

**MOLECULAR-LEVEL KINETIC MODELING OF
HYDROPROCESSING FOR GREEN DIESEL PRODUCTION**

by

Thomas Bollen

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

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by

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ABSTRACT

Green diesel is a promising fuel that is becoming more dominant among other types of fuel. It lowers greenhouse gas emissions by 40-90%[\[1\]](#), has higher energy density than petro-diesels, and can be introduced into any diesel engine or infrastructure without many mechanical modifications. The production process of green diesel consists of two reactors in series. Both reactors are followed by a flash drum. The first reactor, removes oxygen by hydrotreating the triglycerides. The result is a paraffin mix with high cetane number and cloudpoint. The second reactor lowers both cetane number and cloudpoint by isomerization and cracking of the paraffins. The latter is a beneficial change, the former is not. Therefore, a trade-off in either good combustion properties vs. good cloud point emerges.

The objective of this thesis is to deduce a kinetic model for both reactors, using Klein research group[\[2\]](#) in-house software. The software is on a molecular level. Both models are fit to experimental data. First, a reaction network is composed. The extent of this reaction network is controlled by specifying reactant for every specific reaction and by adding a max rank restriction on isomerization. The rank of the reaction is equal to the number of reaction steps from the feed molecules. Together, both models consists of 1963 reactions. Second, properties of all species are computed. Third, for all reactions, a reaction rate constant is determined. The number of parameters is drastically reduced from 1190 to 39 (98% less) by using Linear Free Energy Relationships (LFER). Because a catalyst is involved, Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetics are applied.

The parity plot for the product distribution of the 1st reactor has a R^2 value of 0.9979. It does not include temperature dependency. The parity plot for the product distribution of the 2nd reactor has a R^2 value of 0.8291. Also, it concludes temperature

dependency, its R^2 value for the temperature dependent data is 0.9885. By increasing temperature, the isoparaffin content increases. At about 365°C it reaches a maxima and starts to decrease. This can be related with an increasing thermal cracking and therefore a reduced isoparaffin content.

Chapter 1

INTRODUCTION

Because of growing concerns regarding global warming and oil reserves, study is conducted into the development of a cleaner hydrocarbon fuel. Green diesel and biodiesel are a pay off of these efforts. The focus of this thesis is on the former. Both diesels are produced from natural materials, namely triglycerides. Triglycerides are the main constituent of body fat in humans and animals, as well as vegetable fat.

Biodiesel is produced using a transesterification process, presented in Figure 1.1. Vegetable oils or animal fats are reacting catalytically with a short-chained aliphatic alcohol, typically methanol or ethanol. This produces glycerol as a by-product and ethyl esters of fatty acids. Therefore, biodiesel is also referred to as FAME (fatty acid methyl ester)[3].

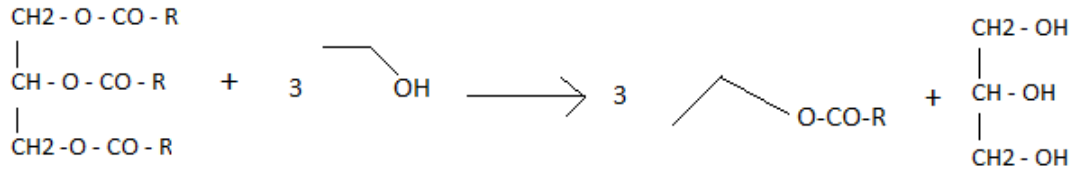


Figure 1.1: Transesterification of triglyceride

Green diesel is a mixture of hydrocarbons, mainly heptadecane and octadecane. It is synthesized by hydroprocessing triglycerides. This already states his main disadvantage: the large consumption of hydrogen increases the production cost. The production process of green diesel will be explained more detailed in Chapter 3.

Two important quality parameters characteristic for diesel are ‘cloudpoint’ and ‘cetane number’. Cloud point refers to the temperature below which wax in diesel starts thickening. The presence of solidified waxes can clog fuel filters and injectors in engines. Cetane number is an indicator of the combustion speed of diesel. It is an inverse of the octane number, a quality parameter for gasoline. Both parameters are greatly influenced by the branching intensity of the paraffins.

Nowadays, the main application of both fuels is as additives to petro-diesel. Biodiesel enhances the lubricity[4] of petro-diesel, while green diesel boost the cetane number. Green diesel can have a cetane number between 65 and 104, what is higher than petrodiesel and biodiesel[4].

In the next Chapter, the objective of this thesis will be further explained. Next, the production process of green diesel will be illustrated more in detail. Chapter 3 discusses molecular kinetic models in general, followed by chapter 5,6 and 7 that discusses 3 different programs used to compose the kinetic model. Chapter 8 explains why an excessive amount of hydrogen is used in the production of green diesel. Subsequently, there is a chapter explaining how the model can be improved in future. Finally, a conclusion is made.

Chapter 2

THESIS OBJECTIVE

This thesis is a small part of a bigger picture. The ultimate goal is to compare petro-, bio- and green diesel via a life cycle assessment (LCA). This is a technique to assess environmental impacts associated with all the stages of a product's life: raw material extraction, materials processing, manufacture, distribution, use, maintenance, and disposal or recycling. Also, at the moment petro-diesel is the most dominant because it is cheaper and its infrastructure is already existing. Therefore, there has to be investigated into potentials to make the bio- and green diesel more competitive.

This focus of the thesis is on green diesel. A small part of its LCA is dependent on cetane number and cloudpoint. As will be explained in Chapter 3, an optimum has to be found between both because doing good for one, does bad for the other. To do so, a kinetic model has to be defined. The latter is exactly what this thesis is about: determine a kinetic model. More specific, the rate constant of every reaction must be derived.

To tackle this problem, kinetic software is used to simulate the process. One way would be using lumped kinetic schemes, i.e. molecules are grouped by physical properties. However, there is chosen to tackle the problem on a molecular level. More specific, the Kinetic Modelers Toolkit (KMT) software is applied, a molecular-level kinetic software. KMT is developed in the Klein research group[2] at the University of Delaware. It consist of several programs, from which three are required to model the green diesel production process.

Obviously, to simulate the process, experimental data is required. As mentioned in the abstract, the process consists of two reactors. The tuning of both reactors is realised by fitting experimental data. The first reactor is based on a paper[5] describing hydrotreatment of Jatropha oil, a triglyceride mix, in a fixed-bed reactor.

The second reactor is based on a paper[6] that discusses isomerization of different paraffin mixtures produced from sunflower oil. They are obtained by hydrotreatment and are isomerized and cracked to green diesel. It might be confusing that this paper mentions 'biofuel', referring to green diesel, and not biodiesel. In future, the kinetic model can be used to predict composition of mixtures obtained by hydrotreating of triglycerides for different feedstocks, reactor conditions, and catalytic systems.

Chapter 3

PRODUCTION PROCESS GREEN DIESEL

The process consists of two steps: hydrotreating followed by hydroisomerization. The first step is executed in a HDO reactor. HDO (Hydrodeoxygenation) is a hydrogenolysis process to remove oxygen from oxygen containing compounds, in this case, the triglycerides. Removing the oxygen atoms is important because oxidation can cause the fuel to become acidic, what is corrosive for the engine. Also, this oxidation can cause the fuel to form insoluble gums and sediments that can plug the filter[8]. However, only using one reactor is not sufficient because a low extent of hydroisomerization occurs. The green diesel obtained directly by the HDO reactor is mainly composed of heptadecane and octadecane. So it has a high cetane number but poor cloud point. To give an idea, pure hepta- and octadecane have a freezing point of respectively 22°C and 28°C.

Therefore, a second reactor is required to boost the quality of the green diesel. In this HI (hydroisomerization) reactor, isomerization and hydrocracking take place. It lowers both cetane number and cloudpoint. The latter is a beneficial change, the former is not. Therefore, a trade-off in either good combustion properties vs. good cloud point emerges. Once green diesel has an improved performance in cold weather, it may be used directly in vehicles. No mechanical changes to the engine has to be made.

Figure 3.1 shows a simplified overview of the reactor set-up.

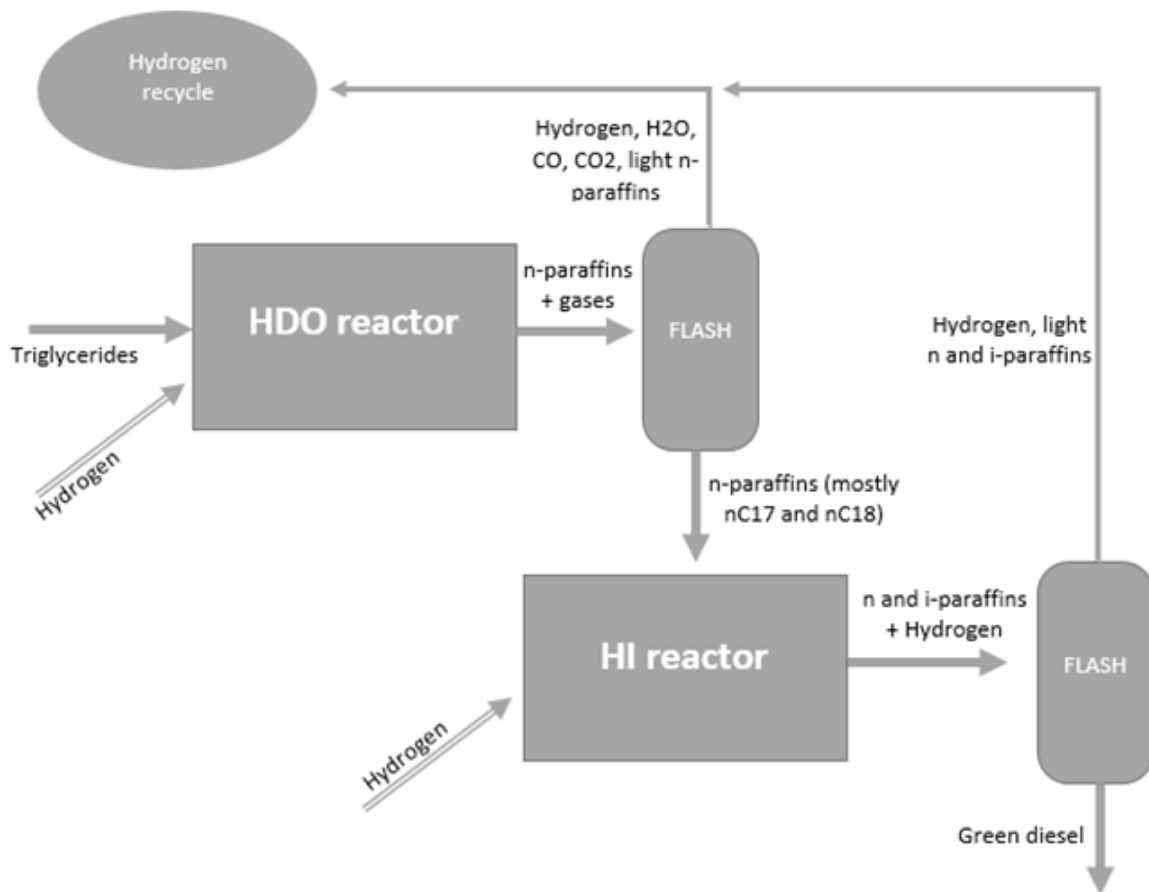


Figure 3.1: Reactor set-up

As can be seen in the set-up, the stream leaving the HDO reactor mentions only ‘n-paraffins + gases’. Note that it also contains some i-paraffins. However, this is not added because the relative quantity is quite low.

3.1 Flash Drum

Figure 3.1 shows two flash drums that recuperate the hydrogen. Also, the 1st flash is an easy way to get the water out. The focus of this thesis is not on this separation technique, so things are simplified. There is assumed the flash is ideal, meaning that every molecule with a boiling point above the flash drum's temperatures evaporates into the gas phase. On the other hand, every molecule with a boiling point lower than this temperature leaves with the flash drum in the liquid stream.

