

**Kinetic Modeling of Hydrodeoxygenation of Methyl Oleate over  
Solid Catalysts to Green Diesel from First Principles**

by

SITI NURNAJWA BINTI NAZERI

Dissertation submitted in partial fulfilment of the requirements for the  
Bachelor of Engineering (Hons)  
(Chemical Engineering)

SEPT 2012

**FINAL YEAR PROJECT II  
DISSERTATION REPORT**

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**CERTIFICATION OF APPROVAL**

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BACHELOR OF ENGINEERING (Hons)  
(CHEMICAL ENGINEERING)

Approved by,

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(Dr. Periyasamy Balasubramaniam)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

SEPT 2012

## **CERTIFICATION OF ORIGINALITY**

This is to certify that I am responsible for the work submitted in this project, and the original work is produced on my own except as specified in the references and acknowledgements, and it has not been undertaken or done by unspecified sources or person.

Produced by,

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SITI NURNAJWA BINTI NAZERI

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## ABSTRACT

This dissertation covers the activities and findings of Final Year Project (FYP) I & II. FYP I activities are mainly on the literature research, elucidation of reaction mechanisms and development of kinetic models. FYP II on the other hands is actually the continuation of the FYP I activities. In clear picture, FYP II covers the simulation of the developed kinetic models using MATLAB software, graphing and tabulation of results and finally, the analysis of the findings. The analysis is concluded based on the related research papers that had been produced by many scholars.

Current development of green diesel production was focusing on the triglycerides as the feedstock. There is no study on the green diesel production using monoglyceride. Because of that, the intent of this paper is to study the trend and variation of optimal operating temperature and initial hydrogen pressure at which reaction route can efficiently hydroconvert methyl oleate, an example of monoglyceride. The research provides insights for future optimal operation and industrial scaling by using monoglyceride as the feedstock to produce green diesel.

The parameters to be identified at the end of the project are methyl oleate conversion, selectivity towards formation of  $C_{18}$  through hydrodeoxygenation reaction (to suppress decarboxylation and decarbonylation), yield for all of the components involved in the conversion, optimum temperature and optimum pressure within 2 hours reaction time.

The project has undergone few stages to achieve the objectives. The stages involved are literature study, elucidation of reaction mechanisms, derivation of rate expressions, pre-exponential factors calculations, reactor model development from first principles and finally, simulation of the model equations using MATLAB software.

Overall, the project has achieved all of the objectives, with optimum operating temperature of 270 °C, pressure of 50 bar in 2 hours reaction time, for 100 % maximum methyl oleate conversion forming 79 mol% of maximum octadecane yield.



# CHAPTER 1: INTRODUCTION

## 1.0 BACKGROUND STUDY

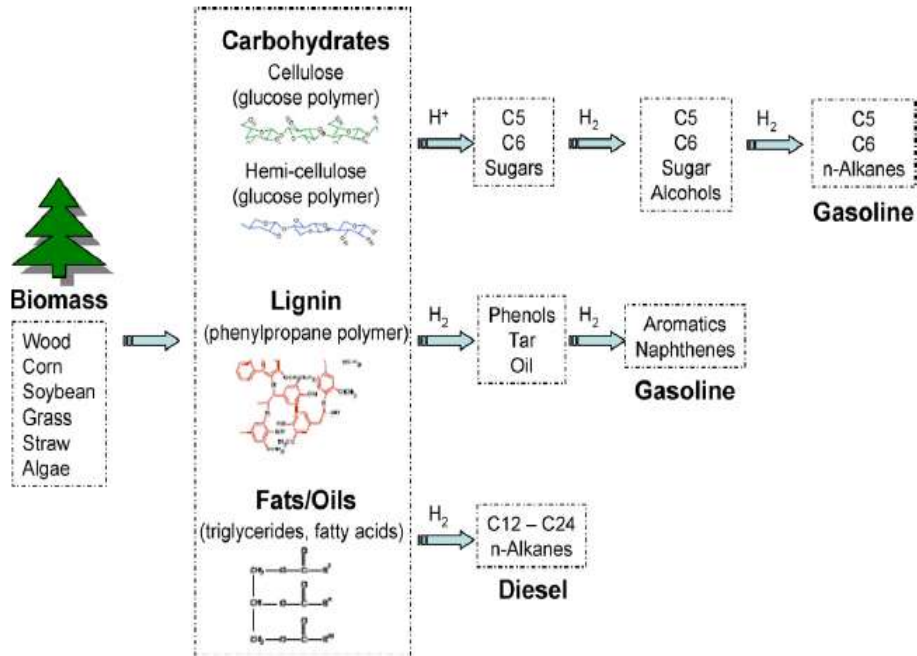
In recent years, concerns on continuous depletion of the non-renewable petroleum reserves, feedstock availability as related to the security of the supply, price volatility and greenhouse gas (GHG) emissions have arisen. Because of that, there are intensified search for alternative sources of energy with special attention on fuel derived from biological sources; such as animal fats and vegetable oils. These raw materials are suitable for the production of transportation fuels because of their chemical structure is relative to the hydrocarbons in the distillation range of diesel fuel. Different processes using fats and oils as feedstocks yield fuels with different compositions and properties. Two most prominent fuels from renewable resources are biodiesel and green diesel (renewable diesel).

Biodiesel can be defined as mono-alkyl esters of vegetable oils or animal fats, obtained by transesterification process with an alcohol under alkaline condition [1]. The obtained Fatty Acid Methyl Ester (FAME) can be blended with conventional petroleum derived diesel fuel (petrodiesel) and used in adapted engines [2]. However, FAME still has the oxygen-to-carbon (O/C) ratio similar to the original triglycerides, a drawback of having lower calorific power, relatively high viscosity, high cloud point, low pour point, poor stability and low volatility.

Alternatively, oxygen can be removed from the biomass-derived molecules via hydrodeoxygenation process (HDO). From this process, various oxygenated bioproducts are able to be transformed into hydrocarbon molecules with composition resemble petrodiesel. By using this method, triglycerides can be converted into green or so-called second generation renewable diesel, with composition of mainly hydrocarbons with a chain length in the range of  $C_{14} - C_{20}$  [3]. Unlike biodiesel, green diesel has higher oxidation stability, lower specific gravity, higher cetane number and it has better cold flow properties when blended with petrodiesel [4]. The most important aspect that favours the option of processing green diesel over biodiesel is the fact that it can be processed using current petrodiesel facilities. In other words, the green diesel can be produced together with petrodiesel on the same time using same facility, whereby the feedstock is the mixture of petroleum and

biological sources (which contain triglycerides). Instead, green diesel also can be processed in a stand-alone facility with only biological sources as the feed stock.

Figure 1.1: Basic building block of biomass to renewable carbon fuel [5].



Biomass decomposes of 3 components; carbohydrates, lignin and fats/oils. Only fats/oils which consist of triglycerides and fatty acids composition is need for the formation of transportation fuel.

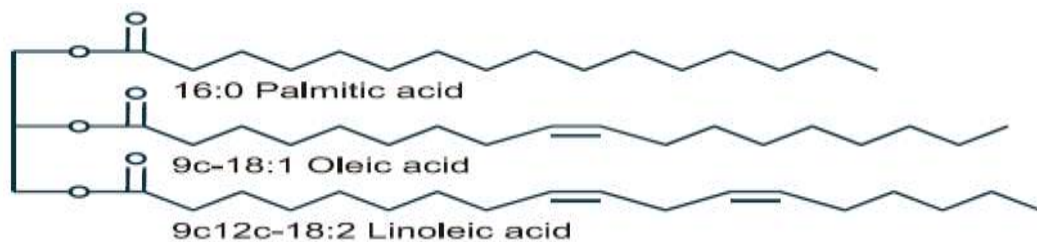


Figure 1.2: Example of triglycerides is a branch of palmitic acid, oleic acid and linoleic acid.

These triglycerides have to be further break down into monoglyceride with the major component that dominates the triglycerides content is taken as a feedstock for the reaction. The weight percent breakdown of a biomass, in for example, rapeseed is as follow:

Table 1.1: Weight percent breakdown of rapeseed oil

fatty acid	structure <sup>a</sup>	wt %
palmitic	C16:0	3.65
palmitoleic	C16:1	0.18
stearic	C18:0	1.65
oleic	C18:1	63.72
linoleic	C18:2	15.42
linolenic	C18:3	14.28
cis-11-eicosenoic	C20:1	1.10

<sup>a</sup> C<sub>x</sub>:<sub>y</sub>, where *x* is the number of carbon atoms; *y* is the number of double bonds.

