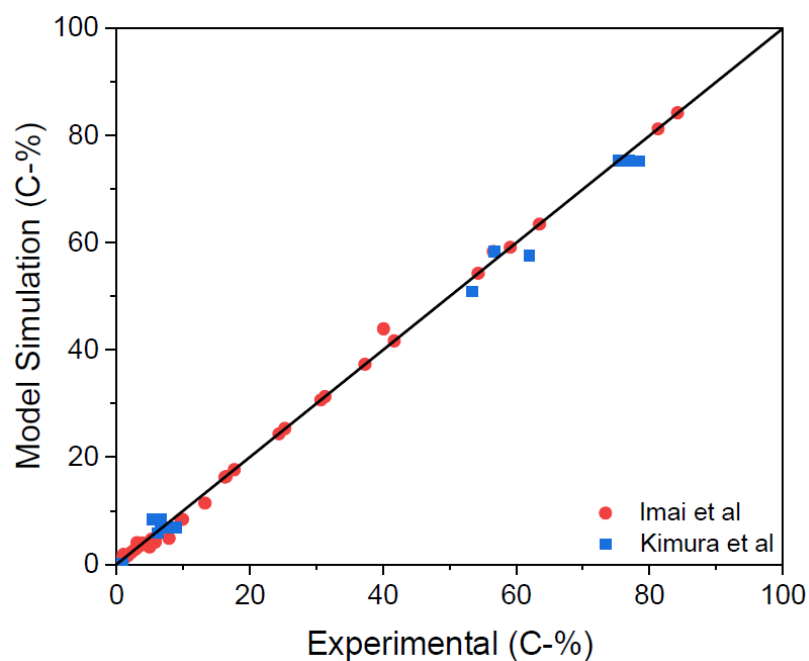


Figure 4.8: Parity plot between experimental and model results for methyl laurate hydroprocessing with $r^2=0.995$.¹

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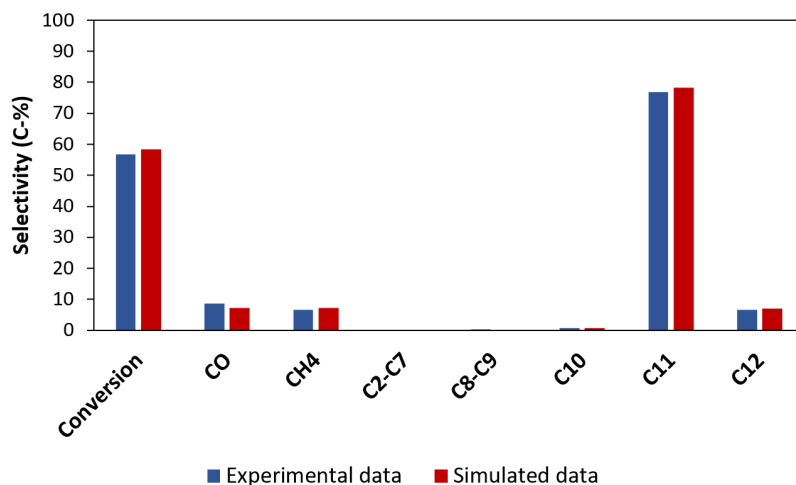


Figure 4.9: Comparison of simulated and experimental methyl laurate conversion and product selectivities for a hydrogen pressure of 0.8 MPa and 20 wt % Ni and 8 wt % Mo alumina catalyst.

Using the simulated product data, another delplot analysis is done as shown in figure 4.10. By comparing the intercept-values of parallel first rank products in a first rank delplot, the ratio of the apparent surface reaction rate coefficients can be determined [43]. Looking at figure 4.10 (a) for the methyl laurate conversion, a $k_1:k_2:k_3$ ratio of 0:83:17 for dodecanal, undecane, and dodecanoic acid formations, respectively, is observed. This indicates that almost all undecane is formed through a direct decarbonylation reaction of methyl laurate. As there is barely any dodecanal predicted as first rank product, all dodecane will be formed with dodecanoic acid as intermediate. Figure 4.10 (b) shows the first rank delplot for the conversion of the intermediate dodecanoic acid. The intercept values indicate that the reaction rate constants of the formation of dodecanal, dodecanol, and undecane have a ratio of 0:72:13 respectively. Therefore, the dodecanoic acid mostly hydrodeoxygenates to the alcohol with a small fraction decarbonylating to undecane as well. Dodecanal is barely formed in both conversion processes and can be ignored in the network. These conclusions coincide well with the earlier delplot analysis from figure 4.1 and the high

selectivity towards undecane as seen in the experimental results.