Because the 1st flash is to get rid of the water, its temperature is set slightly above 100°C. Consequently, some light n-paraffins also become evaporated into the gas stream. For the 2nd flash, a debutanizer is used. Butane and all lighter components evaporate. Its temperature is slight above 0°C. Table 3.1 gives a list of all molecules retained in the gas stream of the flash drum.

FLASH 1		FLASH 2	
Species	Boiling point (°C)	Species	Boiling point (°C)
hydrogen	-252.72	hydrogen	-252.72
carbon monoxide	-191.4	propane	-42
carbon dioxide	-78.5	methyl propane	-11.6
propane	-42	butane	0
butane	0		
pentane	36.2		
hexane	69		
heptane	98.5		
water	100		

Table 3.1: Species retained by flash drums

Chapter 4

APPLIED MOLECULAR KINETIC MODELS

Both the HDO and HI reactor are modelled using molecular-level kinetic models. First of all, there is INGen (Interactive Network Generation), software that is capable of building the reaction network. Second, there is PropGen (Properties Generator). PropGen generates properties of components based on group-contribution. Finally, KME (Kinetic Modeling Editor) is used to solve optimized kinetic models of complex processes. Figure 4.1 gives an idea of the underlying relationship and interdependence of the software.

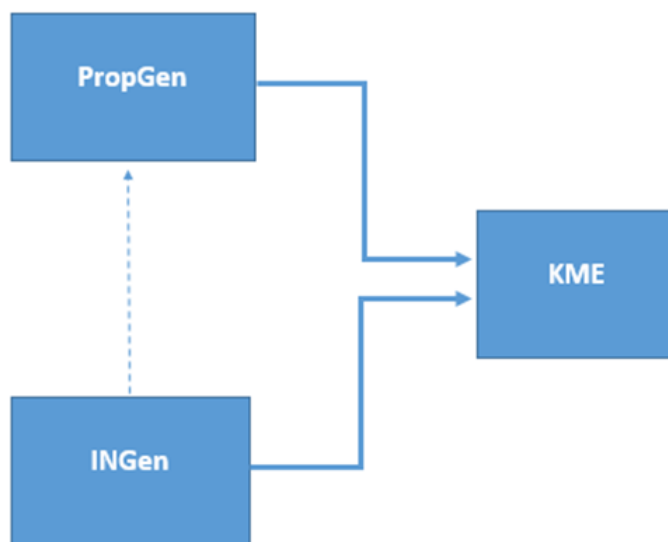


Figure 4.1: interdependence software

A solid arrow means a (full) one way dependence. From the figure is clear that KME relies on the properties and reaction network created by respectively PropGen and INGen. There is a dashed arrow starting from INGen ending in PropGen. This is because PropGen doesn't actually uses the reaction network. It only needs a list of all the molecules created by the network. Therefore this relationship is less strong.

In the following chapters, both the way the software is used and the results are discussed. Also some important assumptions will be mentioned to understand the limitations of the final result. Obviously, these assumptions should have minor influence on the kinetic model. This report will not discuss the detailed working principle of the KMT software.

Chapter 5

INGEN

INGen is used to create a reaction network representing a chemical process and to list all the molecules (reactant, intermediates, and products) involved. There is aimed to build the network as simple as possible, though without distracting from the real-life reaction network. This is done to restrict the growth of the reaction network. Otherwise computing becomes too intense. Furthermore, important to realise is that INGen has nothing to do with quantities. It sums all the molecules involved, also if their appearance is close to zero.

The required input for INGen consists of three things: feed components, reaction families, and restrictions. Figure 5.1 shows a brief overview of inputs and outputs of INGen. All those inputs will be discussed briefly in the following sections.



Figure 5.1: Input and Output INGen

5.1 INPUT

5.1.1 Feed

To start with, the user has to give INGen some chemical components it can use as feed. If the feed components are non-existing in INGen’s species database, they can be added by using Chemdraw[7]. This software is integrated into INGen to visualize the reactions and molecules. Chemdraw prints the chemical components in a Lewis structure. Chemdraw also makes the creation of new species, often required for feed, very user friendly. It allows the user to sketch them.

5.1.2 Reaction Families

INGen consists of some pre-programmed reaction families. A reaction family represents one specific type of reaction. For example, INGen’s reaction family having the name ‘decarboxylation’ removes a carboxyl group and releases carbon dioxide (CO_2) from its reacting component. Adding a new reaction family requires an experienced user. First of all, the user should know how to use the code language C#. Second, it should think of a consistent way to translate a chemical reaction into a mathematical algorithm.

5.1.3 Restrictions

INGen allows to add some standard restrictions. Only one of them is used in this model, namely: ‘Max Rank’. This parameter determines the max rank of the concerned reaction family. The rank of the reaction is equal to the number of reaction steps from the seed molecule. For reactions as hydroisomerization for instance, the reaction network can grow very broad. To restrict this growth, the number of reaction steps from the seed molecule (max rank) is specified. This is a valid assumption because the experimental data used for the HDO product stream and the HI reactant stream only has an isoparaffin content of respectively 6.89%[5] and 0.75%[6]. Therefore, it is

unnecessary to give INGen the opportunity to unlimitedly branch the paraffins.

Another way to limit the extent of the reaction network is by specifying reactant for every specific reaction family. For example, hydrocracking involves the formation of a carbenium ion[9]. The stability of this ion is determined by the number of bonds the ion has with carbon atoms. For an i-paraffin, this are three bonds, so you have a tertiary carbenium ion. For a n-paraffin it are only two bonds, resulting in a binary carbenium ion. The tertiary one is more stable, so is energetically favored. Therefore, hydrocracking will occur mostly on i-paraffin and less on n-paraffins. Hence, commanding the model to execute hydrocracking only on iso-parraffins is acceptable. Not doing this would only make the network unnecessarily complicated.

5.1.4 Applied Input For Reactors

HDO reactor

The feed of the HDO reactor is Jatropha oil, which consists of five triglycerides[5]: Trigondoin, Trilinolein, Triolein, Tripalmitin, and Tristearin. However, more triglycerides are added in INGen to keep the model generic and usable for other feedstocks. Table 5.1 lists all triglycerides used.

Name	Composition
Triarachidin	C20DB0
Tribehenin	C22DB0
Tricaprin	C10DB0
Trierucin	C22DB1
Trigondoin	C20DB1
Trilaurin	C12DB0
Trilignocerin	C24DB0
Trilinolein	C18DB2
Trimyristin	C14DB0
Triolein	C18DB1
Tripalmitin	C16DB0
Tripalmitolein	C16DB1
Tristearin	C18DB0
Linolenic (variant)	C18DB3_C18DB0_C18DB0
hydrogen	H2

Table 5.1: Feed components (triglycerides) HDO reactor

The composition of the triglyceride is formulated as ‘C_xDB_y’, where x denotes the amount of carbon atoms in a fatty acid tail, and y denotes the amount of double bonds in this tail. As an example, C₁₈DB₁ (Triolein) is pictured in figure 5.2.

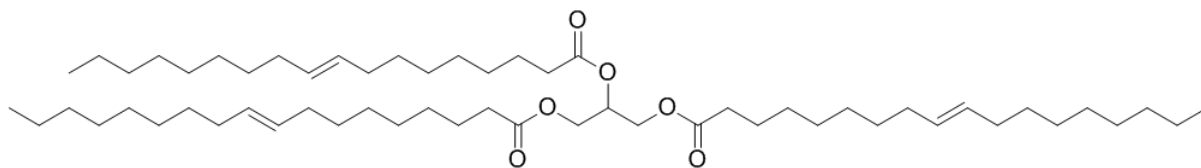


Figure 5.2: Lewis structure Triolein, C₁₈DB₁

The triglyceride ‘Linolenic’ is simplified. Instead of three tails with three double bonds each, only one tail has been given three bonds (C18DB3_C18DB0_C18DB0, see Figure 5.3). The number of double bonds is the number of combinations possible for hydrogenation. If there are 9 double bonds, it would be 9! (9x8x...x2x1=362880). So this simplification makes the computing for INGen faster. Because Linolenic is usually present in very low quantity in common a triglycerides mixtures, this simplification does not affect the result. The highest quantity encountered is 7.9wt% in Canola oil[4].

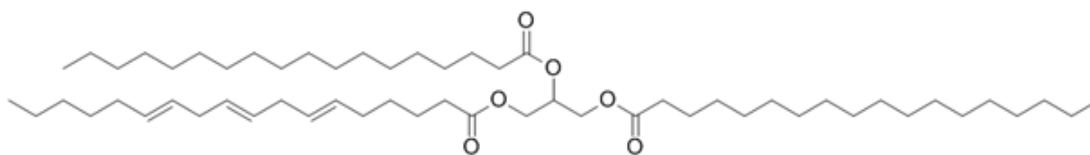


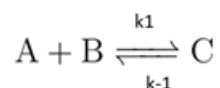
Figure 5.3: Lewis structure Linolenic(simplified), C18DB3_C18DB0_C18DB0

The selected reaction families with their restrictions are listed in Table 5.2. There is only a max rank restriction on hydroisomerization. The validity of this is discussed in the previous subsection. Notice that all following tables will mention ‘cracking’. To clarify, hydrocracking is meant with it, not thermal cracking. Same for isomerization, which is actually hydroisomerization.

HDO	REACTION	REACT WITH	RESTRICTIONS
with H2:	Triglyceride hydrogenolysis	All species	/
	Hydrogenation (eq. rxn)	All species	/
	Hydrodeoxygenation	All species	/
	Decarbonylation	All species	/
	Cracking	Iso-Paraffins	/
without H2:	Decarboxylation	All species	/
	Isomerization (eq. rxn)	N-Paraffins	max Rank: 4

Table 5.2: Reaction families HDO reactor

Note that hydrogenation and isomerization are coded as an equilibrium reaction. The other reactions are assumed to be one-way. The validity of this precondition, can be confirmed by equilibrium constant K_{eq} . Using micro kinetics:



$$\frac{d[A]}{dt} = -k_1[A][B] + k_{-1}[C] \quad (5.1)$$

$$\frac{d[A]}{dt} = -k_1[A][B] + \frac{k_1}{K_{eq}}[C] \quad (5.2)$$

$$\frac{d[A]}{dt} = k_1(-[A][B] + \frac{1}{K_{eq}}[C]) \quad (5.3)$$

If K_{eq} is big, the last term becomes zero. So high equilibrium constant implies a one-way reaction. However, those constants are determined only after using KME. They will be presented in Chapter 8 in Table 8.1. K_{eq} will turn out to be bigger than $O(10^3)$ for all reaction except isomerization. Therefore the assumption is valid.

There can be concluded this assumption is all right, the equilibrium constants of those reaction are indeed the smallest. Also K_{eq} for cracking is quite small. However, this reaction occurs mostly in one direction. A molecule that is cracked will not easily become repaired.

HI reactor

To make a 100% consistent model, the feed of the HI reactor should be the paraffins of the HDO reactor's output. However, this is not possible because experimental data for a HI reactor for this specific paraffin mixture is not available. Instead, a paraffin mixture produced from sun flower oil is used. This mixture comprises mainly n- and i-paraffins between 14 and 19 carbon atoms. The i-paraffins are subdivided in a mono-branched and multi-branched group. The used feed components in INGen are listed in Table 5.3.

Name	Composition
n-pentadecane	C15H32
n-hexadecane	C16H34
n-heptadecane	C17H36
n-octadecane	C18H38
i-pentadecane (mono)	C15H32
i-pentadecane (multi)	C15H32
i-hexadecane (mono)	C16H34
i-hexadecane (multi)	C16H34
i-heptadecane (mono)	C17H36
i-heptadecane (multi)	C17H36
i-octadecane (mono)	C18H38
i-octadecane (multi)	C18H38
hydrogen	H2

Table 5.3: Feed components (paraffin mixture) HI reactor[6]

The HI reactor only consists two reaction reaction families. They are presented with their restrictions in Table 5.4. Again, isomerizaion is restricted with a max rank with the same explanation as for the HDO reactor.