For this research, oleic acid, thus methyl oleate is used as the feedstock because it dominates the composition of biomass. From table above, oleic acid has the highest composition of 63.72% over the other components. That is why, methyl oleate is selected as the feedstock for the production of green diesel.

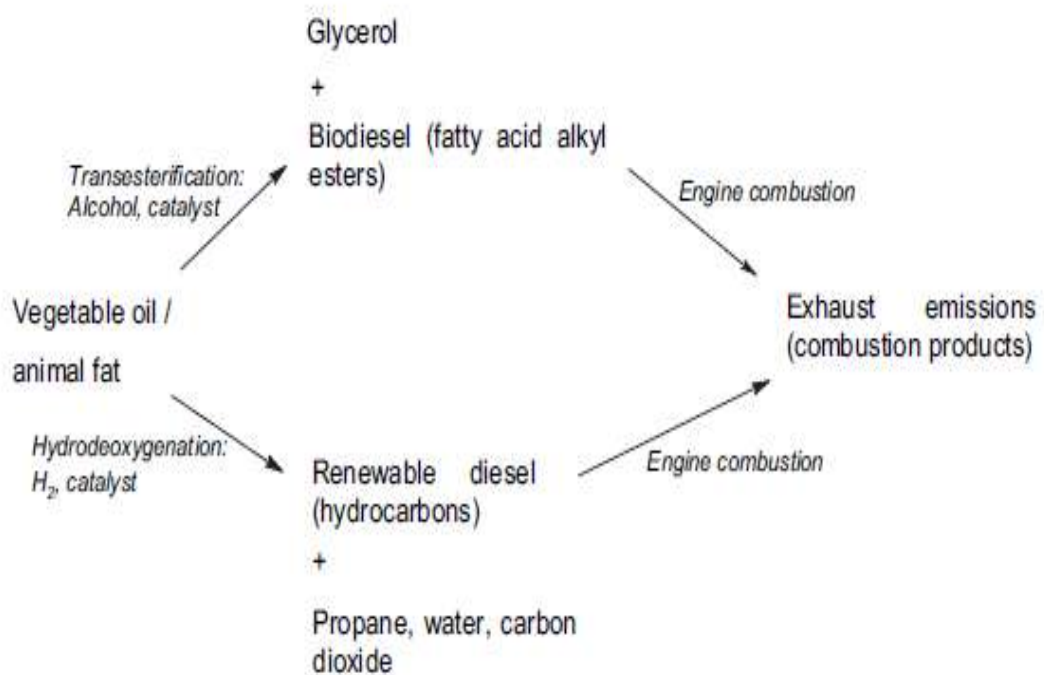


Figure 1.3: The flow chart for transformation of lipid materials to biodiesel and green diesel

Hydrodeoxygenation is a process in which feedstock that contains double bond and oxygen is converted to hydrocarbons by saturation of the double bonds and the removal of oxygen. The process includes decarboxylation (DCX), decarbonylation (DCN), dehydration and cracking. Decarboxylation of the unreactive carboxylic acid

is exothermic and requires elevated temperature and pressure. In this research project, the analysis on the kinetic reactions is based on  $NiMo/\gamma - Al_2O_3$  in solid form, as catalyst and Methyl Oleate (MO) as the feedstock. The significant of using this type of catalyst is discussed in Literature Review section, based on previous researches done by scholars.  $NiMo/\gamma - Al_2O_3$  catalyst refer to metal oxides ( $NiO, MoO_3$ , etc.) supported on alumina. The catalyst has been sulfided with elemental sulphur or  $H_2S$  as this could help to increase the catalyst activity [6]. The partial pressure of  $H_2S$  during the reaction can preserve the catalytic sites [7].

A few companies have developed technologies to produce green diesel. Neste Oil NExBTL technology has been used by hydrotreating vegetable oils or waste fats as the feedstocks [8]. Neste Oil recently opened a plant in Singapore by using this technology that capable producing more than 800 000 tons of green diesel per year [9]. Dynamic Fuels, a joint venture company between Syntroleum and Tyson Foods recently opened a plant at Geismar, LA with capacity up to 75 million gallons of renewable fuel per year from non-food grade animal fats [10]. The animal fat includes beef tallow, pork lard, chicken fat and greases. Syntroleum reported that the carbon footprint of the renewable diesel produces at the plant is 75% below petroleum diesel.

## 1.1 Problem Statement

The problem that has initiated author to come up with this research project is due to current development of green diesel production that is only focusing on the triglycerides as the feedstock. There is less study on green diesel production using monoglyceride. In addition, from literature research, author found out that monoglyceride as the feedstock might require even low operating temperature and hydrogen pressure as compared to triglyceride. Because of that, author conducted the research to verify this statement and to identify the optimum temperature and hydrogen pressure for the reaction.

## 1.2 Objectives

1.2.1 To elucidate the reaction mechanisms involved in the hydrodeoxygenation of methyl oleate to green diesel (FYP I).

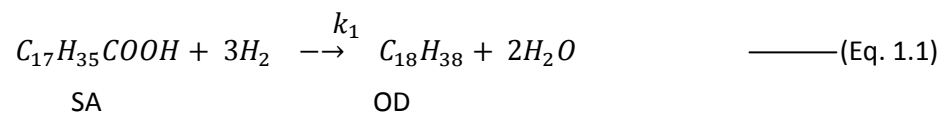
1.2.2 To develop a kinetic model for the hydrodeoxygenation of methyl oleate to green diesel (FYP I).

1.2.3 To study the effect of operating parameters on hydrodeoxygenation of methyl oleate to green diesel by MATLAB simulation. (FYP II).

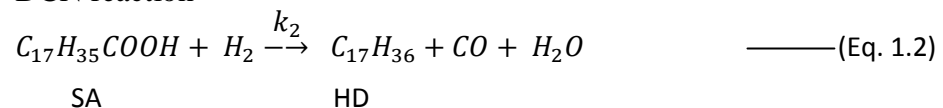
## 1.3 Scope of study

The research project is guided based on the reaction of methyl oleate to produce green diesel. Green diesel compositions are mainly octadecane and heptadecane. However, octadecane formation is desired over heptadecane formation due to its contribution towards high cetane number which is good for engine combustion system. Because of that, the scope of the analysis is basically to maximise the hydrodeoxygenation route which mainly produced octadecane and to suppress decarboxylation and decarbonylation reactions which produced heptadecane. The abovementioned three reactions, forming both methyl stearate and stearic acid as intermediates. The overall reactions is as follow:

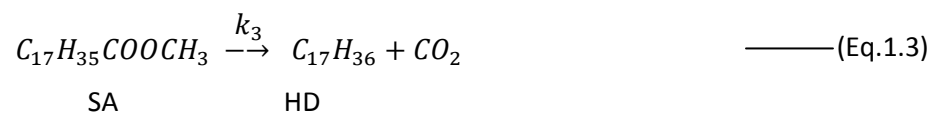
- HDO reaction



- DCN reaction



- DCX reaction



The reaction is assumed to proceed in batch reactor with the presence of conventional solid acid catalysts, NiMo/  $\gamma$ - $Al_2O_3$ . Reaction time is limited to 2 hours. The analysis on both catalyst and time effects are not considered in the research.

#### **1.4 Relevancy of the project**

The project is relevance with current situation where the future of fuel from renewable sources is seen appealing due to the depletion of fuel derived from non-renewable sources. Besides that, the drawback of the well developed biodiesel has shifted the researchers focus on green diesel production which contains no oxygen atom which contributed to better properties especially high cetane number.

#### **1.5 Feasibility of the project within the scope and time frame**

Two semesters has been allocated for this research project, which author has successfully managed the time carefully. The narrower scope of the research made the author managed to achieve the desired objectives and outcomes. However, author would propose another semester if the analysis on continuous plug flow reactor to be conducted.

## CHAPTER 2: LITERATURE REVIEW

Up to now, there are various studies have been devoted to identify the best parameters, including reaction temperature, hydrogen pressure, and type of catalysts that are capable to efficiently hydroconvert various biomass feedstock for the production of green diesel. However, most of the studies use triglycerides as the feedstock and had been conducted experimentally. As for this research paper, the monoglyceride feedstock is used and the analysis was conducted using kinetic models.

Studies on the previous green diesel production-related literatures are crucial because it provides author with current progress and updates in this area. Author capable to compare the findings of the previous literatures with the gathered results from the developed kinetic models.