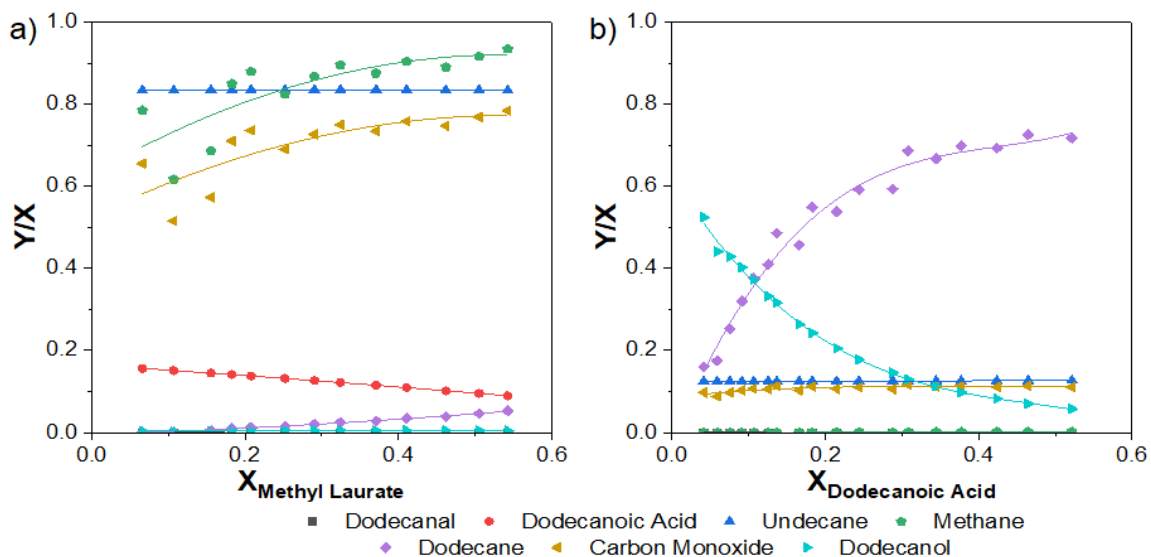


Figure 4.10: First-rank delplots of the kinetic model simulation of hydroprocessing a) methyl laurate and b) dodecanoic acid with 0.25 mL of 8 wt % Mo, 20 wt % Ni on alumina catalyst at 300 °C and 0.4 MPa hydrogen pressure.¹

Table 4.7 tabulates the obtained log A values for catalyst with 20 wt % nickel and variable molybdenum content. Table 4.8 gives the kinetic constants in case the catalyst contains 10 wt % nickel. The 8 reactions types as defined in section 4.1 are expanded to 13 reaction families as the activity of reactions of the same reaction type can be different for different feed molecules types. Additionally, the acid and metal site hydrogen pressure dependent β exponents are determined to be 1.26 and 0.472, respectively, based on the experiments done at different hydrogen pressure. Looking at the dependency of the Arrhenius constant A on metal site composition, trends can be identified. Both for the 20 as 10 wt % Ni catalyst, the decarbonylation, hydrogenation and HDO (hydrodeoxygenation) activity increases with increasing molybdenum concentration. This explains the increase in methyl laurate conversion and paraffin yield

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observed experimentally with increasing Mo content. Also the CO hydrogenolysis reaction seemed to increase in speed, despite a small decrease for the conversion from esters to aldehydes. In contrary, the methanation activity decreases spectacularly with increasing Mo wt %. For the 20 wt % Ni, 0 wt % Mo case, the absence of any CO in the product is achieved by a very fast methanation reaction. Similarly, hydrogenolysis, which represents metal-site cracking of the paraffin products, becomes less significant with increasing Mo content. As expected, the reactions taking place on the acid sites aren't influenced by the variation in metal site composition. This includes the paraffin isomerisation and paraffin cracking reactions. Finally, when comparing catalysts with the same Ni:Mo ratio, e.g. 20:08 and 10:04, the same trends are witnessed and the activities for most of the metal sites reaction families increase slightly with increasing metal content.

Table 4.7: Kinetic parameters for the reaction families in the hydroprocessing of methyl laurate, catalyst with 20 wt % Ni.¹

Reaction Family	log A, cat. wt% Ni: wt% Mo			
	20:00	20:02	20:06	20:08
CO Hydrogenolysis (Ester $\rightarrow$ Aldehyde)	5.97	5.97	5.9	5.8
CO Hydrogenolysis (Ester $\rightarrow$ Carboxylic Acid)	6.11	6.38	6.61	6.93
Decarbonylation (Aldehyde)	4.73	4.73	4.81	4.87
Decarbonylation (Carboxylic Acid)	10.04	10.05	10.05	10.07
Decarbonylation (Ester)	8.8	8.69	9.09	9.35
HDO (Alcohol $\rightarrow$ Paraffin)	9.8	9.99	10.43	11.08
HDO (Carboxylic Acid $\rightarrow$ Alcohol)	8.67	8.97	9.64	10
HDO (Carboxylic Acid $\rightarrow$ Aldehyde)	7.85	7.85	7.85	7.85
Hydrogenolysis (Paraffin)	8.12	7.61	7.28	6.66
Methanation	10.76	7.91	7.48	0
Paraffin Isomerization (Paraffin)	6.71	6.71	6.71	6.71
Paraffin Cracking (Paraffin)	7.75	7.75	7.75	7.75
Hydrogenation (Aldehyde)	9.15	9.46	9.61	9.86

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Table 4.8: Kinetic parameters for the reaction families in the hydroprocessing of methyl laurate, catalyst with 10 wt % Ni.¹

Reaction Family	log A, cat. wt% Ni: wt% Mo			
	10:00	10:01	10:03	10:04
CO Hydrogenolysis (Ester $\rightarrow$ Aldehyde)	5.77	5.71	5.71	5.71
CO Hydrogenolysis (Ester $\rightarrow$ Carboxylic Acid)	6.04	6.36	6.79	6.8
Decarbonylation (Aldehyde)	4.73	4.73	4.73	4.73
Decarbonylation (Carboxylic Acid)	9.68	9.68	9.68	9.68
Decarbonylation (Ester)	8.2	8.74	9.29	9.15
HDO (Alcohol $\rightarrow$ Paraffin)	8.81	9.89	10.3	10.55
HDO (Carboxylic Acid $\rightarrow$ Alcohol)	7.78	8.52	9.02	9.16
HDO (Carboxylic Acid $\rightarrow$ Aldehyde)	7.85	7.85	7.85	7.85
Hydrogenolysis (Paraffin)	7.37	7.24	6.97	6.61
Methanation	10.09	10.09	7.55	6.83
Paraffin Isomerization (Paraffin)	6.71	6.71	6.71	6.71
Paraffin Cracking (Paraffin)	7.75	7.75	7.75	7.75
Hydrogenation (Aldehyde)	9.05	9.15	9.23	9.44