HI	REACTION	REACT WITH	RESTRICTIONS
with H2:	Cracking	Iso-Paraffins	/
without H2:	Isomerization (eq. rxn)	N-Paraffins	max Rank: 5

Table 5.4: Reaction families HI reactor

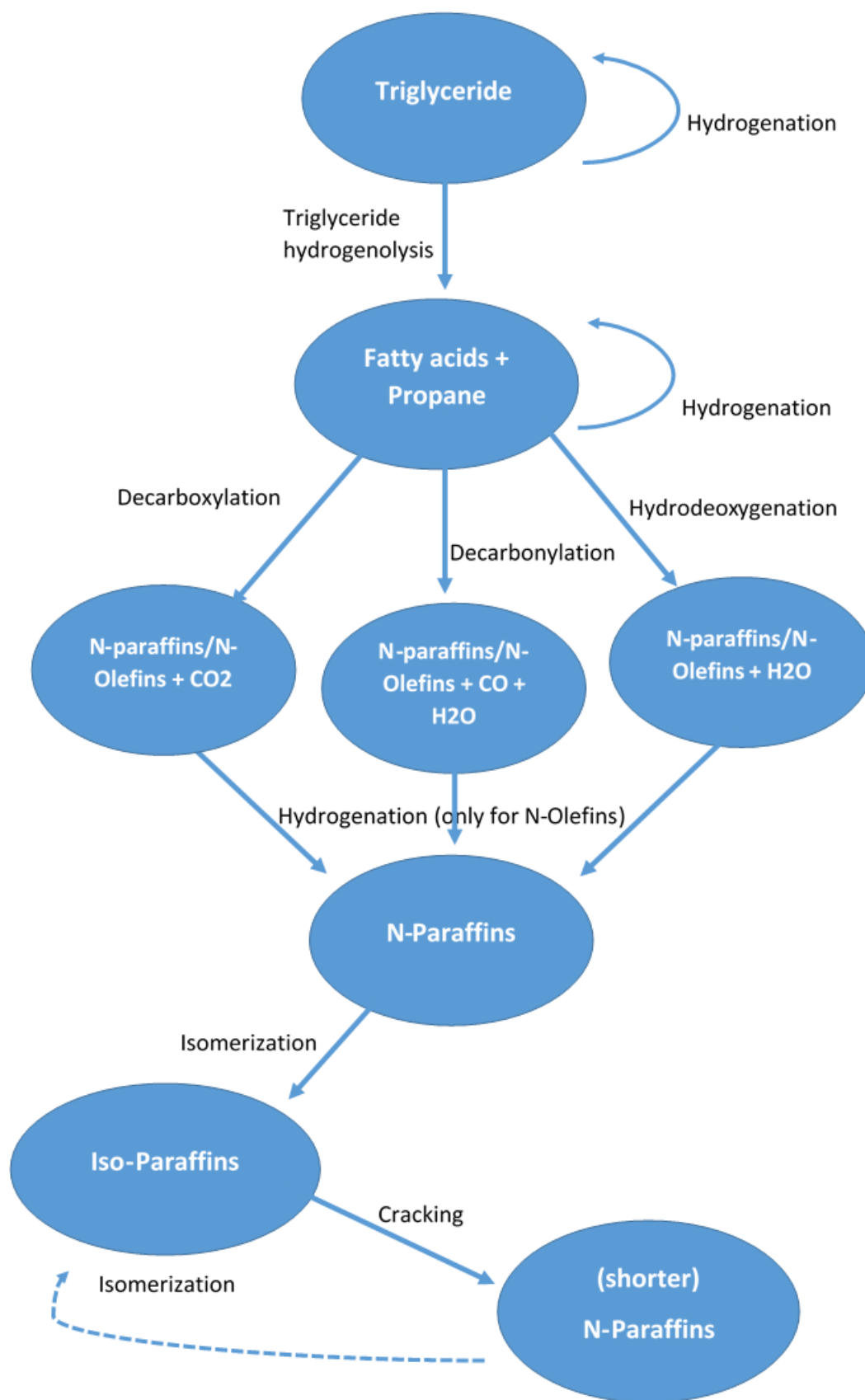
5.2 OUTPUT

In this section, the results of both INGen models will be further explained.

5.2.1 HDO reactor

The reaction network INGen creates, consist usually of a several hundred reactions. Figure 5.4 gives a general overview of the reactions that occur. Most of them take place in a consecutive order. Except for hydrogenation, this reaction can act on all species with a double bond.

The dashed arrow in the end shows a reaction that would occur on a small scale in real life. However, because this model has given isomerization a max rank of 4, this reaction does not take place in INGen's reaction network.



19
Figure 5.4: General reaction network HDO

To give an idea what atom transfers are occurring, the first five ovals of the reaction network are applied on the triglyceride Triolein in Figure 5.5.

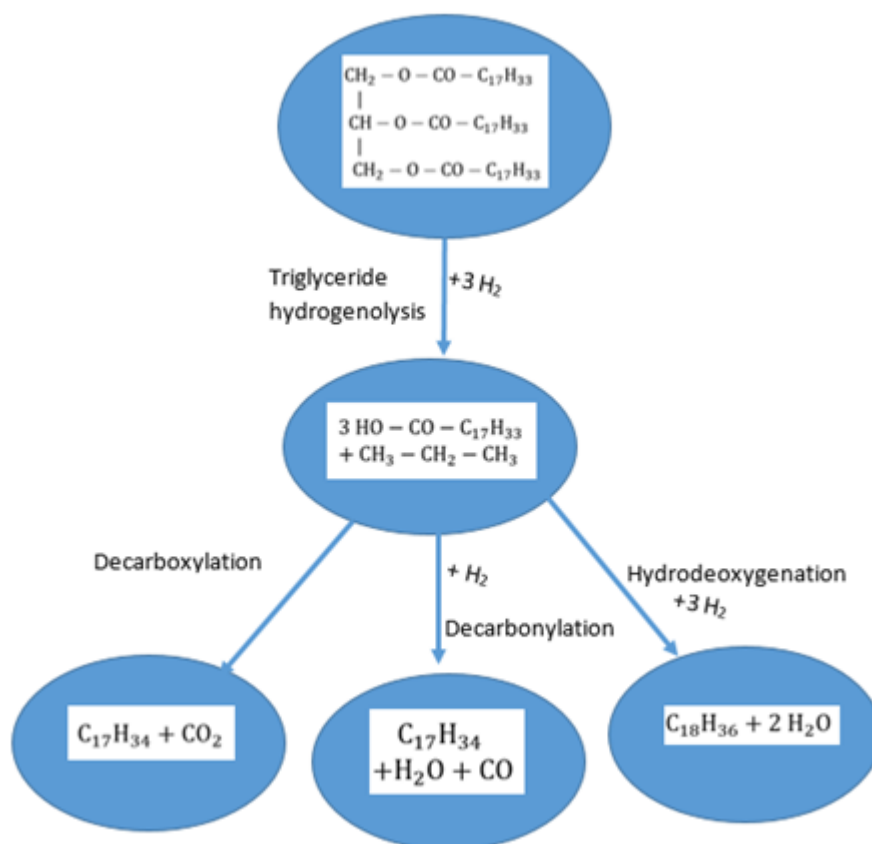


Figure 5.5: Molecular reactions occurring in hydroconversion of triolein

For this example, there is assumed hydrogenation will occur after decarboxylation, decarbonylation, or hydrodeoxygenation. Notice that there are three different pathways: decarboxylation, decarbonylation, or hydrodeoxygenation.

The product of decarboxylation and decarbonylation (heptadecane) has one carbon atom less than the parent fatty acid, while the product of hydrodeoxygenation (octadecane) has the same number of carbon atoms. In addition, Table 5.1 showed that

all triglycerides of the HDO model have an even number of carbon atoms. Therefore, if the fatty acids originated from the oil only consist of triglycerides with max 18 carbon atoms, the C18/C17 ratio is a way to determine the dominant pathway[5]. Figure 5.5 shows a possible continuation of reaction path for Triolein via decarboxylation. It shows that, via isomerization and cracking, a product following one of the three pathways can lose at least three carbon atoms. It can't lose one atom, because that would involve forming a primary carbenium ion, what is energetically not favorable. Therefore, there can be concluded for sure that all C17 and C18 paraffins originate from respectively decarboxylation/decarbonylation or hydrodeoxygenation. Using a C16/C15 ratio is not possible because there is a possibility C15 paraffins are derived from C18 paraffins.

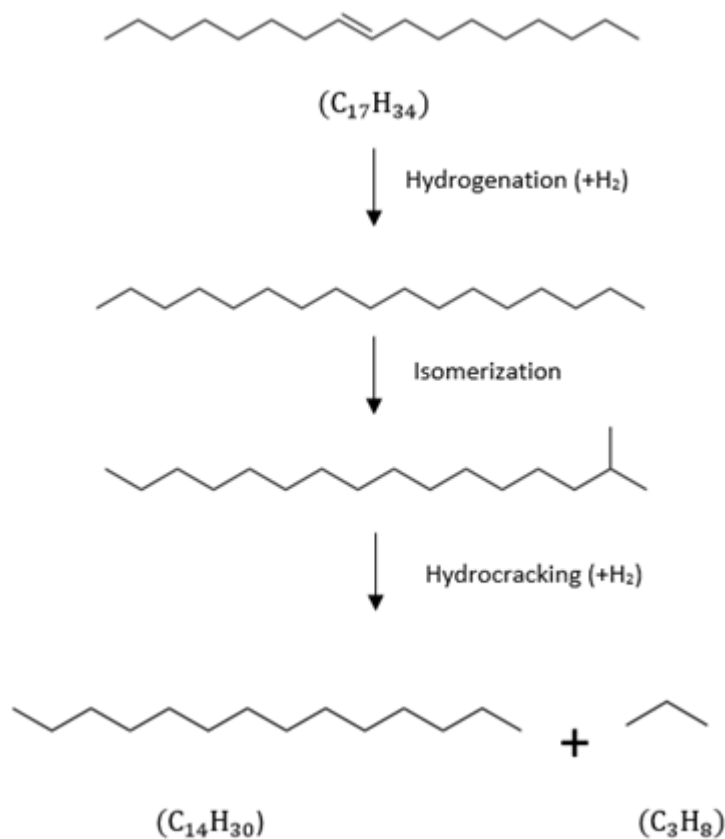


Figure 5.6: Continued decarboxylation pathway of Triolein

To check whether decarboxylation or decarbonylation is most dominant, the CO₂/CO ratio of the product distribution can be used because they are the only reactions that produce CO₂ or CO.

Table 5.5 presents the absolute count of each reaction (excluding adsorption and desorption reactions on catalyst) and the total species count. Note that the equilibrium reactions occur in both directions, so they have to be counted double for total reaction count. As should be the case, decarboxylation, decarbonylation, and hydrodeoxygenation have the same count.

HDO	REACTION	COUNT
with H2:	Triglyceride hydrogenolysis	66
	Hydrogenation (eq. rxn)	173
	Hydrodeoxygenation	18
	Decarbonylation	18
	Cracking	184
without H2:	Decarboxylation	18
	Isomerization (eq. rxn)	112
	Total reaction count:	874
	Total species count:	85

Table 5.5: Reaction en species count HDO

5.2.2 HI reactor

Figure 5.7 gives a general overview of the reactions that occur in the HI reactor

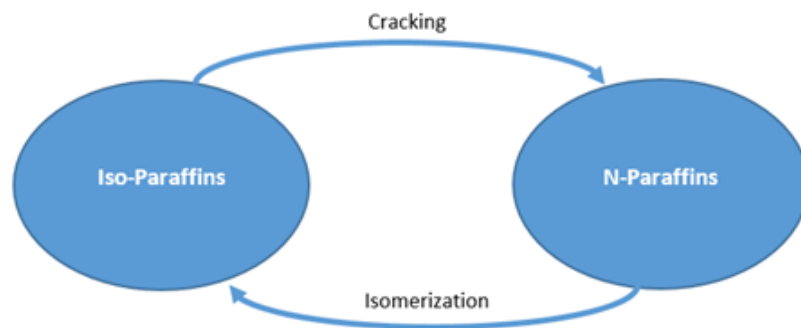


Figure 5.7: General reaction network HI

Table 5.6 presents the absolute count of each reaction (excluding adsorption and desorption reactions on catalyst) and the total species count.