### 2.1 Hydrotreating of rapeseed oil to produce green diesel.

A study on three different types of bi-functional catalysts to produce hydrocarbon in the range of diesel fraction was done by Regolio Sotelo et al [4]. The catalysts involved are Pt/H-Y, Pt/H-ZSM-5 and sulfided NiMo/  $\gamma$ - $Al_2O_3$ . The reaction with NiMo/  $\gamma$ - $Al_2O_3$  catalyst is emphasized because the kinetic model is assumed to use this type of catalyst. The scope of the study is basically to study the optimal operating conditions that capable to hydroconvert rapeseed oil, a triglycerides into green diesel.

Experiments were carried out in a batch reactor at a temperature range of 300 - 400 °C with initial hydrogen pressure of 50 to 100 bar for 3 hours. The temperature and pressure effects were identified and analysed. There are 3 main reactions involved in the transformation; decarboxylation (DCX), decarbonylation (DCN) and hydrodeoxygenation (HDO). These three reactions occurred simultaneously (parallel reactions). DCX and DCN reactions favoured the formation of mainly n-heptadecane,  $C_{17}$ . On the other hands, HDO favoured the formation of mainly n-octadecane,  $C_{18}$ . The transformation started on the formation of intermediate stearic acid (SA), and the by-products produced include water, carbon monoxide, carbon dioxide and propane. Reaction of triglycerides produce propane, however the reaction of monoglyceride produces methane as the by-product.





Sotelo et al, author expected that the monoglyceride requires operating temperature of less than  $350^{\circ}\text{C}$  and initial hydrogen pressure of 50 bar and below.

## **2.2 Second Generation Diesel Fuel from Renewable Sources**

This paper had been produced by Jozef Mikulec et al with the aim to study the direct transformation of triglycerides (TAG) to diesel fuels using NiMo and NiW hydrofining catalysts [11]. Experiments are conducted to achieve the objectives. The reactions involved are desulphurization, HDO, DCX and DCN and is started by the addition of 6.5 vol% of triglycerides into Atmospheric Gas Oil (AGO).

Operating conditions for the transformation is basically in the temperature range of 320 to  $360^{\circ}\text{C}$ , hydrogen pressure of 35 to 55 bar, Liquid hourly space velocity, LHSV of  $1\text{h}^{-1}$ , and  $\text{H}_2:\text{HC}$  ratio of  $500\text{-}1000\text{ Nm}^3/\text{m}^3$ . By products produced includes carbon dioxide, propane and water.

From the experiment, increasing temperatures shows the DCX prevails over HDO reaction, while higher partial pressure suppresses the formation of olefins, cyclones and aromates. However, HDO is the key reaction route and the hydrocracking products can be separated into 3 fractions by distillation; petrol (gasoline), renewable diesel fuel and distillation residue.

The experiments conducted is to search for the optimal condition for the conversion of rapeseed oil, sunflower oil, palm oil & lard on conventional NiMo/ $\text{Al}_2\text{O}_3$  catalyst. Crude vegetable oils and animal fats contain high amount of TAG (95 -97 wt%). On the other hands, refined oils contain more than 99 wt% of TAG. Fatty acid (lard) is obtained as a by-product of the Kraft process of pulp manufacture which contains Free Fatty Acid (FFA) mainly oleic and linoleic acids (30 - 50 wt%), Rosin acids like pimaric & abietic acid.

Table 2.1: Feedstock compositions [11]

Acyl profile of materials used by hydroprocessing study, wt. %.

Fatty acid	Rapeseed oil, refined	Sunflower oil, refined	Palm oil, refined	Lard
C14:0	0.06	0.07	1.0	1.5
C14:1	0.00	0.00	0	0
C16:0	4.64	6.15	35.4	31.2
C16:1	0.24	0.07	0.3	0
C18:0	1.96	3.80	3.8	16.5
C18:1	63.47	22.09	45.1	42
C18:2	20.01	66.62	13.4	6.6
C18:3	6.97	0.12	0.3	0
C20:0	0.60	0.25	0.3	undetectable
C20:1	1.18	0.23	0	undetectable
C22:0	0.15	0.05	0	undetectable
C22:1	0.07	0.08	0	undetectable
C24:0	0.13	0.03	0	undetectable
C24:1	0.14	0.18	0	undetectable

In line with the intent of this research paper which to maximize the production of n-octadecane, author focus on the feed highlighted by Jozef Mikulec that contains maximum amount of saturated  $C_{18}$  hydrocarbon. From table 2.1, rapeseed oil is dominated by saturated n-octadecane composition (63.46 wt%).

For temperature effects, at increasing temperature and constant pressure of 30 bar, the n-heptadecane increases which indicates that DCX favours at high temperature. Besides that, high temperature also leads to second reaction forming aromatics ring.

Table 2.2: Temperature effects at 30 bar

Hydroconversion conditions			
Temperature, °C	330	340	350
Pressure, MPa	3		
LHSV, h <sup>-1</sup>	1.0		
H <sub>2</sub> :TAG, Nm <sup>3</sup> /m <sup>3</sup>	250		
Catalyst	NiMo/γ-Al <sub>2</sub> O <sub>3</sub>		
Liquid product yield, wt%	89.8	92.9	90.5
Product:	Composition, % wt.:		
<n-C <sub>14</sub>	0.26	0.31	0.35
n-C <sub>15</sub>	2.84	3.09	3.35
n-C <sub>16</sub>	2.51	2.43	2.27
n-C <sub>17</sub>	49.35	51.16	53.32
n-C <sub>18</sub>	35.95	33.40	29.09
> n-C <sub>18</sub>	1.51	1.54	1.50
Isoalkanes, cycloalkanes, olefins	5.59	6.34	8.31
Aromatics	0.95	1.27	1.54
Polar substances	1.06	0.45	0.26
Bromine index, mg Br <sub>2</sub> /100 g	692	465	351

For pressure effect, at higher hydrogen pressure, HDO reaction is favoured, as it shows by increasing octadecane formation. High pressure also suppresses olefins formation.

Table 2.3: Pressure effect at 340°C

Hydroconversion conditions			
Pressure, MPa	3.5	4.0	4.5
Temperature, °C	340		
LHSV, h <sup>-1</sup>	1.0		
H <sub>2</sub> :TAG, Nm <sup>3</sup> /m <sup>3</sup>	250		
Catalyst	NiMo/γ-Al <sub>2</sub> O <sub>3</sub>		
Liquid product yield, wt%	90,9	93,0	93,5
Product:	Composition, % wt.:		
<n-C <sub>14</sub>	0.40	0.27	0.37
n-C <sub>15</sub>	3.81	2.54	2.86
n-C <sub>16</sub>	3.39	2.70	3.00
n-C <sub>17</sub>	49.12	49.28	46.26
n-C <sub>18</sub>	34.06	37.12	38.94
>n-C <sub>18</sub>	0.84	1.80	1.29
Isoalkanes, cycloalkanes, olefins	7.02	5.03	5.96
Aromatics	1.15	1.09	1.17
Polar substances	0.20	0.18	0.13
Bromine index, mg Br <sub>2</sub> /100 g	466	410	328

For clear picture,  $C_{17}/C_{18}$  ratio was plotted against temperature to verify the trend. The graph is as follow. At increasing temperature,  $C_{17}/C_{18}$  ratio shows increasing trend which explained the DCX reaction is favoured and heptadecane formation is prevails. On the other hands, at increasing pressure from 30 to 55 bar, the  $C_{17}/C_{18}$  ratio (showing by graph's gradients) is decreasing.

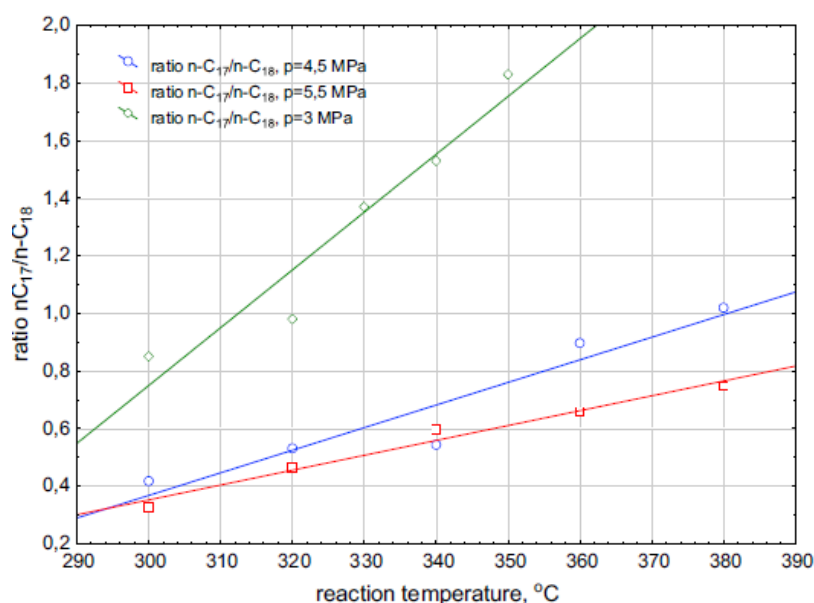


Figure 2.1:  $C_{17}/C_{18}$  ratio vs. temperature.