The parameters in tables 4.7 and 4.8 can be used to predict the kinetic constants for the same processes, but with other members of the same catalyst family. For each reaction family, relations can be found between the parameters by curve fitting the

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parameters as a function of the Mo and Ni content of the catalyst. As an example, this is done for the log A value of the CO hydrogenolysis converting methyl laurate into dodecanoic acid and methane. Equation 4.2 gives this correlation. This equation can be used to extrapolate the CO hydrogenolysis activity of a catalyst with different Ni and Mo concentration, without further experimental studies. Extending this to all of the reaction families subsequently defines all parameters needed to study the hydroprocessing activity of catalysts with different Ni:Mo ratios. The concept should also apply to other catalysts with different metals and different acid supports, given some information about the activity on those catalysts with relations based on fundamental properties of the metal or acid sites.

$$\log A_{CO \text{ hydrogenolysis}} = 6.48 - 0.0216(\text{wt } \% \text{ Ni}) + 0.114(\text{wt } \% \text{ Mo}) \quad (4.2)$$

4.3.2 Coconut Oil Hydroconversion

To verify the hypothesis that a whole vegetable oil feedstock undergoes the same intrinsic reactions as the methyl laurate model compound, the obtained kinetics from section 4.3.1 are used as starting point for the coconut oil hydroprocessing. Kimura *et al.* [31] studied the hydroconversion of coconut oil at 350 °C, 0.8 MPa hydrogen pressure and a molar feed ratio of H_2 to coconut oil of 15. Again a Ni-Mo/ Al_2O_3 catalyst is used, although this time containing 9.1 wt % Ni and 5 wt % Mo. Similarly to equation 4.2 for the CO hydrogenolysis, the Arrhenius constant for all reaction families can be determined by extrapolating the values for the same catalyst family, but different Ni:Mo ratio. All experiments of the methyl laurate study were done at 300 °C. As the coconut oil hydroprocessing is done at 350 °C, the temperature dependence of the kinetics is improved by making small corrections to the activation energy. The LFER coefficient α is still kept constant at 0.01. The coconut oil experiment is performed with contact times between 0.05 and 1 hour.

Table 4.9: Kinetic parameters for the reaction families in the hydroprocessing of coconut oil [51].

Reaction Family	log A	E ₀ (kcal/mol)
CO Hydrogenolysis (Ester → Aldehyde)	5.77	20.07
CO Hydrogenolysis (Ester → Carboxylic Acid)	4.46	17.33
Decarbonylation (Aldehyde)	4.91	20.21
Decarbonylation (Carboxylic Acid)	2.85	12.22
Decarbonylation (Ester)	6.87	17.40
HDO (Alcohol → Paraffin)	11.62	21.22
HDO (Carboxylic Acid → Alcohol)	5.81	16.18
HDO (Carboxylic Acid → Aldehyde)	7.85	20.00
Hydrogenolysis (Paraffin)	5.84	19.12
Methanation	-0.361	11.81
Paraffin Isomerization (Paraffin)	3.94	16.84
Paraffin Cracking (Paraffin)	4.57	16.38
Hydrogenation (Aldehyde)	7.96	18.32

While a thorough optimization of the kinetics is still work in progress, some preliminary result make it possible to justify the earlier derived methyl laurate kinetics. Table 4.9 contains the kinetic parameters derived with the methyl laurate kinetics as starting point. The removal of each individual chain from a triglyceride is modeled independently. A constant log A increase of 0.37 and 0.20 for diglyceride and monoglyceride reactions, is implemented to achieve the reported hydrocarbon yields. Figure 4.11 shows a parity plot comparing the conversion and yields obtained experimentally and through simulation. This plot shows only the results for a contact time of 0.1 h, but the good agreement is clear. This proves that the kinetics determined with the fatty acid methyl ester model compound are a good representation for a complete

vegetable oil feedstock hydroconversion.

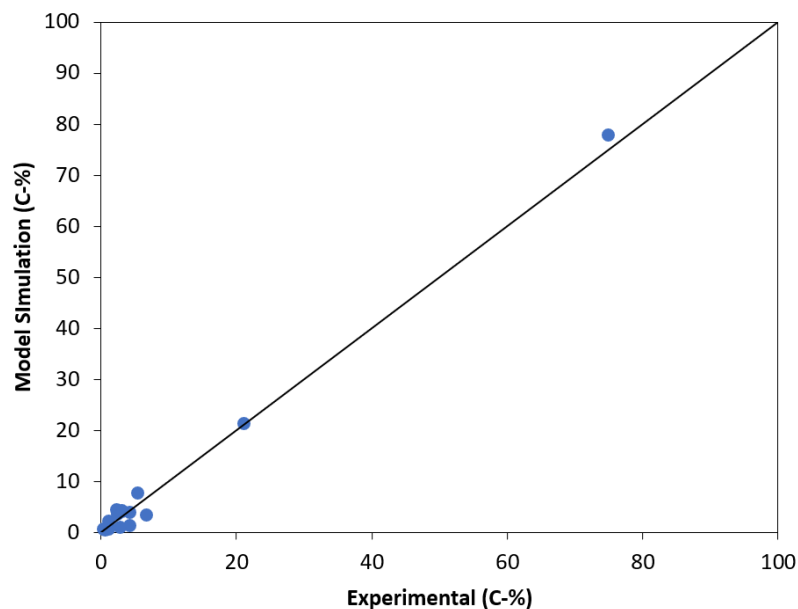


Figure 4.11: Parity plot comparing experimental and simulated hydrocarbon yields and reactant conversion for a contact time of 0.1 h with $r^2=0.993$.