HI	REACTION	COUNT
with H2:	Cracking	103
without H2:	Isomerization (eq. rxn)	64
	Total reaction count:	231
	Total species count:	85

Table 5.6: Reaction en species count HI

Ingen shows the rank of every species. After studying this data, it is noticed that the max rank obtained is 3. This implies the restriction of ‘max rank 5’ for isomerization is unnecessary. After 3 consecutive reactions on a seed, all possible combinations have already been formed. To verify this, table 5.7 sums all possible combinations for forming a new i-paraffin. Every combination is unique, all symmetric molecules are taken out. Also, forming new multi-branched species is not possible, only mono-branched species are formed. The exception are the i-paraffins with a carbon number 15 up to 18, they have ‘+1 combination’ because there exists a multi-branched form of them in the feed.

Carbon atoms	Combinations	Carbon atoms	Combinations
2	0	11	4
3	0	12	5
4	1	13	5
5	1	14	6
6	2	15	6+1
7	2	16	7+1
8	3	17	7+1
9	3	18	8+1
10	4	SUM	68

Iso-Paraffins	68
N-paraffins	17
Total species	85

Table 5.7: max number of species

The max number of unique i-paraffins and n-paraffins formed is respectively 68 and 17. So in total, max 85 paraffins can be included in the model, which is exactly the same as the total species count (see Table 5.6). This proves the statement that INGen is done creating the entire reaction network after reaching rank 3.

Chapter 6

PROPGEN

PropGen generates properties of pure components based on group-contribution. Therefore, the result for small components is not accurate. For them, online sources as NIST[10] and Cheric[11] are consulted. They provide a large database of properties for many components. Their values have to be added manually.

Figure 6.1 gives an overview of input and output of PropGen.



Figure 6.1: Input and Output PropGen

6.1 INPUT

In this chapter, there is not made a distinction between HDO and HI reactor because both have exactly the same approach. PropGen generates all properties for the species it receives from the INGen file. As mentioned, small species are added manually. They are listed in Table 6.1.

Manually added	
Hydrogen	Butane
Water	Pentane
Carbon monoxide	Hexane
Carbon dioxide	Heptane
Propane	Octane

Table 6.1: Manually added species in PropGen

The main difference between Cheric and NIST is that the former is more user friendly, though NIST is more correct. However, both sources are consulted and their results corresponds well. Cheric is reliable enough for non-exotic species such as listed in [Table 6.1](#).

6.2 OUTPUT

PropGen returns a table with all possible properties. These are used by KME. Carefully, PropGen and KME use different units, so some values have to be converted.

Chapter 7

KME

After reaction network generation and properties determination, the final step is to build the reactor model. The main purpose of KME is to determine all the reaction rate constants by fitting experimental data. Therefore, it is in KME that quantities of the species show up for the first time.

The basis of this model is a large system of ODEs (ordinary differential equations) with 1 material balance per species and an overall energy balance. KME automatically writes these equations for the given reaction network and process conditions, e.g. reactor type, feed, temperature, input flow rates/concentrations, etc.

These equations make us of a certain rate law, for which KME offers a choice between 3 types: law of mass-action (micro kinetics), power-law, and Langmuir-Hinshelwood-Hougen-Watson (LHHW) model. Our process consist of catalytic reactions, what implies LHHW has to be used. More information about this is given in the next section.

KME can work in two modes: simulation or tuning mode. The former is a once through solution. It solves the equations taking the given inputs (including kinetic parameters) into account, and returns product flow rates and properties, reaction rates, etc. This allows the user to compare KME's solution with experimental data to evaluate the obtained output. Second, the tuning mode minimizes a chosen objective function by randomly changing a set of kinetic parameters within boundaries which are selected by the user. It repeatedly solves the kinetic model, as in simulation mode, to optimize these kinetic parameters.

When tuning, it is essential to start from nearly-correct values of rate constants or the solver may not find a global minimum. This can be done by relying the initial

conditions on literature ones and by manually tuning in simulation mode before going to tuning mode. This way, KME can find the best fit of the model to the experimental data.

Reducing number of parameters by LFER

An important concept involved in both modes is Linear Free Energy Relationships (LFER). The HDO model contains 874 reactions ($O(10^2)$), but some models can go even up to $O(10^4)$ reactions. Every reaction rate consists of two parameters, the pre-exponential factor (A_i) and the activation energy (E_i). Their relationship is described via the Arrhenius equation:

$$\log(k_i) = \log(A_i) - \frac{E_i^*}{2.303RT} \quad (7.1)$$

with: i = reaction

This implies several thousand parameters for one model, what results into two problems. First, if the number of adjustable parameters is greater than the number of measurements, it is impossible to obtain a unique solution. Second, there is danger of overfitting. An overfitted model will have poor predictive performance, it describes random error or noise instead of the underlying relationship. It generally occurs when a model has too many parameters relative to the number of observations. In essence, tuning would become impossible because of both the amount of required data and computational complexity.

Therefore LFER comes in, its major impact is the massive reduction in the number of adjustable parameters. The basic assumption of LFER's is that the rate constants of reaction families are dependent on the thermodynamic properties of the reactants and products. This is based on a phenomenon that is observed in literature[12][13][14].

More specific, KME uses the the Bell-Evans-Polanyi[15][16] LFER:

$$E_{i,j}^* = E_j + \alpha_j \cdot \Delta H_{rxn,i} \quad (7.2)$$

with: i = reaction, and j = family

This relation correlates the activation energy ($E_{i,j}^*$) of a given *reaction* i in a *reaction family* j , to the reaction enthalpy ($\Delta H_{rxn,i}$). E_j is the standard activation energy for *reaction family* j . Also α_j is a parameter specific to a reaction family. It gives weight to the only reaction specific value $\Delta H_{rxn,i}$, which is determined by the enthalpy of the reactants and products. If α_j is zero, all reactions within a reaction family have the same value for activation energy.

Next, the pre-exponential factor of equation (7.1) is assumed to be only dependent of the reaction family[12]:

$$A_{i,j} \rightarrow A_j \tag{7.3}$$

Substitution of equation (7.2) and (7.3) into (7.1) results in

$$\log(k_{i,j}) = \log(A_j) + \frac{\alpha_j}{2.303RT} \cdot \Delta H_{rxn,i} - \frac{E_j}{2.303RT} \tag{7.4}$$

with: i = reaction, and j = family

As the only reaction specific parameter left ($\Delta H_{rxn,i}$) is determined by Prop-Gen's values for enthalpy of reactants and products, it is clear that the number of adjustable parameters is massively reduced. The total set of adjustable parameters are three per reaction family: $\log(A_j)$, α_j , and E_j . However, one may note that it becomes impossible to discriminate between $\log(A_j)$ and E_j if all experimental data is at a single temperature.

Table 7.1 summarizes the reduction in number of parameters using LFER. Recall from Table 5.5 and 5.6 the 'total reaction count', representing 'non-adsorption reactions' here. The number of parameters is reduced with 99%. However, don't forget that KME only uses 5 of the fourteen seeds assigned to INGen for HDO (Table 5.1). So

actually the reduction is less. Taking 5/14th of the number of reactions of HDO, it yields a total reactions of 959, so a reduction of approximately 98%.

Initially		with LFER	
	HDO HI		HDO HI
non adsorption reactions	874 231	reaction families	8 2
adsorption reactions	688 170	adsorption constants	2 1
TOTAL REACTIONS	1963	TOTAL EXPRESSIONS	13
parameters for each reaction	2	parameters for each expression	3
TOTAL PARAMETERS	3926	TOTAL PARAMETERS	39

Figure 7.1: Reduction of parameters using LFER

Figure 7.2 shows a brief overview of inputs and outputs of KME. Those will be discussed in the following chapters.

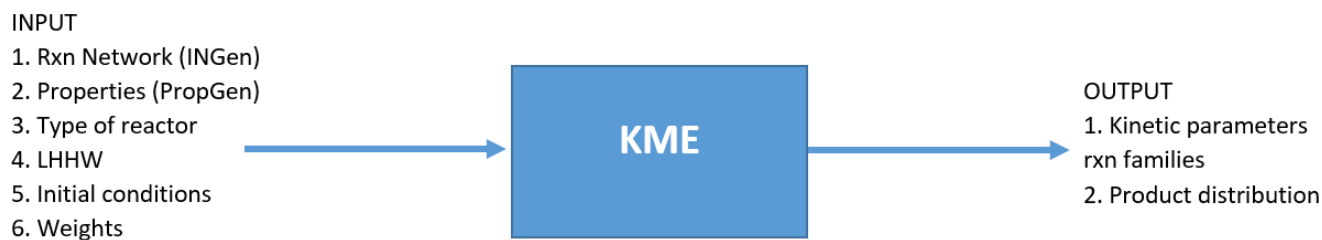


Figure 7.2: Input and Output KME

7.1 INPUT

7.1.1 Type of Reactor

KME offers the choice between several types of reactors. For both the HDO and the HI reactor, the experimental data is valid for a PFR. However, KME has an important limitation: it treats every feed as if it is a gas. Therefore a liquid feed can cause implications. For both reactors, temperature and pressure are more or less 350°C and 30 atm[5][6]. The temperature is quite elevated, nonetheless, the pressure is that high that there can be assumed the feed is a liquid. Therefore the volumetric flow rate q [$\frac{m^3}{s}$] should be more or less constant. If KME treats the feed as a gas, q would not be constant at all because of changing mole quantities.

As already mentioned, the model consists of 1 material balance per species and an overall energy balance. This material balance for a PFR in steady state is[12]:

$$\frac{dF}{dV} = \sum_i^{n \text{ reactions}} \bar{v}_i \cdot r_i \quad (7.5)$$

with F denoting molar flow [$\frac{mol}{s}$] of every specific molecular species, V the volume [m^3], \bar{v}_i stoichiometric coefficients, and r_i reaction rate [$\frac{mol}{s \cdot m^3}$] of reaction i .

Because q is constant: $F = q \cdot dC$, with C denoting molar concentration [$\frac{mol}{m^3}$]. This simplifies equation (7.5) to:

$$q \cdot \frac{dC}{dV} = \sum_i^{n \text{ reactions}} \bar{v}_i \cdot r_i \Leftrightarrow \frac{dC}{dt} = \sum_i^{n \text{ reactions}} \bar{v}_i \cdot r_i \quad (7.6)$$

The latter is the material balance for a batch reactor. Position in a PFR is equivalent to time in a batch reactor. So by using a batch instead of a PFR, KME is forced to suppose q is constant. Therefore, there is chosen to execute the model in a batch reactor. Obviously, there should not be forgotten to convert the initial conditions:

molar flow rates [mol/s]	→	molar concentration [mol/L]
diameter [dm] + reactor length [dm]	→	reactor volume [L]
reactor volume [L] + volumetric flowrate [L/s]	→	reaction time [s]

7.1.2 LHHW and Bifunctional Catalyst

LHHW For both reactors, the reaction takes place on a catalyst site. Nowadays, the most common way to describe the kinetics of catalysis is through the Langmuir-Hinshelwood-Hougen-Watson (LHHW) theory[12]. LHHW is generally formulated as[17]:

$$r = \frac{(kinetic\ group)(driving\ force\ group)}{(adsorption\ group)^n} \quad (7.7)$$

A simplistic overview of this reaction mechanism is depicted in Figure 7.3. It is valid for the reaction $A + B \rightarrow C$. It consist of three consecutive steps:

1. A and B adsorb to catalyst surface L
2. Reaction occurs at catalyst surface, an adsorbed product species is the result
3. Product species desorbs from catalyst surface

Kinetics can be controlled by any of these three step. In KME, surface reaction control is applied.