Jozef Mikulec in this ‘Second Generation Diesel Fuel from Renewable Sources’ also analysed possible reaction mechanisms. Reported, DCX reaction is favoured at lower pressure, higher temperature and involves carbon dioxide elimination and the formation of alkane with odd number (n-heptadecane). Increase hydrogen pressure will shift reaction towards HDO. Besides that, it is also found that cracking of alkanes occurs at higher temperature, exceeding 380°C.

### 2.3 Biodiesel Hydrodeoxygenation in the Presence of Catalyst Based on Precious Metal

Both V.O Dundich and V.A Yakovlev has conducted a study on catalytic HDO of biodiesel (that represents mixture of FAME) aiming at obtaining linear alkanes. The experiment employed 5 different type of catalysts; Ru, Rh, Pd, Pt, Ir [12].

Alkane distribution at 330 and 370 °C shows that at this high temperature, DCX is favoured and  $C_{14} - C_{17}$  formation do not exceed 20 by wt%. With Pd and Pt catalyst, cracking happened with the formation of light hydrocarbon (green gasoline) ranging from  $C_6 - C_{13}$  (gasoline range). Yet, at this operating range, n-heptadecane dominates the products composition. The formation of methane is due to undesirable side reaction causing an increase in hydrogen consumption and decrease in hydrocarbon yield. The trend is shows at figure 2.2.

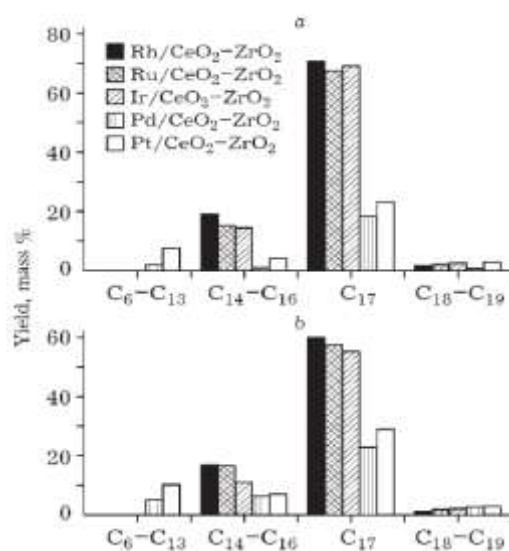


Figure 2.2: Hydrogen consumption

V.O Dundich and V.A Yakovlev summarised HDO of fatty acid ester into a reactions scheme, starting with saturation of double bond by HDO reaction forming stearic acid. The, the reaction proceed with the DCX reaction with the subsequent hydrogenation of carboxylic fragment. The result is the formation of linear alkanes (mainly heptadecane), methane and water. Finally, the conversion involves hydrocracking forming lighter hydrocarbons.

#### **2.4 NiP/SBA-15 as a hydrodeoxygenation catalyst with enhanced selectivity for the conversion of methyl oleate to n-octadecane**

Yangxing Yang has conducted an experiment on methyl oleate conversion to n-octadecane (green diesel's main composition) by using NiP/SBA-15 through HDO reaction [3]. Because the scope is almost the same as the research project that author is working on, the results is chosen as the basis for comparison. The comparison is discussed at chapter 4 in this paper.

The experiment was performed in a fixed-bed continuous reactor, PFR with methyl oleate (surrogate of triglycerides molecules present in vegetable oils) as a feedstock. Catalysts used are NiP/SBA-15 and Ni/SBA-15 with hydrogen pressure of 30 to 40 bar and operating temperature of higher than 290 °C. Ni/SBA-15 is for the pyurpose of comparison. From the experiment, Yangxing Yang found that hydrogenation of methyl oleate double bond under mild condition yields methyl stearate (intermediate). On this basis, author included this finding in detailed reactions scheme 3.1 and 3.2.

At pressure of 30 bar and temperature range of 250 to 340 °C, nearly complete conversion is achieved at temperature of 290°C. However, at operating temperature of 250°C and below, the conversion drops to below 20% due to accumulation of by-product that partially blocks the active site of the catalyst. The trend is as follow:

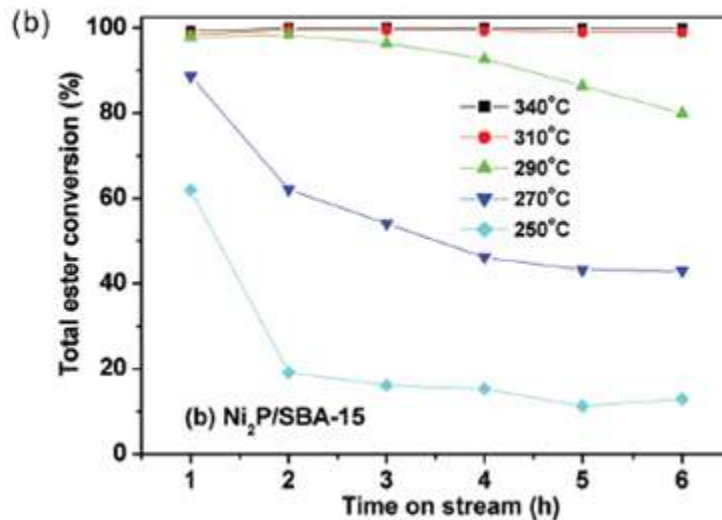


Figure 2.3: Temperature and pressure effect.

For n-octadecane formation at varying temperature, the maximum yield is at 290°C, shows by figure 2.4. Decline in n-octadecane yield as the increasing temperature is due to DCX process which favour at high temperature.

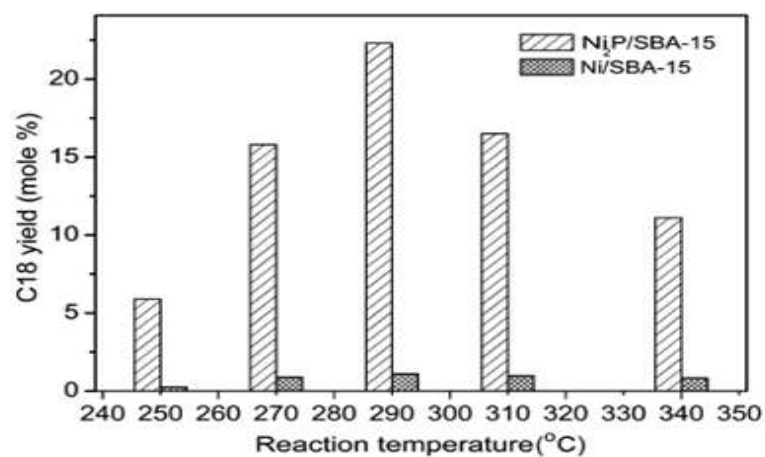


Figure 2.4: n-octadecane yield

The analysis also had been done on hydrocarbon distribution at 250°C and 40 bar. Figure x.0 shows the trend. At 250 °C, and pressure of 40 bar, cracking is limited and Ni-SBA-15 yields mostly DCX products, C<sub>17</sub> hydrocarbon. Yangxing Yang proposed to operate the reaction at moderate pressure of 20-30 bar and at lower temperature to provide adequate HDO reaction yield with lower hydrogen consumption.