4.3.3 Lube Base Oil Hydroprocessing

The kinetics of the lube oil hydroprocessing are optimized by matching the experimental data reported by Wang *et al.* [32]. Three experiments were done at reaction temperatures of 360, 370 and 380 °C. The space velocity, pressure, hydrogen/oil volumetric ratio and catalyst loading were kept constant at 0.8 h⁻¹, 9.0 MPa, 800 v/v and 100 mL respectively. The catalyst was an advanced hydrowaxing bifunctional catalyst containing platinum and phosphate on silica-alumina with a similar functionality as the Ni-Mo/Al₂O₃ catalyst, but a very strong acidity. For each reaction temperature, the study reports the hydrocarbon type analysis and carbon number distribution of the lube base oil product. For the experiment at 380 °C, more detailed product properties were reported including sulfur fractions. The hydrotreating process was followed by a vacuum distillation to divide the product in different distillation cuts based on the boiling point distribution. Only the high overall boiling point cuts (> 350 °C) are useful as

lube base oil and are crucial in evaluating the model optimization. For the low overall boiling point cuts ($< 350\text{ }^{\circ}\text{C}$), detailed hydrocarbon type and carbon number analysis are given as well, but as the boiling ranges of the different cuts overlap and only a small fraction of the total product has a boiling point in this range, it is less useful for tuning. Finally, also the gaseous product properties are used to optimize the model. In total 141 data points were extracted to develop the reaction kinetics. Figure 4.12 shows the good agreement between the experimental and simulated properties. There are still some small randomly distributed deviations which are (partially) caused by the fact that the experimental data reports that a significant portion of the lube base oil product was lost during the distillation or had a boiling point of more than $540\text{ }^{\circ}\text{C}$.

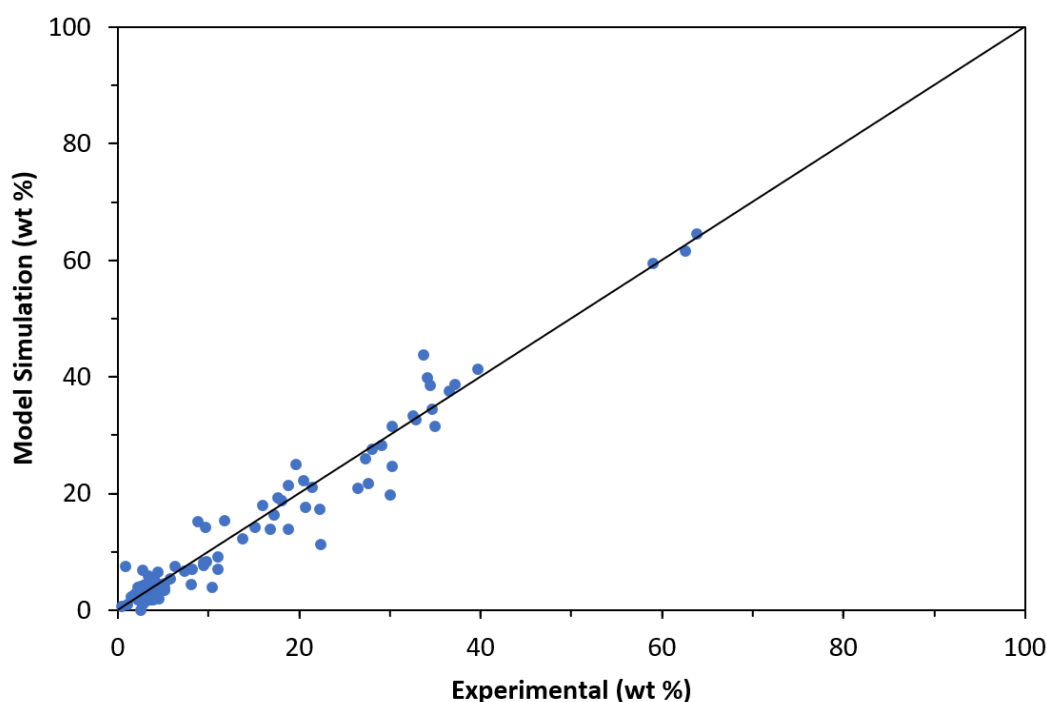


Figure 4.12: Parity plot between all experimental and model results for lube base oil hydroprocessing with $r^2=0.9588$.

While there are some small errors simulating the detailed boiling point cut properties, the overall carbon number distribution and hydrocarbon type analysis of

the lube base oil is predicted very accurately. Figure 4.13 shows the parity plots of these global properties for the three reaction temperatures. In contrast with section 4.3.1, the experimental data at different temperatures makes it possible to include temperature dependence in the simulated kinetics by optimizing both the log A and E values. Table 4.10 tabulates the optimized kinetic parameters for this reaction network. As mentioned earlier, the deasphalted vacuum residue feed has gone through a hydrotreatment before entering the hydrocracker reactor to reduce the sulfur and nitrog fractions. This results in a low sensitivity of the total kinetics on the kinetic parameters for the heteroatom removal reactions, but taking the severe reaction conditions in account, the low reaction rate coefficient for desulfurization and heterocyclic saturation were expected. The denitrogenation reactions are even completely neglected as the feed only contains 1 wppm nitrogen and no nitrogen level of the product was reported. Denitrogenation kinetics can be added when optimizing the model with additional experimental data. Also the olefin hydrogenation reactions were excluded in this optimization process as the feed didn't contain any olefins. As expected due to the high hydrogen pressure and temperature, it appears from the $\ln k_{sr}$ values in table 4.10 that the destructive hydrogenation reaction on the acid sites of the catalyst are the dominating reactions. This includes the paraffin isomerization and cracking, sidechain cracking, hydrodealkylations, ring opening and ring isomerization reactions. On the other hand, all ring saturation reactions happened very slowly, due to the unfavorable reaction conditions (and the low aromatic content (7.2 wt %) of the feed).