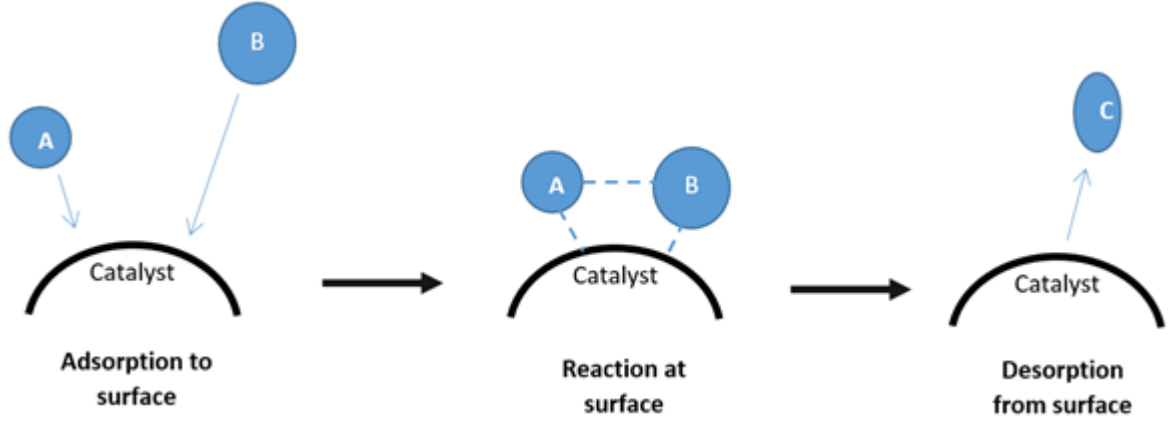


Figure 7.3: Catalytic reaction mechanism[12]

The reaction rate constant of adsorption and desorption on the catalyst site is formulated through K_{ad} , the adsorption equilibrium constant. It is the ratio of both reaction rate constants. K_{ad} is formulated as:

$$\log(K_{ad}) = A_j + \frac{B_j \cdot CN_i + C_j \cdot ON_i}{R.T} \quad \text{with } K_{ad} = \frac{k_{adsorption}}{k_{desorption}} \quad (7.8)$$

with: i = reaction, j = family, CN = carbon number, ON = oxygen number. KME tunes on the parameters A_j , B_j , and C_j .

Bifunctional Catalyst

Characteristic for production of green diesel is the use of a bifunctional catalyst. This is a catalytic substance that possesses two catalytic sites. There is an acid and a metal (base) site. Although most of reactions are only supported by one site, it might occur

that a reaction can take place on both acid and metal site[4]. This is not only dependent on reaction type, another important influence is the ratio of availability of acid sites to metal ones. However, KME requires to assign every reaction family to one of the two sites. This means a simplification of the real life situation must be made by choosing one of the two sites. Table 7.1 shows the assigned catalyst sites in KME.

REACTION	CATALYST SITE
Triglyceride hydrogenolysis	acid
Hydrogenation (eq. rxn)	metal
Hydrodeoxygenation	metal
Decarbonylation	acid
Cracking	acid
Decarboxylation	acid
Isomerization (eq. rxn)	acid

Table 7.1: Catalyst site in KME[4][18]

7.1.3 Initial Conditions: feedstock and reactor conditions

HDO reactor

The feed for the HDO reactor is Jatropha oil, which consists of triglycerides. Through hydrogenolysis, these are converted into three fatty acid molecules and a propane. Linoleic, oleic, palmitic, stearic, and gadoleic acid are the fatty acids mainly found in Jatropha oil. The fatty acid composition of Jatropha oil and their contents are presented in Table 7.2. The notation ‘CxDBy’ denotes the same as is explained for Table 5.1, x denotes the amount of carbon atoms and y denotes number of double bonds. The fatty acids with 16, 18 or 20 carbon atoms have a content of respectively 15.56%, 84.21%, and .23%. The saturated and unsaturated fatty acid contents are respectively 22.85% and 77.15%.

Fatty acid	Structure	Formula	Composition (C%)
palmitic acid	C16DB0	C16H32O2	15.56
linoleic acid	D18DB2	C18H32O2	34.06
oleic acid	C18DB1	C18H34O2	42.86
stearic acid	C18DB0	C18H36O2	7.29
gadoleic acid	C20DB1	C20H36O2	0.23

Table 7.2: Fatty acid composition of Jatropha oil[5], HDO reactor

The reactor conditions for a batch type HDO reactor are listed in Table 7.3. It is important to note that the process is executed isothermal.

HDO REACTOR	
Temperature [°C]	350.15
Pressure [atm]	29.61
Reaction Time [s]	1800
Volume [L]	0.0020096
Volumetric ratio H2/feed	600

Table 7.3: Initial conditions HDO[5], Batch

HI reactor

The feed for the HI reactor consists of a paraffin mixture produced from sunflower oil. This oil is mainly composed out of palmitic acid 4.5%, stearic acid 2.1%, oleic acid 63.2%, linoleic acid 20.6%, linolenic 6.8%, and other carbon acids 2.8%.

The content of the paraffin mixture is presented in Table 7.4. The content consists of several hydrocarbon-groups nC_x or iC_x . Such a group consists of hydrocarbons with the same amount of carbon atoms x , and hydrocarbons in one group are all n (no

branches) or i (branched). E.g. ‘iC16’ is equivalent for all hydrocarbons composed of 16 carbon atoms and at least one branch. ‘nC14minus’ denotes all paraffins with 14 or less carbon atoms. The mixture has an isoparaffin content of 0.75%.

Hydrocarbon-group	mol% (at 360°C)
nC14minus	1.80
nC15	3.10
nC16	3.15
nC17	47.30
nC18	43.90
iC14minus	0.07
iC15	0.05
iC16	0.04
iC17	0.26
iC18	0.33

Table 7.4: Composition of paraffin mixture produced from sunflower oil[6], HI reactor

The reactor conditions for a batch type HI reactor are listed in Table 7.5. It is important to note that the process is executed isothermal.

HI REACTOR	
Temperature [°C]	360
Pressure [atm]	39.48
Reaction Time [s]	3600
Volume [L]	0.1
Volumetric ratio H2/feed	400

Table 7.5: Initial conditions HI[6], Batch

Catching the eye might be the fact that the volume of the HDO reactor is more or less 50 times smaller compared to HI. The reason for this is explained in Appendix B.

Furthermore, KME can have numerical difficulties with solving the material balances due to poorly initial conditions. First, very small (close to zero) numerical values of reactants [mol/L] can cause issues. For example, the HDO model species range from $O(10^{-1})$ up to $O(10^{-4})$ (excluding hydrogen). This causes a physically impossible result when using simulation mode as some of the products molar concentration becomes negative. To solve this, the model is scaled up. Specifically in this model, all triglycerides concentrations are multiplied with 10^4 . Obviously, the volume has to be scaled up with the same magnitude as well. This results in mathematically the same result if product concentrations are divided by the same factor in the end. The HI model does not have this problem.

Second, there is the possibility that the set of differential equations becomes too stiff due to the relatively very high quantity of hydrogen. A stiff equation is one for which certain numerical methods for solving them become numerically unstable. To tackle this, one could make the step size smaller, what implies slower computations. Another possibility is choosing a lower quantity of hydrogen in KME to avoid stiffness. However, this should be done carefully because several reactions (e.g. hydroisomerization) are promoted by hydrogen pressure. So lowering the quantity could affect the final result of the kinetic parameters.

7.1.4 Objective Function

As mentioned, KME's tuning mode minimizes a chosen objective function by randomly changing a set of kinetic parameters. The objective function is a measure of how well the output stream matches experimental measurements. KME uses a least

squares objective function:

$$f(\bar{x}) = \sum_i^{\text{experimental data}} \left(\frac{y_{\text{exp data}} - y_{\text{kme}}(\bar{x})}{w_i} \right)^2 \quad (7.9)$$

with: $f(\bar{x})$ denoting the objective function, \bar{x} the kinetic parameters, $y_{\text{exp data}}$ the experimental output data, y_{kme} the corresponding data from KME, and w_i the weight placed on a data point.

The user can arbitrarily set the weight for each data point. A common way to set this value, is by taking the exact same value as the experimental data. In this case, each term in the objective function becomes a measure of relative error. Therefore all experimental data, regardless of their magnitude, are equally weighted. However, for this model it is preferred to give more weight to species present in high quantity [mol/l]. Therefore, they are given small w_i values, what makes them more significant for the objective function.

7.2 OUTPUT

Kinetic parameter tuning allows the model to match experimental data. The initial guesses of kinetic parameters are of paramount importance for the tuning procedure. Initial guesses can be obtained by analyzing the experimental data and applying prior chemical knowledge. For example, it would make sense that most triclycerides are broken down into fatty acids. Therefore it is advisable to start with relatively big $\log(A)$ values for the reaction family ‘triglyceride hydrogenolysis’.

7.2.1 HDO reactor

There is no experimental data on each specific isomer in the reactor. Only data of liquid hydrocarbon product composition (in C%) in terms of hydrocarbon-groups is available. Every hydrocarbon-group consists of hydrocarbons with the same amount of

carbon atoms, and hydrocarbons in one group are all n (no branches) or iso (branched). E.g. 'iC16' is equivalent for all hydrocarbons composed of 16 carbon atoms and at least one branch. Figure 7.4 shows a parity plot of the product composition. The coefficient of determination (R^2) for a linear trendline equals 0.9979.

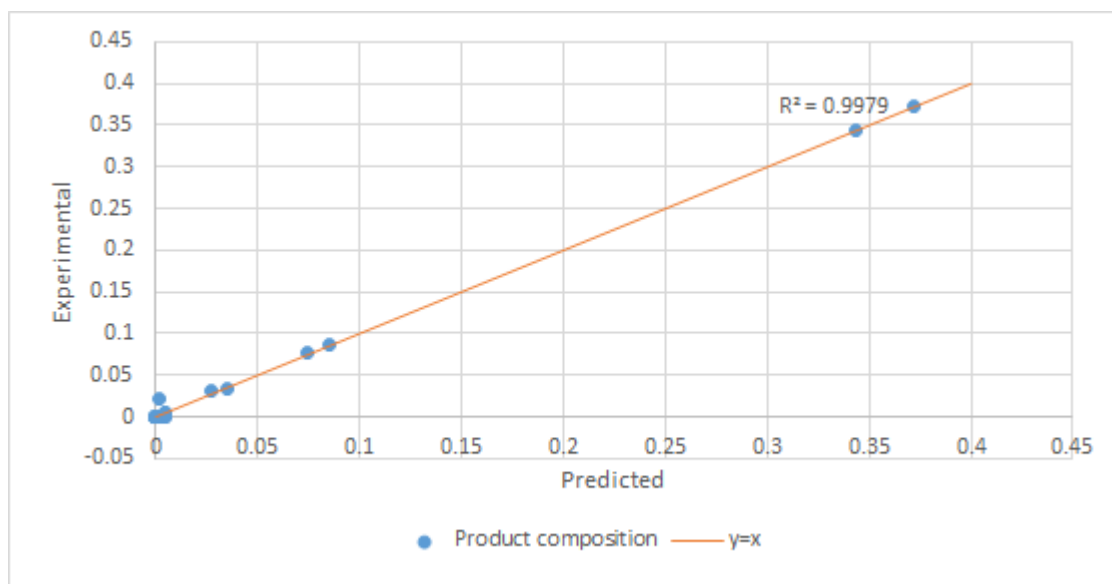


Figure 7.4: Parity Plot product composition hydrocarbon-groups HDO reactor[5]

To give a better overview of the datapoints close to the origin, there is zoomed-in on this region in Figure 7.5.