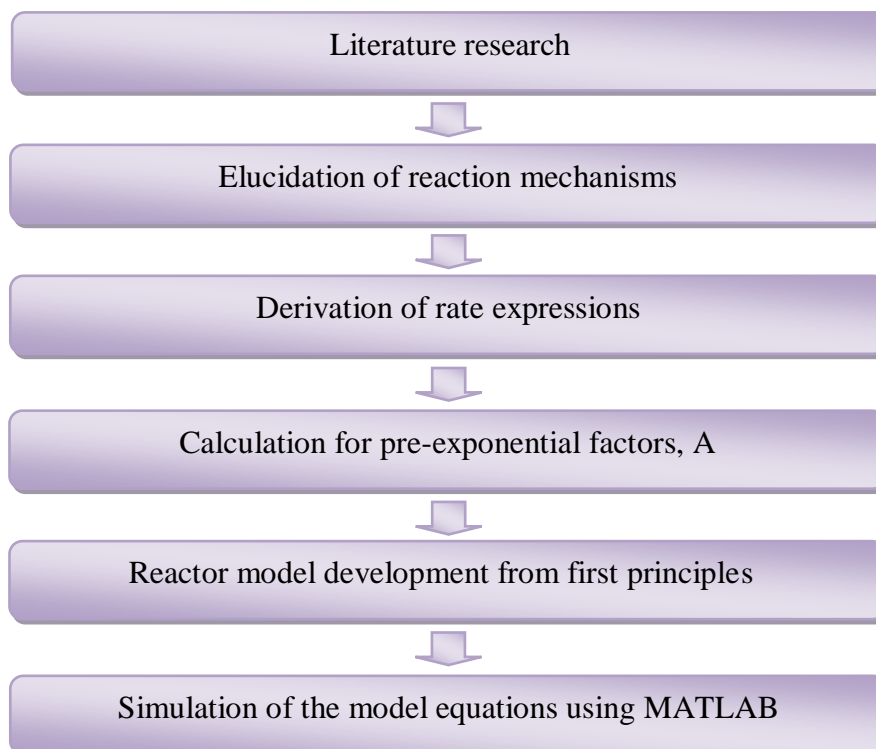
## CHAPTER 3: METHODOLOGY & PROJECT WORK

The methodology implemented in this research project is waterfall methodology where, it is a rigid step-by step approach for project continuation. With waterfall method, the whole project is planned at the very beginning with each phase was given a fixed deadline in accordance to Gantt chart, attached at the end of this chapter, page 32. The model derives its name from the cascading effect from one phase to the other as illustrated in figure 3.1 below.

Project activities were conducted according to the outlined research methodology, which involves literature study, elucidation of reaction mechanisms, derivation of rate expressions, pre-exponential factors calculations, reactor model development from first principles and finally, simulation of the model equations using MATLAB software.

### 3.1 Research Methodology/ milestones

Research methodology comprises of work activities throughout the development of this research project to achieve the desired objectives.



*Figure 3.1: Research methodology.*

### 3.1.1 Literature Research

This research project started with literature research by using keywords of kinetic modeling, green diesel, monoglyceride, hydrodeoxygenation, biodiesel, methyl oleate and etc. Due to the presence of various routes to produce green diesel, focus was given on the literatures that present the reaction within the outlined project's scope. Various types of models presented on the past literatures, which mostly are experiment-based were studied to see whether the models can be employed for the reaction using monoglyceride as the feedstock. Besides that, the outcomes of the analysis based on the past papers for example, the trend for operating temperature and initial hydrogen pressure are set to be compared with the results that were obtained by author.

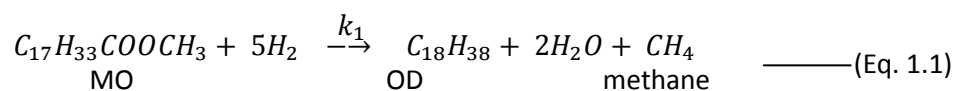
### 3.1.2 Elucidation of reaction mechanisms

Reaction of methyl oleate to green diesel can be divided into two reaction schemes; overall and detailed reactions. On the following sections until the end of project research, the project activities and analysis were discussed according to these two separate schemes.

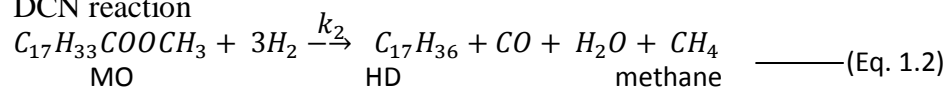
#### Overall reactions scheme

Overall reactions show the direct transformation of methyl oleate to green diesel through 3 parallel reactions; hydrodeoxygenation (HDO), decarbonylation (DCN), and decarboxylation (DCX). No intermediates formations were considered. The overall reaction mechanisms are as follow:

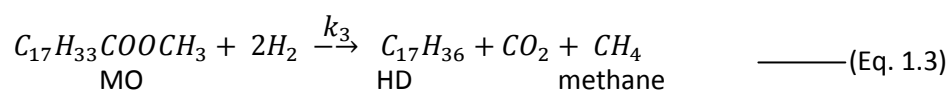
- HDO reaction



- DCN reaction



- DCX reaction

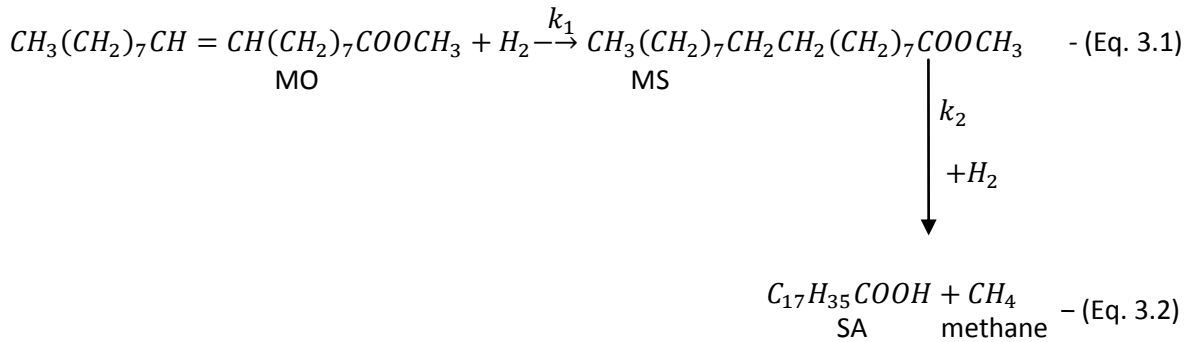




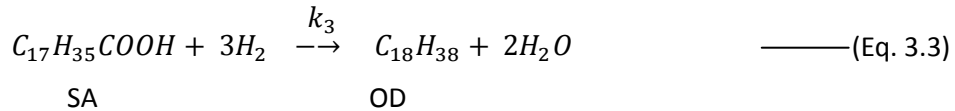
## Detailed reactions scheme

Detailed reactions scheme involves two series intermediate formation reactions; methyl oleate to methyl stearate (MS) and methyl stearate to stearic acid (SA). Hydrogenation of MO is basically to saturate the double bond forming saturated single bond MS. Just after SA formation, the abovementioned 3 main reactions; HDO, DCN and DCX take place. The detailed reaction mechanisms are as follow:

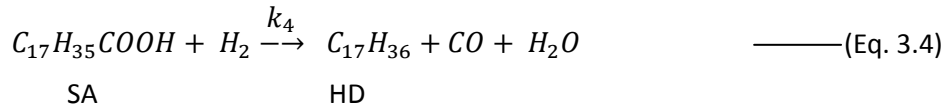
- Intermediates formation



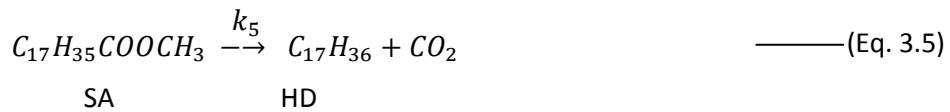
- HDO reaction



- DCN reaction



- DCX reaction



### 3.1.3 Derivation of rate expressions

#### Overall reactions scheme

- Rate of methyl oleate consumption

$$r_{MO} = -(k_1 + k_2 + k_3)C_{MO} \left( \frac{P_{H_2}}{RT} \right)^\alpha \quad \text{————(Eq. 3.6)}$$

- Rate of ocatadecane formation

$$r_{OD} = k_1 C_{MO} \left( \frac{P_{H_2}}{RT} \right)^\alpha \quad \text{————(Eq. 3.7)}$$

- Rate of heptadecane formation

$$r_{HD} = (k_2 + k_3)C_{MO} \left( \frac{P_{H_2}}{RT} \right)^\alpha \quad \text{————(Eq. 3.8)}$$

- Rate of methane formation

$$r_{CH_4} = (k_1 + k_2 + k_3)C_{MO} \left( \frac{P_{H_2}}{RT} \right)^\alpha \quad \text{————(Eq. 3.9)}$$

- Rate of water formation

$$r_{H_2O} = (2k_1 + k_2)C_{MO} \left( \frac{P_{H_2}}{RT} \right)^\alpha \quad \text{————(Eq. 3.10)}$$