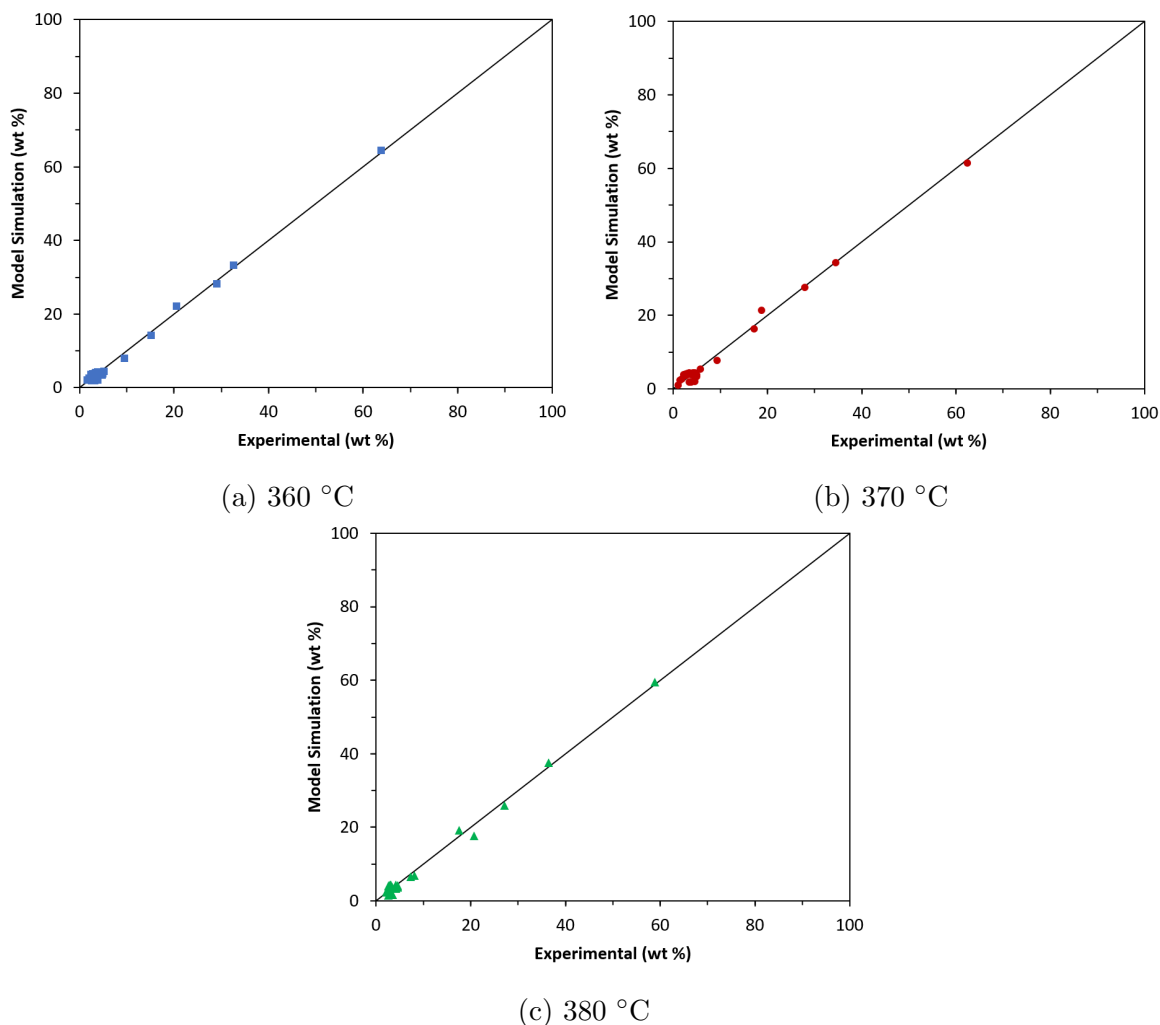


Figure 4.13: Parity plot between experimental and simulated product properties of lube base oil cut obtained by hydrocracking at different temperatures with a) $r^2=0.9951$, b) $r^2=0.9898$ and c) $r^2=0.9911$.

To take in account the temperature dependency of the kinetics, the activation energy of each reaction family was set to 20 kcal/mol as starting point for further optimization. Due to the low reaction activity of the metal site, only for the acid site reactions corrections of this activation energy was necessary to match the data at the three reaction temperatures. Especially the hydrodealkylation of aromatic and multiring naphthenic compounds is very temperature sensitive as shown by the low activation energy. For the other acid site reactions the temperature sensitivity had to

be reduced.

Table 4.10: Kinetic parameters for the reaction families in the hydroprocessing of lube base oil. The $\ln k$ values are calculated at 380 °C. (Only for paraffin cracking, α is included in the $\ln k$ calculation by using an average reaction enthalpy.)