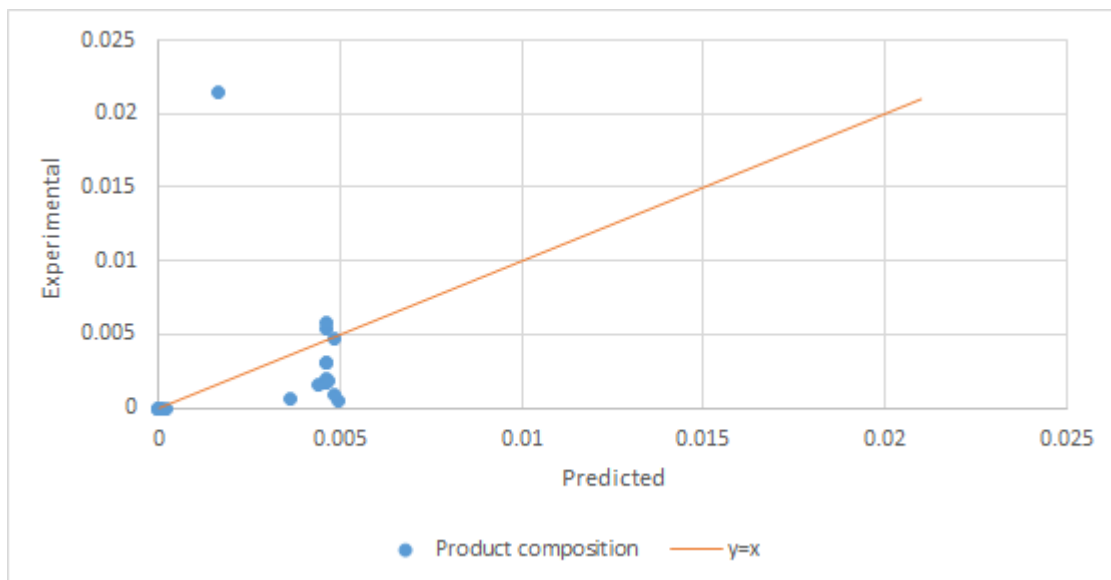


Figure 7.5: Zoomed-in Parity Plot product composition hydrocarbon-groups HDO reactor[5]

To compare the hydrocarbon-groups mutually, the absolute error (in C%) between the predicted and experimental value is studied. The absolute error is defined as:

$$absolute\ error = |predicted\ value - experimental\ value| \quad (7.10)$$

Figure 7.6 shows the share of the 4 hydrocarbon-group with the highest error, the 10 that are having one between 0.001 and 0.003, and the 18 that have one smaller than 0.001.

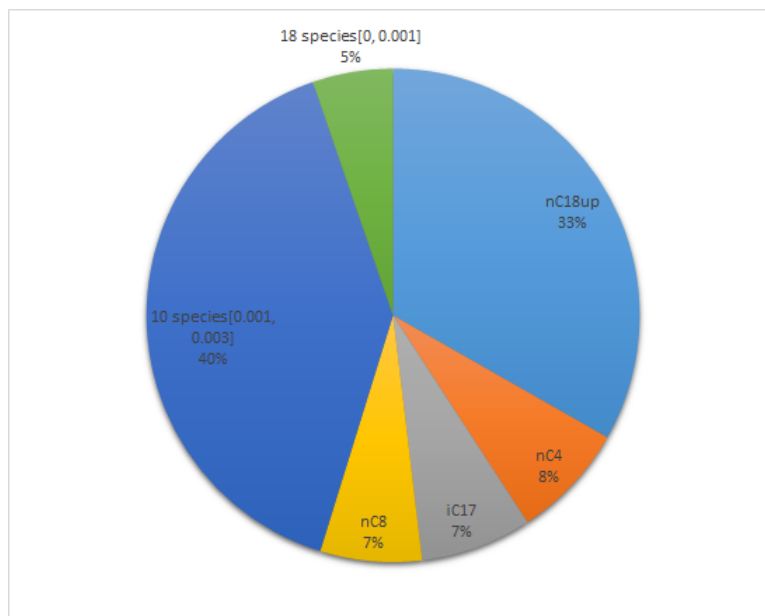


Figure 7.6: Absolute error share of hydrocarbon-groups, HDO reactor

When studying Figure 7.4, 7.5 and 7.6, there can be concluded the overall fit is good, except for some errors in the lower values (Figure 7.5). However, this error is less important as the components themselves are a relatively small fraction. Note that the value of the objective function is not given, because it is dependent of the applied weights. This means it can be influenced easily, so its value is not meaningful.

Now, a general idea of the precession of KME's HDO model is formed. Keeping this in mind, the kinetic parameters for every reaction family are presented in Table 7.6.

REACTION	log A /	E kcal/mol	alpha /	$\Delta H(i)_{rxn,av}$ kcal/mol	log k /
Triglyceride hydrogenolysis	8.91	10.51	0.26	-51.14	-10.18
Hydrogenation of triglycerides/fatty acids	2.66	8.58	0.23	-27.89	-9.49
Hydrogenation of olefins	10.27	4.77	0.21	-27.99	1.73
Hydrodeoxygenation	-2.92	12.02	0.15	-67.79	-21.01
Decarbonylation	12.94	3.78	0.56	-29.80	-3.70
Cracking	6.70	10.52	0.15	-11.23	-3.23
Decarboxylation	10.62	5.49	0.57	-39.04	-11.78
Isomerization	5.78	10.72	0.07	-0.64	-2.94
	A	B	C		
K(ad) acid site	0.81	0.30	0.10		
K(ad) on metal site	2.65	0.14	0.10		

T = 350.15°C

K(ad) is adsorption equilibrium constant, $K(ad) = k(\text{adsorption})/k(\text{desorption})$

units of A and k: $1/(s \cdot \text{atm}^{(n-1)})$ where n is reaction order

Table 7.6: Kinetic Parameters HDO

$\Delta H(i)_{rxn,av}$ is an average value of all reactions i in that specific reaction family j. It is acceptable to use an average value because all the reaction enthalpies within one reaction family differ only slightly. Appendix C shows a table with the standard deviation of the reaction enthalpies within a reaction family.

Kinetic parameter E (activation energy) is a measure of the relative impact of temperature on reaction rate. An increasing temperature will give an increasing effect on reaction rate k due to the ' $-E_j/RT$ ' term of the rate constant expression (equation (7.4)). If E is big, a change in temperature will have a bigger chance in k compared to a small E. The term ' $\alpha_j/RT \cdot \Delta H_{rxn,i}$ ' is affected by temperature as well. However,

because the HDO paper only contains experimental data for one temperature, it is not possible to tune in a useful sense on E. In this case, equation (7.4) should be regarded as:

$$\begin{aligned} \log(k_{i,j}) &= \log(A_j) + \frac{\alpha_j}{2.303RT} \cdot \Delta H_{rxn,i} - \frac{E_j}{2.303RT} \text{ and } T = ct. \\ &\rightarrow \log(k_{i,j}) = C_{A\&E} + \frac{\alpha_j}{2.303RT} \cdot \Delta H_{rxn,i} \end{aligned}$$

with: i = reaction, and j = family, $C_{A\&E}$ is a constant.

First, the adsorption equilibrium constants of Table 7.6 are evaluated. However, no relevant experimental data is found related to hydrotreating of triglycerides. Therefore, a comparison is made with data related to hydrocracking of a mixture of naphthalene and phenanthrene[18]. Clearly, there cannot be made an absolute comparison as this are cyclic compounds. But it can be used to suggest a trends or relative orders of magnitude. The bifunctional hydrocracking catalysts also consist of an acid and metal site. The adsorption constant on the acid site is formulated as:

$$\ln(K_{ads}) = Z_1 + \frac{Z_2 \cdot N_{AR} + Z_3 \cdot N_{SC}}{RT} \rightarrow \ln(K_{ads}) = 0.182 + \frac{1.934N_{AR} + 0.187N_{SC}}{RT} [18] \quad (7.11)$$

with N_{AR} denoting number of aromatic rings and N_{SC} the number of saturated carbons. The adsorption constant on the metal site is formulated as:

$$\ln(K_{ads}) = M_1 + \frac{M_2 \cdot N_{AR} + M_3 \cdot N_{SC}}{RT} \rightarrow \ln(K_{ads}) = 1.324 + \frac{0.887N_{AR} + 0.123N_{SC}}{RT} [18] \quad (7.12)$$

The equations are valid between a temperature interval of 300-370°C.

For the HDO reactor, the K_{ad} expressions become:

$$\log(K_{ad,acid}) = 0.81 + \frac{0.30 CN_i + 0.10 ON_i}{R.T} \quad (7.13)$$

$$\log(K_{ad,metal}) = 2.65 + \frac{0.14 CN_i + 0.10 ON_i}{R.T} \quad (7.14)$$

with: i = reaction, CN = carbon number, ON = oxygen number.

They show more or less the same trend as the mixture of naphthalene and phenanthrene, and their order of magnitude is the same. At a temperature of 350.15°C, the denominator equals 1.24 kcal/mol. $K_{ad,acid}$ becomes bigger than $K_{ad,metal}$ for a carbon number of 15 or higher (assuming oxygen number is the same for both).

Second, the $\log(k)$'s of the reaction families are evaluated. As explained in Figure 5.4, there exist three different pathways: decarboxylation, decarbonylation, and hydrodeoxygenation. Because the first two are the only reactions that produce respectively CO₂ and CO, there can be determined which one of those two is the most dominant using the CO₂/CO ratio. Using the species output sheet [mol/l] of KME, it is found that this ratio equals 0.128. This means decarbonylation should be more dominant than decarboxylation. This is the case, its $\log(k)$ is 3 times bigger.

The C18/C17 ratio is a way to determine if hydrodeoxygenation is dominant compared to decarboxylation and decarbonylation[4]. The produced paraffin of decarboxylation and decarbonylation has one carbon atom less than the parent fatty acid, while the one of hydrodeoxygenation has the same number of carbon atoms (see also Figure 5.5). As mentioned in the previous section, Jatropha oil consists of several fatty acids. For these acids, the one with 16, 18 or 20 carbon atoms have a content of respectively 15.56%, 84.21%, and .23%. The contribution of the 20 carbon atom acids is really low, so there can be assumed the max carbon atoms present in the acids is 18. This is important for the C18/C17 ratio. Table 7.7 shows the liquid hydrocarbon product composition. From this data, the C18/C17 ratio is computed.

Hydrocarbon-group	Predicted Value	Hydrocarbon-group	Predicted Value
nC4	0.00496	iC4	0
nC5	0.00463	iC5	0
nC6	0.00462	iC6	0
nC7	0.00463	iC7	0
nC8	0.00483	iC8	0
nC9	0.00462	iC9	0.00001
nC10	0.00481	iC10	0.00002
nC11	0.00461	iC11	0.00002
nC12	0.00460	iC12	0.00003
nC13	0.00454	iC13	0.00004
nC14	0.00442	iC14	0.00006
nC15	0.08547	iC15	0.00363
nC16	0.07439	iC16	0.00465
nC17	0.37200	iC17	0.02748
nC18	0.34365	iC18	0.03546
nC18up	0.00165	iC18up	0.00019

C18/C17 ratio	95%
isoparaffin content	7.16%

Table 7.7: liquid hydrocarbon product composition, HDO

In this case, C18/C17 equals 95%. This means hydrodeoxygenation counts slightly less than decarboxylation and decarbonylation together. However, $\log(k)$ of hydrodeoxygenation is double as low as the one of decarboxylation. This is a bit contradictory. A higher $\log(k)$ for hydrodeoxygenation is expected.

7.2.2 HI reactor

As it was the case for HDO, there is no experimental data on each specific isomer for the HI reactor available. Only data of product composition in terms of

hydrocarbon-groups (in mol%) of the paraffin mixture is available. In addition, temperature dependent data is available[6] for HI. More specific, the isoparaffin content (mol%) of the products is given at four different temperatures. Figure 7.7 shows a parity plot of the product composition and the isoparaffin content. The coefficient of determination (R^2) for a linear trendline for product composition and isoparaffin content equals respectively 0.8291 and 0.9985.