- Rate of carbon monoxide formation

$$r_{CO} = k_2 C_{MO} \left( \frac{P_{H_2}}{RT} \right)^\alpha \quad \text{————(Eq. 3.11)}$$

- Rate of carbon dioxide formation

$$r_{CO_2} = k_3 C_{MO} \left( \frac{P_{H_2}}{RT} \right)^\alpha \quad \text{————(Eq. 3.12)}$$

- Rate of hydrogen gas consumption

$$r_{H_2} = -(5k_1 + 3k_2 + 2k_3)C_{MO} \left( \frac{P_{H_2}}{RT} \right)^\alpha \quad \text{————(Eq. 3.13)}$$

### Detailed reactions scheme

- Rate of methyl oleate consumption

$$r_{MO} = -k_1 C_{MO} \left( \frac{P_{H_2}}{RT} \right)^{\alpha_1} \quad \text{———— (Eq. 3.14)}$$

- Rate of methyl stearate formation

$$r_{MS} = k_1 C_{MO} \left( \frac{P_{H_2}}{RT} \right)^{\alpha_1} - k_2 C_{MS} \left( \frac{P_{H_2}}{RT} \right)^{\alpha_2} \quad \text{———— (Eq. 3.15)}$$

- Rate of stearic acid formation

$$r_{SA} = k_2 C_{MS} \left( \frac{P_{H_2}}{RT} \right)^{\alpha_2} - k_3 C_{SA} \left( \frac{P_{H_2}}{RT} \right)^{\alpha_3} - k_4 C_{SA} \left( \frac{P_{H_2}}{RT} \right)^{\alpha_4} - k_5 C_{SA} \quad \text{———— (Eq. 3.16)}$$

- Rate of octadecane formation

$$r_{OD} = k_3 C_{SA} \left( \frac{P_{H_2}}{RT} \right)^{\alpha_3} \quad \text{———— (Eq. 3.17)}$$

- Rate of heptadecane formation

$$r_{HD} = k_4 C_{SA} \left( \frac{P_{H_2}}{RT} \right)^{\alpha_4} + k_5 C_{SA} \quad \text{———— (Eq. 3.18)}$$

- Rate of methane formation

$$r_{CH_4} = k_2 C_{SA} \left( \frac{P_{H_2}}{RT} \right)^{\alpha_4} \quad \text{———— (Eq. 3.19)}$$

- Rate of carbon monoxide formation

$$r_{CO} = k_4 C_{SA} \left( \frac{P_{H_2}}{RT} \right)^{\alpha_4} \quad \text{———— (Eq. 3.20)}$$

- Rate of carbon dioxide formation

$$r_{CO_2} = k_5 C_{SA} \quad \text{———— (Eq. 3.21)}$$

- Rate of water formation

$$r_{H_2O} = 2k_3 C_{SA} \left( \frac{P_{H_2}}{RT} \right)^{\alpha_3} + k_4 C_{SA} \left( \frac{P_{H_2}}{RT} \right)^{\alpha_4} \quad \text{———— (Eq. 3.22)}$$

- Rate of hydrogen consumption

$$r_{H_2} = -k_1 C_{MO} \left( \frac{P_{H_2}}{RT} \right)^{\alpha_1} - k_2 C_{MS} \left( \frac{P_{H_2}}{RT} \right)^{\alpha_2} - 3k_3 C_{SA} \left( \frac{P_{H_2}}{RT} \right)^{\alpha_3} - k_4 C_{SA} \left( \frac{P_{H_2}}{RT} \right)^{\alpha_4} \quad \text{(Eq. 3.33)}$$

### 3.1.3 Reactor model development

#### Overall reactions scheme

- Rate of methyl oleate consumption

$$\frac{dC_{MO}}{dt} = -(k_1 + k_2 + k_3)C_{MO} \left( \frac{P_{H_2}}{RT} \right)^\alpha \quad \text{————(Eq. 3.34)}$$

- Rate of ocatadecane formation

$$\frac{dC_{OD}}{dt} = k_1 C_{MO} \left( \frac{P_{H_2}}{RT} \right)^\alpha \quad \text{————(Eq. 3.35)}$$

- Rate of heptadecane formation

$$\frac{dC_{HD}}{dt} = (k_2 + k_3) C_{MO} \left( \frac{P_{H_2}}{RT} \right)^\alpha \quad \text{————(Eq. 3.36)}$$

- Rate of methane formation

$$\frac{dC_{CH_4}}{dt} = (k_1 + k_2 + k_3) C_{MO} \left( \frac{P_{H_2}}{RT} \right)^\alpha \quad \text{————(Eq. 3.37)}$$

- Rate of water formation

$$\frac{dC_{H_2O}}{dt} = (2k_1 + k_2) C_{MO} \left( \frac{P_{H_2}}{RT} \right)^\alpha \quad \text{————(Eq. 3.38)}$$

- Rate of carbon monoxide formation

$$\frac{dC_{CO}}{dt} = k_2 C_{MO} \left( \frac{P_{H_2}}{RT} \right)^\alpha \quad \text{————(Eq. 3.39)}$$

- Rate of carbon dioxide formation

$$\frac{dC_{CO_2}}{dt} = k_3 C_{MO} \left( \frac{P_{H_2}}{RT} \right)^\alpha \quad \text{————(Eq. 3.40)}$$

- Rate of hydrogen gas consumption

$$\frac{dC_{H_2}}{dt} = -(5k_1 + 3k_2 + 2k_3) C_{MO} \left( \frac{P_{H_2}}{RT} \right)^\alpha \quad \text{————(Eq. 3.41)}$$

## Detailed reactions scheme

- Rate of methyl oleate consumption

$$\frac{dC_{MO}}{dt} = -k_1 C_{MO} \left( \frac{P_{H_2}}{RT} \right)^{\alpha_1} \quad \text{———— (Eq. 3.42)}$$

- Rate of methyl stearate formation

$$\frac{dC_{MS}}{dt} = k_1 C_{MO} \left( \frac{P_{H_2}}{RT} \right)^{\alpha_1} - k_2 C_{MS} \left( \frac{P_{H_2}}{RT} \right)^{\alpha_2} \quad \text{———— (Eq. 3.43)}$$

- Rate of stearic acid formation

$$\frac{dC_{SA}}{dt} = k_2 C_{MS} \left( \frac{P_{H_2}}{RT} \right)^{\alpha_2} - k_3 C_{SA} \left( \frac{P_{H_2}}{RT} \right)^{\alpha_3} - k_4 C_{SA} \left( \frac{P_{H_2}}{RT} \right)^{\alpha_4} - k_5 C_{SA} \quad \text{———— (Eq. 3.44)}$$

- Rate of octadecane formation

$$\frac{dC_{OD}}{dt} = k_3 C_{SA} \left( \frac{P_{H_2}}{RT} \right)^{\alpha_3} \quad \text{———— (Eq. 3.45)}$$

- Rate of heptadecane formation

$$\frac{dC_{HD}}{dt} = k_4 C_{SA} \left( \frac{P_{H_2}}{RT} \right)^{\alpha_4} + k_5 C_{SA} \quad \text{———— (Eq. 3.46)}$$

- Rate of methane formation

$$\frac{dC_{CH_4}}{dt} = k_2 C_{MS} \left( \frac{P_{H_2}}{RT} \right)^{\alpha_2} \quad \text{———— (Eq. 3.47)}$$

- Rate of carbon monoxide formation

$$\frac{dC_{CO}}{dt} = k_4 C_{SA} \left( \frac{P_{H_2}}{RT} \right)^{\alpha_4} \quad \text{———— (Eq. 3.48)}$$

- Rate of carbon dioxide formation

$$\frac{dC_{CO_2}}{dt} = k_5 C_{SA} \quad \text{———— (Eq. 3.49)}$$

- Rate of water formation

$$\frac{dC_{H_2O}}{dt} = 2k_3 C_{SA} \left( \frac{P_{H_2}}{RT} \right)^{\alpha_3} + k_4 C_{SA} \left( \frac{P_{H_2}}{RT} \right)^{\alpha_4} \quad \text{———— (Eq. 3.50)}$$

- Rate of hydrogen consumption

$$\frac{dC_{H_2}}{dt} = -k_1 C_{MO} \left( \frac{P_{H_2}}{RT} \right)^{\alpha_1} - k_2 C_{MS} \left( \frac{P_{H_2}}{RT} \right)^{\alpha_2} - 3k_3 C_{SA} \left( \frac{P_{H_2}}{RT} \right)^{\alpha_3} - k_4 C_{SA} \left( \frac{P_{H_2}}{RT} \right)^{\alpha_4} \quad \text{(Eq. 3.51)}$$