Reaction family	$\log A$	E (kcal/mol)	α	$\ln k_{sr}$
Desulfurization	2.00	20.00	0.01	-10.81
Heterocyclic Saturation $2H_2$	1.00	20.00	0.01	-13.11
Hydrodealkylation (Aromatic + Multiring Naphthene)	1.83	10.54	0.01	-3.90
Hydrodealkylation (Monoring Naphthene)	10.17	29.46	0.01	0.71
Paraffin Isomerisation	10.00	20.00	0.01	7.62
Paraffin Cracking	2.30	22.84	2.40	13.59
Ring Isomerisation	7.00	20.00	0.01	0.71
Ring Opening	8.50	20.00	0.01	4.16
Ring Saturation $2H_2$	1.00	20.00	0.01	-13.11
Ring Saturation $3H_2$ (Monoring Aromatic)	3.00	20.00	0.01	-8.50
Ring Saturarion $3H_2$ (Multiring Aromatic)	3.00	20.00	0.01	-8.50
Sidechain Cracking (Aromatic + Multiring Naphthene)	5.00	20.00	0.01	-3.90
Sidechain Cracking (Monoring Naphthene)	8.17	29.46	0.01	-3.90

Finally, also the linear free energy relationship factor α is a variable parameter in the optimization process. To start off, a value of 0.01 is given for every reaction family.

This appears to be a good estimation for all families except for the isoparaffin cracking reactions. To optimize the agreement with the experimentally obtained lube base oil and gaseous product composition, an optimal value of 2.40 is found. While this high value is a stretch of the thermodynamical linear free energy relationship concept, it can be explained based on the carbon distribution of the paraffins in the feed and products and the reaction enthalpy differences between the different paraffin cracking reactions. Figure 4.14 shows the gaseous phase product composition and the good agreement between the simulated and experimental values. For all three temperatures, the gaseous product yield is slightly underpredicted, but the paraffin distribution is matched very well. Without a reaction enthalpy dependency, the paraffin cracking to propane, butane, pentane, hexane and heptane would be all equally fast and the gaseous product would have had an approximate equimolar paraffin composition. Table 4.11 shows the reaction enthalpies obtained using group contribution theory as described in section 3.2.2. The cracking reactions resulting in butane as product are the most exothermic, followed closely by propane forming reactions. The formation of pentane appears less thermodynamically favorable. By increasing the reaction enthalpy dependence, this difference in thermodynamics between the different cracking reactions is exploited to match the gaseous product data. Looking back at figure 4.14, butane composes indeed the largest fraction followed by propane and pentane. The large LFER factor also makes the cracking of larger chains more favorable than the cracking of shorter chains which makes sure that a lot of the larger molecules are cracked while the cracking of small molecules is less active, avoiding all butane, pentane and hexane getting isomerized and cracked to propane.

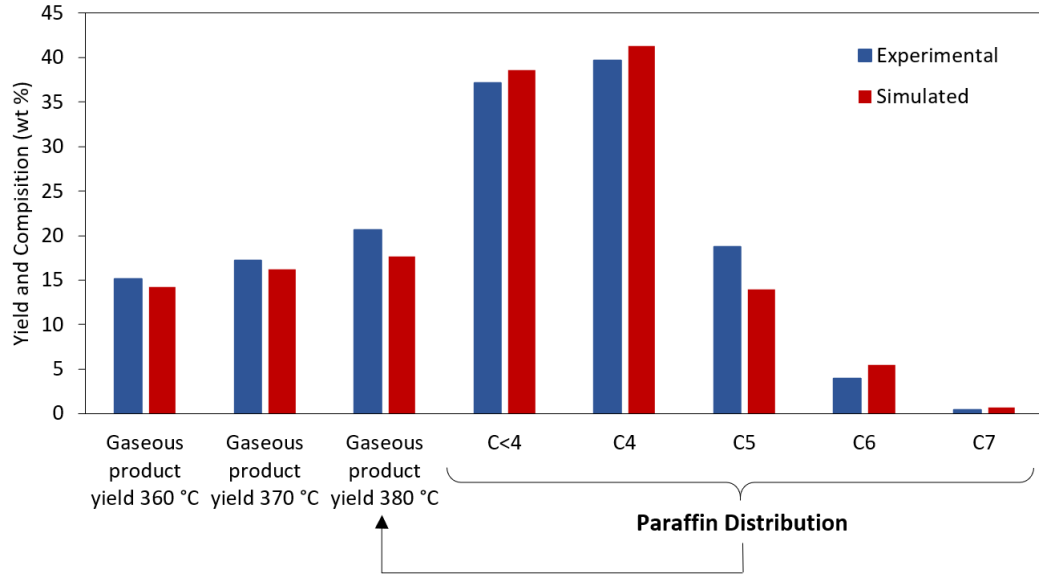


Figure 4.14: Evaluation of experimental and simulated gaseous product data of the lube base oil hydroprocessing at 380 °C.

Table 4.11: Reaction enthalpies of different cracking reactions of isoparaffins with carbon number 10 and 50. ($\Delta H_{reaction} < 0$ for exothermic reactions.)