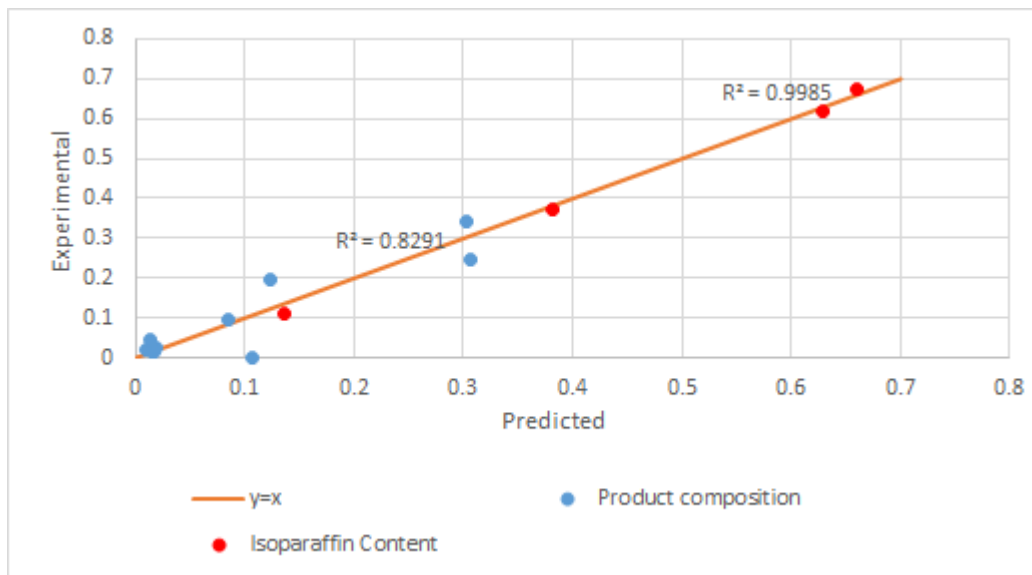


Figure 7.7: Parity Plot product composition and isoparaffin content HI reactor[6]

Figure 7.8 shows the share of the 4 hydrocarbon-groups with the highest absolute error, the 2 that have one between 0.01 and 0.035, and the 4 having one smaller than 0.01. The absolute error is defined the same way as for the HDO reactor (equation (7.10)). ‘nC14minus’ denotes all paraffins with 14 or less carbon atoms.

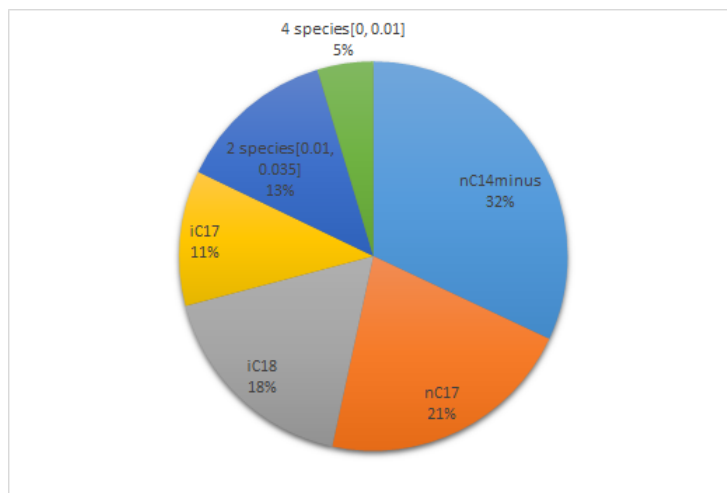


Figure 7.8: Absolute error share of hydrocarbon-groups, HI reactor

Figure 7.9 shows the trend of the isoparaffin composition as function of temperature. Both experimental and predicted results are plotted.

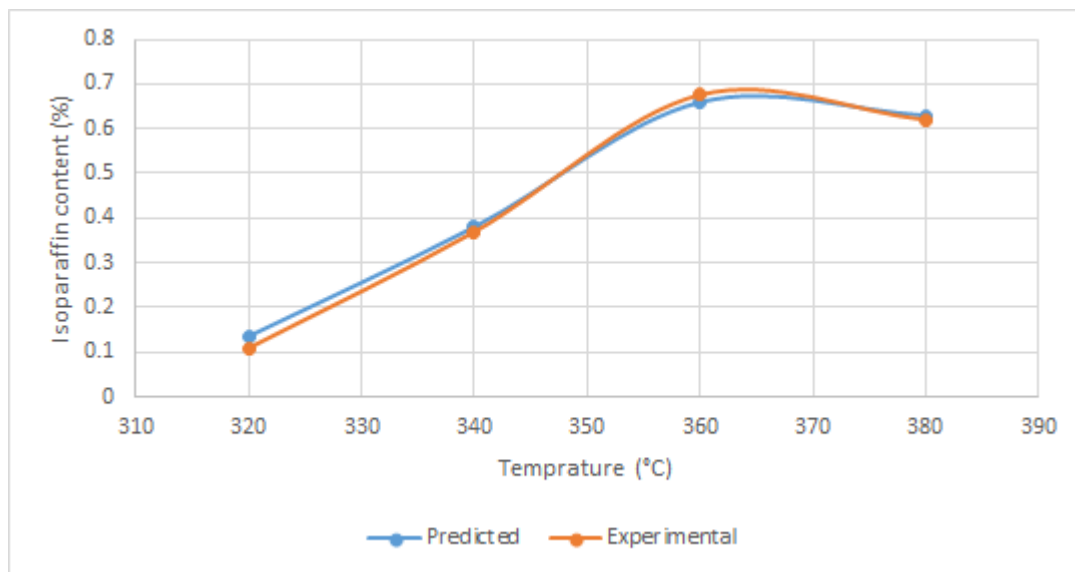


Figure 7.9: Isoparaffin content of products as function of temperature

As can be seen on Figure 7.9, by increasing temperature the isoparaffin content increases. However, at about 365°C it reaches a maxima and starts to decrease. This can be related with an increasing thermal cracking and therefore a reduced isoparaffin content[6].

Now a general idea of the precession of KME's HI model is formed, the kinetic parameters for every reaction family can be evaluated. They are listed in Table 7.8.

REACTION	log A /	E kcal/mol	alpha /	$\Delta H(i)_{rxn,av}$ kcal/mol	log k /
Cracking	10.87	50.28	0.84	-18.72	-41.78
Isomerization	17.18	51.15	0.42	-0.73	-23.88
	A	B	C		
K(ad) on acid site	2.41	0.20	/		

T = 360°C

K(ad) is adsorption equilibrium constant, $K(ad) = k(\text{adsorption})/k(\text{desorption})$

units of A and k: $1/(\text{s}\cdot\text{atm}^{(n-1)})$ where n is reaction order

Table 7.8: Kinetic Parameters HI

Again, $\Delta H(i)_{rxn,av}$ is an average value of all *reactions* i in that specific *reaction family* j . Appendix C shows a table with the standard deviation of the reaction enthalpies within a reaction family. Also, when comparing $\Delta H(i)_{rxn,av}$ of cracking and isomerization of both kinetic models (Table 7.6 and 7.8), one sees that $\Delta H(i)_{rxn,av}$ is of the same magnitude for both. This make sense because the reaction enthalpy is independent of reactor and dependent of temperature, which differs slightly for both reactors. The remainder parameters (log(A), E and alpha) are not the same. This makes sense as well. The remainder depends on the catalyst, which is different for both cases, so they don't have to be the same.

First of all, recall that the equilibrium constant is computed as:

$$\log(K_{ad}) = A_j + \frac{B_j \cdot CN_i + C_j \cdot ON_i}{R \cdot T} \quad \text{with } K_{ad} = \frac{k_{adsorption}}{k_{desorption}} \quad (7.15)$$

with: i = reaction, j = family, CN = carbon number, ON = oxygen number. Because

there are no oxygen containing compounds in the HI reactor, parameter C_j becomes insignificant.

Furthermore, it is noticed that the $\log(A)$ value of isomerization is quite big. KME tends to push it higher and higher (up to a $\log(A)$ of 26) to match the papers predicted results. It is found in the literature that pyrolysis of ethane has an pre-exponential factor A of $4 \cdot 10^{16} \text{ s}^{-1}$ [19] for cracking ethane under non-isothermal and non-isobaric conditions in a pilot plant. As this involves radicals, it is a fast reaction. Isomerization is assumed to be slower. Therefore, there is chosen to keep the result physically meaningful by limiting the $\log(A)$ at 17.18.

Third, when studying Figure 7.7, it is noticed that $\log(k)$ of cracking is extremely low. It looks like no reaction is happening at all. The fact that the reaction rate of cracking is smaller than isomerization, relatively speaking, sounds reasonable by looking at Table 7.9. It shows the shift in share of ‘carbon number i ’ (e.g. how much C_{15} there is in input vs. output) compared to the shift in isoparaffin content. Indeed, isoparaffin content is affected more drastically compared to number of carbons. However, absolutely speaking, the $\log(k)$ seems still quite low.

	INPUT	OUTPUT	difference
n- and i-C14 (%)	1.87	4.69	2.82
n- and i-C15 (%)	3.15	3.15	0
n- and i-C16 (%)	3.19	4.55	1.36
n- and i-C17 (%)	47.56	53.5	5.94
n- and i-C18 (%)	44.23	34.2	-10.03
Isoparaffin content (%)	0.75	67.57	66.82

Table 7.9: Change in carbon number and isoparaffin content, HI reactor

Chapter 8

HYDROGEN PRESSURE

An excessive amount of hydrogen is required to produce green diesel, making the production process very expensive. Therefore, this chapter will explain why such a huge amount of hydrogen is required. Recall from Table 7.3 and 7.5, the volumetric flow ratio of H₂/feed for HDO and HI is respectively 600[5] and 400[6]. A plausible explanation for such a high hydrogen flow rate could be to assure equilibrium limited reactions (small K_{eq}) still proceed sufficient. It pushes those reactions to the direction to the right, in accordance with the principle of le Chatelier Brown.

To check this statement, the average equilibrium constants for reaction family j are listed in Table 8.1. The table with standard deviation of the K_{eq} 's within a reaction family are added in Appendix D. Compared to $\Delta H(i)_{rxn,av}$, the standard deviations are relatively bigger. However, $K_{eq,av}$ still gives an acceptable general idea of the magnitude of an equilibrium constant for a reaction family.

HDO		HI	
REACTION	Keq,av(350.15°C)	REACTION	Keq,av(360°C)
Triglyceride hydrogenolysis	8.52E+17	Cracking	3.32E+03
Hydrogenation of triglycerides/fatty acids	1.87E+03	Isomerization	9.24E-01
Hydrogenation of olefins	1.68E+03		
Hydrodeoxygenation	2.72E+23		
Decarbonylation	1.20E+23		
Cracking	3.74E+04		
Decarboxylation	2.28E+24		
Isomerization	8.78E-01		

Table 8.1: Average equilibrium constants returned by KME

In addition, K_{eq} is manually calculated for one reaction, namely hydrogenolysis of the triglyceride Trigondoin (C20DB1, see also Table 5.1). This makes it possible to check if KME does not calculate things wrongly because e.g. the user made an error while building the model. The complete calculation is added in Appendix E. KME's and the manually calculated result is respectively 8.34E+17 and 8.94E+16. The small difference is due to the fact that KME's result is more precise because it uses atomic correction factors on ΔH_{rxn} and ΔG_{rxn} .

When studying Table 8.1, apparently most of the equilibrium values are already quite big. This implies that such a huge amount of hydrogen is not required to stimulate equilibrium limited reactions (assuming PropGen's properties are accurate). Another possible explanation of the high H₂/feed ratio is that hydrogen minimizes coke formation and reduces pore blockage. This increases catalyst lifetime.[4].