### 3.1.4 Calculation for pre-exponential factor, A

#### Step 1: Critical temperature ( $T_c$ ), critical pressure ( $P_c$ ) and critical volume ( $V_c$ )

$T_c$ ,  $P_c$  and  $V_c$  were calculated using Marrero-Marejon & Pardillo-Fontdevila method [13]. This method uses contribution of group interaction in pairs, known as bond contribution to get the critical values. The critical properties of all the groups present in methyl oleate, methyl stearate and stearic acid molecules given by Marrero & Pardillo are as follow:

- Methyl oleate

*Table 3.1: Critical properties for methyl oleate*

Pair number	Group pair	$N_k$	Tcbk	Pcbk	Vcbk	Tbbk
2	$CH_3 - \& - CH_2 -$	1	-0.0227	-0.043	88.6	194.25
29	$-CH_2 - \& - CH_2 -$	6	-0.0206	-0.0272	56.6	244.88
32	$-CH_2 - \& = CH -$	2	0.8636	0.0818	50.7	201.8
88	$-CH[=]\& - CH[=]$	1	-1.766	-0.2291	47.8	334.64
47	$-CH_2 - \& - COO[-]$	1	0.0276	0.1561	69.9	475.65
20	$-CH_3 - \& - COO[-]$	1	0.0267	0.1462	93.3	456.92
<b>Total</b>	$\sum N_k \times (\text{properties})$		<b>-0.131</b>	<b>0.0306</b>	<b>740.6</b>	<b>3334.34</b>

- Methyl stearate

*Table 3.2: Critical properties for methyl stearate*

Pair number	Group pair	$N_k$	Tcbk	Pcbk	Vcbk	Tbbk
2	$CH_3 - \& - CH_2 -$	1	-0.0227	-0.043	88.6	194.25
29	$-CH_2 - \& - CH_2 -$	7	-0.0206	-0.0272	56.6	244.88
47	$-CH_2 - \& - COO[-]$	1	0.0276	0.1561	69.9	475.65
20	$-CH_3 - \& - COO[-]$	1	0.0267	0.1462	93.3	456.92
<b>Total</b>	$\sum N_k \times (\text{properties})$		<b>-0.1126</b>	<b>0.0689</b>	<b>648</b>	<b>2840.98</b>

- Stearic acid

*\*Critical properties for stearic acid has to be calculated using different method.*

Based on above critical properties, Marrero and Pardillo came up with equations to calculate boiling point temperature, critical temperature, critical pressure and critical volume. The equations introduced by Marrero & Pardillo are:

$$T_b = M_w^{-0.404} \sum N_k (tbbk) + 156.0 \quad \text{————(Eq. 3.52)}$$

$$T_c = T_b / [0.5851 - 0.9286(\sum N_k tcbk) - (\sum N_k tcbk)^2] \quad \text{————(Eq. 3.53)}$$

$$P_c = [0.1285 - 0.0059N_{atom} - \sum N_k pcbk]^{-2} \quad \text{————(Eq. 3.54)}$$

$$V_c = 25.1 + \sum N_k vcbk \quad \text{————(Eq. 3.55)}$$

Where,

$T_b$  = boiling point temperature

$N_k$  = number of atoms of type k

$N_{atom}$  = number of atoms in compound

$M_w$  = molecular weight

### **Step 2: Acentric factor, $\omega$**

Acentric factor is obtained by using Edmister correlation and is given by:

$$\omega = \frac{3}{7} \times \frac{\log \left( \frac{P_c}{14.7} \right)}{\frac{T_c}{T_b} - 1} - 1 \quad \text{————(Eq. 3.56)}$$

Where,

*Both  $T_c$  and  $T_b$  are in rankine ( $^{\circ}R$ ) while  $P_c$  in Psi unit.*

### Step 3: Molar volume, $V_m$

The molar volume with unit  $cm^3/mol$  is obtained from Yamada and Gunn (1973) correlation:

$$V_m = V_c(0.29056 - 0.08775\omega)^{(1-T_b/T_c)^{2/7}} \quad \text{————(Eq. 3.57)}$$

### Step 4: Absolute translation entropy, $S_{trans}^0$

Absolute translation entropy is calculated using Sackur-Tetrode equation:

$$S_{trans}^0 = R \ln \left( \frac{V_m}{N_A} \left( \frac{2\pi(M_w/N_A)k_B T}{h^2} \right)^{3/2} \right) + \frac{5}{2} R \quad \text{————(Eq. 3.58)}$$

Where,

$N_A = \text{avogadro number}, 6.02214 \times 10^{23}$

$\pi = 3.14159$

$M_w = \text{molecular weight}$

$K_B = \text{Boltzman constant}, 1.38065 \times 10^{-23}$

$h = \text{planck's constant}, 6.62607 \times 10^{-34}$

$T = \text{average temperature}, 565.65 \text{ } ^\circ K$

### Step 5: Change in absolute translation entropy, $\Delta S_{trans}^0$

Delta absolute translation entropy is calculated using:

$$\Delta S_{trans}^0 = - \left( \frac{2}{3} \right) S_{trans}^0 \quad \text{————(Eq. 3.59)}$$



### Step 6: Pre-exponential factor, A

Pre-exponential factor is calculated using eq. 1.0 below. The results are then converted in  $h^{-1}$  unit and are plug in the MATLAB formulation.

$$A = \frac{k_B T}{h} \exp \frac{\Delta S_{trans}^\circ}{R} \quad \text{————(Eq. 3.60)}$$

### 3.1.5 MATLAB simulation

#### Step 1: Identify equations involved

As stated earlier, parameters to be identified are temperature and initial hydrogen pressure variations as the reaction proceed in 2 hours residence time. Because of that, Arrhenius equation is used to demonstrate these relationships. Theoretically, the higher the temperature, the higher the rate of collision between the atoms and the molecules of the substances due to higher kinetic energy, results in the higher the rate of reaction. Pressure terms are added to Arrhenius equation to see the pressure variations, forming Modified Arrhenius equation.

- Arrhenius equation

$$k = A \exp\left(\frac{-E_a}{RT}\right) \quad \text{————(Eq. 3.60)}$$

- Modified Arrhenius equation

$$k = A \exp\left(\frac{-E_a}{RT}\right) \left(\frac{P}{P_{ref}}\right)^\beta \quad \text{————(Eq. 3.61)}$$

Where,

$k$  = rate coefficient/ rate constant

$A$  = pre-exponential factor

$E_a$  = activation energy in kJ/mol

$R$  = universal gas constant ( $8.314 \times 10^{-3} \text{ kJ mol}^{-1}\text{K}^{-1}$ )

$T$  = temperature in Kelvin

$P$  = pressure in bar

$P_{ref}$  = reference pressure in bar

Pre-exponential factors for both overall and detailed reactions were calculated using Marrero & Pardillo method as discussed in section 3.14. While, activation energy is defined as the amount of energy that must be overcome for the reaction to proceed.

The values shall be obtained from experiment. However in this research project due to scope of study which is simulation-based, the activation energy values were assumed with respect to the MATLAB simulation graphs. Means, the plugged in activation energy values that produced smooth graphs were selected.

Both A and  $E_a$  are unique for each rate constants. For overall reactions scheme, there are three rate constants involved, with  $k_1$  as the rate constant for HDO,  $k_2$  as the rate constant for DCN and  $k_3$  as the rate constant for DCX reaction. The assumed  $E_a$  and calculated A values are as follow:

*Table 3.3: Assumed  $E_a$  values for overall reactions scheme*

Rate constants	Activation energy, $E_a$	Pre-exponential factor, A
$k_1$	125800	$2.3 \times 10^7$
$k_2$	132300	
$k_3$	141400	

On the other hands, there are in total of five rate constants which involved in detailed reactions scheme with  $k_1$  is the rate constant for saturation of double bond together with the formation of MS,  $k_2$  is the reaction forming SA,  $k_3$  is the rate constant for HDO reaction,  $k_4$  is the rate constant for DCN and finally,  $k_5$  is the rate constant for DCX reaction. The assumed  $E_a$  and calculated A values are as follow:

*Table 3.4: Assumed  $E_a$  values for detailed reactions scheme*

Rate constants	Activation energy, $E_a$	Pre-exponential factor, A
$k_1$	121657	$2.3 \times 10^7$
$k_2$	128200	$9.66 \times 10^{10}$
$k_3$	76400	$1.53 \times 10^6$
$k_4$	82300	
$k_5$	83800	

Based on literature research, author found that the reaction forming green diesel using triglyceride as the feedstock can proceed at the temperature range of 250 °C up

to 400°C and initial hydrogen pressure of 50 - 100 bar [4]. Unwanted cracking is the prevailing reaction occurred beyond this temperature range. Because of that, the analysis using monoglyceride as the feedstock were conducted at the temperature of 220, 250, 270, 300 °C and initial hydrogen pressure of 20, 30, 40 and 50 bar. Reference pressure of 60 bar was selected.