Cracking reaction	$\Delta H_{reaction}$ (kJ/mol)
$iC_{10}H_{22}(2 - methyl) + H_2 \leftrightarrow nC_7H_{16} + Propane$	-11.2432
$iC_{10}H_{22}(3 - methyl) + H_2 \leftrightarrow nC_6H_{14} + Butane$	-14.7518
$iC_{10}H_{22}(4 - methyl) + H_2 \leftrightarrow nC_5H_{12} + Pentane$	-8.6065
$iC_{50}H_{102}(2 - methyl) + H_2 \leftrightarrow nC_{47}H_{96} + Propane$	-32.0836
$iC_{50}H_{102}(3 - methyl) + H_2 \leftrightarrow nC_{46}H_{94} + Butane$	-35.5919
$iC_{50}H_{102}(4 - methyl) + H_2 \leftrightarrow nC_{45}H_{92} + Pentane$	-29.4469

4.4 Comparison Kinetics of Hydrotreating Processes

While the discussed processes are all hydrotreating processes catalyzed by a bifunctional catalyst, there is a significant difference in reaction kinetics. This was expected looking at the reaction conditions and confirmed by the kinetic parameter

values. Table 4.12 shows a comparison of the average surface reaction rate coefficients of the three different hydroprocessing functionalities of the methyl laurate and lube base oil hydrotreatments. For methyl laurate, the parameters for the 20 wt % Ni, 8 wt % Mo catalyst and reaction temperature of 300 °C are used while for the lube base oil hydroprocessing, the average values of the experiment at 380 °C are tabulated. During the hydroconversion of methyl laurate, the saturation and heteroatoms removing reactions appear to be the most active. There is way less hydrocracking and hydroisomerisation happening. (Notice that the natural logarithms of the reaction rate coefficients are tabulated instead of the reaction rate coefficients themselves.) On the other hand, for the lube oil hydroprocessing there is a huge difference in activity as well, but this time the destructive hydrocracking and hydroisomerization reactions are way faster. This difference can be explained based on the feed properties, catalyst type and reaction conditions. The methyl laurate hydrotreatment happens at a moderate pressure of 0.4 MPa. The lube base oil hydrocracking is done at 9.0 MPa. The higher pressure favors the more destructive hydrocracking reactions happening on the acid sites. Additionally, the hydrocracking catalyst has a very strong acidity [31]. Methyl laurate has a high oxygen content, so a catalyst is chosen which promotes hydrodeoxygenation reactions. Ni-Mo/Al₂O₃ has a high hydrogenation activity and mild acidity which is ideal for these reactions [53]. While the reaction rate coefficient should be independent of the reactant concentration, the lack of heteroatoms in the lube base oil feedstock made it impossible to accurately simulate the denitrogenation and desulfurization kinetics. Nevertheless, the low activity was expected due to the catalyst choice and severe reaction conditions.

Table 4.12: Comparison of the average kinetic rate coefficients of three hydroprocessing functionalities for the methyl laurate and lube base oil hydrotreatment.

Hydroprocessing functionality	$\ln k_{sr}$	
	Methyl Laurate	Lube Base Oil
Saturation	5.14	-10.81
Removing of heteroatoms	1.02	-13.11
Hydrocracking/Isomerization	-0.91	1.89

As mentioned in the introduction, there is growing interest in co-processing biomass and petroleum derived feed. This study shows that both hydroprocesses are designed for other main purposes and a compromise in reaction condition and catalyst choice will have to be made to combine both processes.

Chapter 5

CONCLUSIONS

This thesis shows that molecular-level kinetic modeling is a suitable technique to model all kind of hydrotreating processes on bifunctional catalysts. The Kinetic Modeler's Toolbox with his four submodels, ICG, INGen, KME and PropGen, was an ideal tool to develop these models. Both the methyl laurate and coconut oil hydrotreatment for green diesel production and lube base oil hydroprocessing can be modeled using the LHHW kinetics formalism.

A delplot analysis was found to be an excellent approach to find the major reaction pathways of the hydroconversion of pure compounds. In addition to experimental studies, this information was used to develop the reaction network for the methyl laurate and coconut oil hydroconversion. The methyl laurate network consists of 45 species and 83 total reactions. For the hydrotreatment of a whole coconut oil feed, this was expanded to 150 species and 309 reactions. The lube base oil hydroprocessing is the most complex process with 1 690 species and 24 754 reactions in the reaction network, developed based on experimental studies.

By matching experimentally obtained bulk properties using the ICG tool, it was possible to accurately recreate the molecular composition of the deasphalted oil feed for the lube base oil hydroprocessing. The use of probability density function trees was a good way to optimize the molecular composition in a feasible way. Especially density, heteroatomic content, carbon distribution and hydrocarbon type data can be matched very accurately. Only the boiling point estimations based on simulated distillation experiments appeared less accurate and adjustment to the group contribution theory for this thermodynamic data had to be made. This is something to work on in future studies.

Using the KME tool, this study proved that the developed reaction networks and feed composition are a reliable representation of the hydrotreating processes and it showed how this kinetic-level approach made it possible to obtain the reaction kinetics. For all studied hydroprocessing operations, good agreement between experimentally obtained and simulated product compositions was found. The Bell-Evans-Polanyi linear free energy relationship formalism appeared a feasible tool to group the individual reactions in a small number of reaction families. For the methyl laurate hydroprocessing experiments at various reaction conditions, optimizing kinetic parameters for 8 reaction types (expanded to 13 reaction families) resulted in a parity plot with a r^2 value of 0.995. The kinetics of this fatty acid methyl ester hydroconversion is proven to be a good representation of the hydrotreatment of whole vegetable oil feeds as the coconut oil hydrotreatment product composition was predicted with an r^2 value of 0.993. Based on the obtained kinetics of processes with Ni-Mo/ Al_2O_3 catalysts with different Ni and Mo content, a catalyst family concept is developed, predicting the reaction rate constants based on the metal content of the catalyst.

For the lube base oil production operation, the network kinetics can be reliably approximated using 11 reaction types, which are expanded to 13 reaction families for optimization. The lube base oil product composition was predicted accurately with an average r^2 value of 0.992 for three reaction temperatures. Despite experimental uncertainty, a total of 141 product data points including detailed hydrocarbon composition of different boiling point cuts of the lube base oil product and the gaseous and low boiling byproduct composition, were matched well with an r^2 value of 0.9588. A high reaction enthalpy dependence was found for the paraffin cracking reactions in the network due to a relatively big gaseous product yield.