Chapter 9

FUTURE WORK

Several things are mentioned in this chapter that could improve the quality of the kinetic models. First, an important way to improve the model is by adding an expression in KME that takes the effect of hydrogen pressure on the reaction rate constants into account. E.g. hydroisomeriation is affected by hydrogen pressure[20]. In this model, the isomerization process in the reactors is considered by KME as a normal isomerization process, and not a hydro one. Both have a different mechanism, however, the result for KME is the same. Updating ‘normal isomerization’ to ‘hydro isomerization’ can be done by adding the following expression:

$$k^{new} = k^{original} \cdot P_{hydrogen}^{\beta} [21] \quad (9.1)$$

KME tunes on the parameter β . Obviously, the equilibrium is not altered, it becomes:

$$K_{eq} = \frac{k_1 \cdot P_{hydrogen}^{\beta}}{k_{-1} \cdot P_{hydrogen}^{\beta}}$$

Second, the kinetic models becomes more reliable by using several different sources of experimental data. For the moment, every reactor is based just on one source of experimental data. Also, a limitation of the HDO model is the fact that the kinetic parameters are only valid at 350.15°C. They are not tuned for temperature dependence. Therefore, data sets at different temperatures are required to add temperature dependence.

Third, as mentioned, KME treats every species as if it is a gas. To force KME to assume volumetric flowrate is constant, a batch reactor is used instead of a PFR. However, an extension of KME making it possible to treat liquids, should make it more convenient.

Chapter 10

CONCLUSION

Currently, green diesel is not suited for direct use. But it is useful as an additive to boost performance of petro-diesel. Converting triglycerides in green diesel is a prominent technology that likely will continue to develop in future. This thesis is devoted to contribute to this development. More specific, it contributes in determining a trade-off between cetane number and cloudpoint.

The production process of green diesel consists of two consecutive reactors. First the HDO reactor, followed by the HI reactor. In the former, hydrotreating of triglycerides takes place to remove oxygen. The latter makes sure the diesel's cloudpoint is not too low by branching the paraffins. Both reactors are followed by a flash drum at respectively a temperature slightly above 100°C and 0°C.

For both reactors, a kinetic model is derived. This is accomplished by using molecular-level kinetic software. First, a reaction network is composed through INGen. The growth of this reaction network is curbed by specifying reactant for every specific reaction family and by adding a max rank restriction on hydroisomerization. Second, properties of all species are computed through PropGen based on group-contribution. For small components online sources are consulted. Third, kinetic parameters are determined through fitting to experimental data. Because KME only works with gases, a batch type reactor is used instead of a PFR. This obligates KME to treat volumetric flow rate as a constant. The number of parameters is reduced by 98% using Linear Free Energy Relationships (LFER). Because a catalyst is involved, Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetics are applied.

The fit of the product distribution of the HDO model has a R^2 value of 0.9979. However, it does not include temperature dependency. For the HI reactor, the fit of the

product distribution and the temperature dependent data has a R^2 value of respectively 0.8291 and 0.9985. By increasing temperature, the isoparaffin content increases. At about 365°C it reaches a maxima and starts to decrease. This can be related with an increasing thermal cracking and therefore a reduced isoparaffin content.

If both models are optimized in future, they can contribute to the development of a complete life cycle assessment of green diesel. Although green diesel is not dominant yet, people realize that it is both an economical and environmentally efficient way to produce energy and decrease the consumption of fossil fuels.

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Appendix A

COMPARISON CHERIC AND NIST

In this appendix, the C_p value of propane is computed using Cheric and NIST. For both, the experimental data is fitted via least square error function. The result for both corresponds well:

$$C_p = A + B \cdot T + C \cdot T^2 + D \cdot T^3$$

where C_p in $J/(mol \cdot K)$, T in K

Coefficient	unity	Cheric	NIST
A	J/mol	23.12806	36.06752
B	J/molK	0.142338	0.030151
C	J/molK ²	0.000136	0.00043
D	J/molK ³	-1.33E-07	-3.71E-07
		Cheric	NIST
Cp(350.15°C)		132.3052	132.1289

Table A.1: Comparison C_p value Propane using Cheric[11] vs. NIST [10])

Appendix B

EXPLANATION SMALLER REACTOR VOLUME HDO COMPARED TO HI REACTOR

In this appendix is explained why the volume of the HDO reactor is more or less 50 times smaller compared to HI. It is explained in an appendix because it could cause confusion. KME uses a batch type reactor. Here, the reason for the smaller volume is explained using the original reactor, a PFR.

The reason for the smaller volume is that HI's volumetric flow rate is also considerably higher, as can be seen in Table [B.1](#) and [B.2](#) .

HDO REACTOR	
Radius [dm]	0.04
Length Reactor [dm]	0.4
LHSV [1/h]	1.0
Volumetric flow [L/h]	0.0020096

Table B.1: extra data HDO (PFR[5])

HI REACTOR	
Radius [dm]	0.147
Length Reactor [dm]	1.471
LHSV [1/h]	2.0
Volumetric flow [L/h]	0.20

Table B.2: extra data HI (PFR)[6]

Appendix C

POPULATION STANDARD DEVIATION OF $\Delta H_{I,RXN}$

$\Delta H(i)rxn,av$	Mean	Variance	Population standard deviation
Triglyceride hydrogenolysis	-51.137	0.001	0.037
Hydrogenation of triglycerides/fatty acids	-27.892	0.103	0.321
Hydrogenation of olefins	-27.989	0.219	0.468
Hydrodeoxygenation	-67.795	0.000	0.000
Decarbonylation	-29.797	0.000	0.000
Cracking	-11.229	0.084	0.291
Decarboxylation	-39.041	0.000	0.000
Isomerization	-0.644	0.078	0.280

Table C.1: Population standard deviation of $\Delta H_{i,rxn}$ for HDO reactor

$\Delta H(i)rxn,av$	Mean	Variance	Population standard deviation
Isomerization	-0.729	0.140	0.374
Cracking	-18.721	0.071	0.266

Table C.2: Population standard deviation of $\Delta H_{i,rxn}$ for HI reactor

Appendix D

POPULATION STANDARD DEVIATION OF K_{EQ}

Keq(350.15°C) for HDO	Mean	Variance	Population standard deviation
Triglyceride hydrogenolysis	8.52E+17	1.63E+33	4.03E+16
Hydrogenation of triglycerides/fatty acids	1.87E+03	4.67E+05	6.84E+02
Hydrogenation of olefins	1.68E+03	1.11E+06	1.06E+03
Hydrodeoxygenation	2.72E+23	9.12E+45	9.55E+22
Decarbonylation	1.20E+23	1.46E+45	3.83E+22
Cracking	3.74E+04	7.01E+07	8.37E+03
Decarboxylation	2.28E+24	5.31E+47	7.28E+23
Isomerization	8.78E-01	6.11E-02	2.47E-01

Table D.1: Population standard deviation of K_{eq} for HDO reactor

Keq(360°C) for HI	Mean	Variance	Population standard deviation
Isomerization	9.24E-01	8.03E-02	2.83E-01
Cracking	3.32E+03	3.75E+06	1.94E+03

Table D.2: Population standard deviation of K_{eq} for HI reactor

Appendix E

CALCULATION OF K_{EQ} FOR HYDROGENOLYSIS OF TRIGONDOIN

The reaction with properties are:

REACTION				
Trigondoin (C20DB1)	+	3 Hydrogen	->	propane + 3 fatty acid
PROPERTIES				
	<u>SHform(Kcal/mol)</u>	<u>SGform(Kcal/mol)</u>	<u>SSform (kcal/mol)</u>	
Trigondoin (C20DB1)	-3.68E+02	5.42E+01	-1.42E+00	
hydrogen	0.00E+00	0.00E+00	0.00E+00	
fatty acid	-1.30E+02	3.39E+00	-4.47E-01	
propane	-2.48E+01	-5.61E+00	-6.45E-02	
	<u>SCPa(Cal/mol.K)</u>	<u>SCPb(Cal/mol.K^2)</u>	<u>SCPc(Cal/mol.K^3)</u>	<u>SCPd(Cal/mol.K^4)</u>
Trigondoin (C20DB1)	3.02E+01	1.11E+00	-3.90E-04	0.00E+00
hydrogen	6.53E+00	2.20E-03	-3.63E-06	2.19E-09
fatty acid	1.22E+01	3.45E-01	-1.17E-04	0.00E+00
propane	5.53E+00	3.40E-02	3.24E-05	-3.18E-08

Table E.1: reaction and properties

Note that KME does not directly use ‘SSform’.

K_{eq} can be calculated as following:

$$H_{int} = (Cp(1) + Cp(2) * T + Cp(3) * T^2 + Cp(4) * T^3) \quad (E.1)$$

$$S_{int} = ((Cp(1) + Cp(2) * T + Cp(3) * T^2 + Cp(4) * T^3)/T) \quad (E.2)$$

H_{int} and S_{int} are calculated in Matlab:

```

clear all
close all
clc

i=1;
sol=ones(1,999);
Cp = [30.24883915    1.106840583 -0.000390057    0];

fun = @(T) (Cp(1)+Cp(2).*T+Cp(3).*T.^2+Cp(4).*T.^3);

T0=298;
T=623.15;
HintSpec6 = integral(fun,T0,T) %kcal/mol

sol(i)=HintSpec6;
i=i+1

fun = @(T) ((Cp(1)+Cp(2).*T+Cp(3).*T.^2+Cp(4).*T.^3)./T);
SintSpec6 = integral(fun,T0,T) %kcal/mol

sol(i)=SintSpec6;
i=i+1

%*****
Cp = [6.526289948    0.002197837 -3.62972E-06    2.19057E-09];
R=0.001987094*10^3; %cal/mol.K

fun = @(T) (Cp(1)+Cp(2).*T+Cp(3).*T.^2+Cp(4).*T.^3);

T0=298;
T=623.15;
HintSpec15 = integral(fun,T0,T) %kcal/mol

sol(i)=HintSpec15;
i=i+1

fun = @(T) ((Cp(1)+Cp(2).*T+Cp(3).*T.^2+Cp(4).*T.^3)./T);
SintSpec15 = integral(fun,T0,T) %kcal/mol

sol(i)=SintSpec15;
i=i+1

%*****
Cp = [5.527740041    0.034019481 3.24231E-05 -3.18031E-08];
R=0.001987094*10^3; %cal/mol.K

fun = @(T) (Cp(1)+Cp(2).*T+Cp(3).*T.^2+Cp(4).*T.^3);

T0=298;
T=623.15;
HintSpec19 = integral(fun,T0,T) %kcal/mol

```

subsequently:

$$\Delta H_f = SH_{from} + H_{int} \quad (\text{E.3})$$

$$\Delta S_f = SS_{from} + S_{int} \quad (\text{E.4})$$

$$\Delta G_f = \Delta H - T \cdot \Delta S \quad (\text{E.5})$$

$$\Delta G_{rxn} = \sum_{products} \Delta G_f - \sum_{reactants} \Delta G_f \quad (\text{E.6})$$

$$K_{eq} = \exp\left(\frac{-\Delta G_{rxn}}{RT}\right) \quad (\text{E.7})$$

The results of the calculation of Keq for this reaction are summarized in Table E.2. ‘with correction’ denotes the result of KME, who takes atomic correction into account.

Hint (cal/mol)	Sint ((cal/mol))	deltaH (kcal/mol)	deltaS (kcal/mol)	deltaG (kcal/mol)	deltaG with correction
147570.279	323.790	-220.448	-1.093	460.682	538.122
2268.669	5.143	2.269	0.005	-0.936	-0.936
47170.816	103.531	-82.705	-0.344	131.455	156.579
8085.001	17.710	-16.748	-0.047	12.404	17.245
<hr/>					
deltaGrxn (623.15K) kcal/mol		deltaGrxn (623.15K) with correction			
-51.104		-48.332			
<hr/>					
Keq(623.15K)		Keq(623.15K) with correction			
8.39E+17		8.94E+16			

Table E.2: Results of calculation Keq