Finally, the obtained kinetics for the green diesel and lube base oil production were used to discuss the different functionalities of hydroprocessing. It was found that the mild reaction conditions and the high hydrogenation activity of the catalyst for the methyl laurate hydroconversion favored hydrorefining reactions including saturation reactions and the removal of heteroatoms. On the other hand, in the lube base oil

hydrotreating process, the hydrocracking and -isomerization reactions had the fastest intrinsic kinetics due to the very acidic catalyst, high hydrogen pressure and reaction temperature.

In conclusion, this manuscript contains a comprehensive overview of the modeling of the universal kinetics of hydrotreatment of carbon feedstocks on bifunctional catalysts and provides the framework upon which further molecular-level kinetic models of hydroprocessing operations can be build, potentially modeling the co-hydrotreatment of petroleum-derived and biomass feedstocks.

Chapter 6

FUTURE WORK

While the kinetic models developed in this thesis were able to accurately match the experimental data used, there is still room for improvement. The methyl laurate kinetics were optimized based on experiments performed at different hydrogen pressures, but the same reaction temperature and space velocity. The coconut oil experiment was done at a different temperature which made it possible to additionally optimize the activation energy as a variable parameter. However, by including additional experiments with varying temperature and contact time in the optimization process, the reliability of the obtained kinetics can be further improved. The experimental study by Kimura *et al.* [31] studies the coconut oil hydroprocessing with different space velocities which can be used for further optimization. For the lube base oil case on the other hand, temperature dependency is already included in the simulated kinetics, but no hydrogen pressure dependent data was available.

Secondly, the development of the kinetic models on a molecular-level scale had specific purposes in mind. By converting experimental bulk properties into a complete molecular composition, vital properties of the products can be predicted more accurately. For the green diesel production, the cetane number and cloud point are important properties which can be determined based on the molecular composition of the product. In future work, the calculations of these properties can be added to show the reliability and importance of the developed molecular-level kinetic models. A good starting point for the cetane number calculation would be the model developed by Ghosh and Jaffe [1]. A cloud point model can be developed based on solid-liquid mixture phase equilibria [54]. For the lube base oil production an equally important incentive for molecular-level modeling is the prediction of the product viscosity index.

Again, the trustworthiness of the developed models would benefit from the addition of a molecular-level property model. Noh *et al.* [7] developed correlations for the viscosity index based on the hydrocarbon type composition. Two correlations were developed. One is based solely on the weight percentage normal paraffins, multiring naphthenes and multiring aromatics. A second is one also a function of the isoparaffins, monoring naphthenes and aromatics content. Table 6.1 shows how well these correlations predict the viscosity index of the lube base products from the experimental study of Wang *et al.* [32] based on the product composition obtained by the kinetic model simulation. Neither of the correlations are able to accurately predict the viscosity index. Verdier *et al.* [55] was able to predict the viscosity index of vacuum gas oils based on chain length, branching position and aromatic content of the individual molecules. This could be a good lead for future research and shows the added value of the molecular-level approach of this thesis.

Table 6.1: Viscosity index calculation based on lumped product composition.

	Correlation 1[7]	Correlation 2[7]	Experimental data [32]
Viscosity Index	95.01	100.95	110

Finally, some more time could be invested in improving the fundamental equations and concepts of the molecular-level modeling toolbox. The KMT software is capable taking catalyst deactivation in account, so coke formation could be added as a parameter for the hydroprocessing models to make them more accurate. Froment and coworkers [56], [57] describe the single event concept as a way to introduce an entropy contribution term in the Arrhenius equation of elementary reactions. It could be worthwhile implementing a similar concept to improve the models.

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Appendix A

METHYL LAURATE HYDROCONVERSION DATA

Table S1 Hydroconversion of ML over Ni-Mo/Al₂O₃ catalysts at 1.5 h.

Mo content / wt%		0	1	2	3	4
Conversion ^{a)} / %		30.7	54.3	75.6	84.2	81.3
Yield ^{a)} / C-%	CO	0.0	0.0	0.4	1.7	3.9
	CH ₄	5.8	9.9	11.1	13.3	9.7
	C ₂ -C ₁₀	2.8	3.2	2.0	2.3	1.1
	C ₁₁	17.7	37.3	56.8	63.5	59.1
	C ₁₂	0.1	0.6	1.4	1.7	3.6
Mo content / wt%		0	2	6	8	
Conversion ^{b)} / %		25.3	24.4	41.7	56.6	
Yield ^{b)} / C-%	CO	0.0	0.4	1.7	3.9	
	CH ₄	5.8	5.0	5.3	7.9	
	C ₂ -C ₁₀	3.9	1.2	0.9	0.7	
	C ₁₁	16.5	16.3	31.3	40.1	
	C ₁₂	0.1	0.3	1.2	3.1	

^{a)} Reaction conditions: cat., 0.5 mL of Ni-Mo/Al₂O₃ (Ni: 10 wt%); 300 °C; 0.4 MPa; H₂/ML = 15; LHSV = 10 h⁻¹.

^{b)} Reaction conditions: cat., 0.15 mL of Ni-Mo/Al₂O₃ (Ni: 20 wt%); 300 °C; 0.4 MPa; H₂/ML = 15; LHSV = 40 h⁻¹.

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Author: Pratyush Agarwal, Nicholas Evenepoel, Sulaiman S. Al-Khattaf, et al

Publication: Energy & Fuels

Publisher: American Chemical Society

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