## **Step 2: Define functions**

Order of reaction with respect to hydrogen,  $\alpha$  is taken as 1.85 because this study evaluates first order reaction.

- Functions for overall reactions scheme

```
function f = hydrocar_eq(t,c)
global k a
% c(1) = methyl oleate
f(1) = -(k(1)+k(2)+k(3))*c(1)*c(8)^a;
% C(2) = octadecane
f(2) = k(1)*c(1)*(c(8))^a;
% C(3)= heptadecane
f(3)= (k(2)+k(3))*c(1)*(c(8))^a;
% c(4) = methane
f(4)= (k(1)+k(2)+k(3))*c(1)*(c(8))^a;
%c(5) = water
f(5) = (2*k(1)+k(2))*c(1)*(c(8))^a;
%c (6) = carbon monoxide
f(6) = k(2)*c(1)*(c(8))^a;
%f(7) = carbon dioxide
f(7)= k(3)*c(1)*(c(8))^a;
%f(8) = hydrogen
f(8)= -(5*k(1)+3*k(2)+2*k(3))*c(1)*(c(8))^a;
f=f';
```

- Functions for detailed reaction scheme

```
function f = detailed_function(t,c)
global k a
% c(1): disappearance of methyl oleate
f(1) = -k(1)*c(1)*c(10)^a(1);
% c(2): formation of methyl stearate
f(2) = k(1)*c(1)*c(10)^a(1) - k(2)*c(2)*c(10)^a(2);
% c(3): formation of stearic acid
f(3) = k(2)*c(2)*c(10)^a(2) - k(3)*c(3)*c(10)^a(3) - k(4)*c(3)*c(10)^a(4) - k(5)*c(3);
% c(4): formation of octadecane
f(4) = k(3)*c(3)*c(10)^a(3);
```

```

% c(5): formation of heptadecane
f(5) = k(4)*c(3)*c(10)^a(4) + k(5)*c(3);
% c(6): formation of methane
f(6) = k(2)*c(2)*c(10)^a(2);
% c(7): formation of carbon monoxide
f(7) = k(4)*c(3)*c(10)^a(4);
% c(8): formation of carbon dioxide
f(8) = k(5)*c(3);
% c(9): formation of water
f(9) = 2*k(3)*c(3)*c(10)^a(3) + k(4)*c(3)*c(10)^a(4);
% c(10): disappearance of hydrogen
f(10) = -k(1)*c(1)*c(10)^a(1) - k(2)*c(2)*c(10)^a(2) -
3*k(3)*c(3)*c(10)^a(3) - k(4)*c(3)*c(10)^a(4);
f = f';

```

The functions were for each component in terms of concentration (in  $mol/m^3$ ) in 'editor window'.  $F=f'$  indicates that the function is differentiated once. This differentiation is done automatically by MATLAB. The file name is hydrocar\_eq. The file is linked with another 'editor window' which defines the modified Arrhenius equation and related constants.

### **Step 3: Formulation**

Initial methyl oleate concentration considered in present study is  $100 mol/m^3$  and this value is reducing as the reactions proceed. Author fixed the reaction time of 2 hours, at every 0.2 hour increment. After 2 hours, the concentration of all of the products are tabulated and plotted in graphs. Further analysis on the final concentrations will be discussed in the next chapter, results & discussion.

- Formulation for overall reactions scheme

```

% Hydrodeoxygenation of methyl oleate to C14-C18 hydrocarbons
clc
clear
global k a
nk = 3;
Apre = [2.3e7 2.3e7 2.3e7];
Eact = [125800 132300 141400];
R = 8.314; % J/MOL/K
Temp = 300; % deg.C
T = 273+Temp
b = 1.56;
Pref = 60;
P = 50;

```

```

for i = 1:nk
    k(i) = Apre(i)*exp(-Eact(i)/(R*T))*(P/Pref)^b;
end
k
a = 1.85;
ch2= P*1e5/(R*T)
c0 = [100 0 0 0 0 0 0 ch2];
tspan = [0:0.2:2];
[t,c]=ode45(@hydrocar_eq,tspan, c0);
t
c
plot(t,c)
xlabel('t in h')
ylabel('concentration in mol/m^3')

```

- Formulation for detailed reactions scheme


```

hydrodeoxygenation (detailed stoichiometric)
clc
clear
global k a
nk = 5;
Apre = [2.3e7 9.66e10 1.53e6 1.53e6 1.53e6];
Eact = [121657 128200 76400 82300 83800];
R = 8.314; % J/MOL/K
Temp = 300; %degree.C
T = 273+Temp
b = 1.45
Pref = 60;
P = 50
for i = 1:nk
    k(i) = Apre(i)*exp(-Eact(i)/(R*T))*(P/Pref)^b;
end
k
a = [1.7 1.8 1.8 1.8];
ch2 = P*1e5/(R*T)
c0 = [100 0 0 0 0 0 0 0 0 ch2];
tspan = [0:0.2:2];
[t,c]=ode45(@detailed_function,tspan,c0);
t
c
plot(t,c)
xlabel ('t in h')
ylabel ('concentration in mol/m^3')

```

### 3.2 Gantt Chart

No.	Detail/Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15	
1.	Project work continues	■	■	■	■	■	■	■	M I D  S E M E S T E R  B R E A K									
2.	Submission of progress report									■								
3.	Project work continues									■	■	■	■	■				
4.	Pre-EDX												■					
5.	Submission of draft report													■				
6.	Submission of dissertation (soft bound)														■			
7.	Submission of technical paper														■			
8.	Oral presentation																■	
9.	Submission of project dissertation (hard bound)																	■

 Expected completion

## CHAPTER 4: RESULTS & DISCUSSION

The simulation runs were conducted for both overall and detailed reactions separately. As stated earlier, the objective for this research project is to identify the trend and variations of operating temperature and initial hydrogen pressure as the reactions proceed. The changes in concentrations, in  $\text{mol}/\text{m}^3$  for all of the components with respect to 2 hour reaction time were observed. With that, for better understanding, the analysis were done based on the conversion of methyl oleate, selectivity towards octadecane and heptadecane formations, and the yields for all of the components involved in the reactions.

### Conversion of reactant

Conversion of reactant can be defined as concentration of reactant consumed in the reaction over the initial concentration of reactant fed into the reactor. In this research, the reactant is methyl oleate. The conversion is calculated using eq. 4.1 given below. Graph is plotted in terms of mol percent of methyl oleate versus temperature (220, 250, 270, 300 °C) in different initial hydrogen pressures (20, 30, 40, 50 bar).

$$\text{Methyl oleate conversion} = \frac{(C_{mo,i} - C_{mo,f})}{C_{mo,i}} \times 100 \quad \text{---(Eq. 4.1)}$$

Where,

$C_{mo,i}$  = initial methyl oleate concentration in  $\text{mol}/\text{m}^3 = 100 \text{ mol}/\text{m}^3$

$C_{mo,f}$  = final methyl oleate concentration in  $\text{mol}/\text{m}^3$ (after 2 hours)

### Yields of products

Yield can be defined as concentration of each of the component produced from the reactions over the initial amount of reactant fed. For example, the yield for octadecane is the final octadecane concentration over the initial concentration of methyl oleate fed. Yield is represented in mol %.

$$\text{Yield}_{\text{component}} = \frac{C_{\text{component},f}}{C_{mo,i}} \times \text{stoichiometric factor} \times 100 \quad \text{---(Eq. 4.2)}$$



Where,

$$C_{\text{component}} =$$

Concentration of all components mol/m<sup>3</sup> (OD, HD, MS, SA, CH<sub>4</sub>, H<sub>2</sub>O, CO, CO<sub>2</sub>)

$$\text{Stoichiometric factor} = \frac{\text{no. of moles of reactant consumed}}{\text{no. of moles of product formed}} \quad \text{---(Eq. 4.3)}$$

Stoichiometric factors for all of the components involved in the reactions are listed in table x.0

Table 4.1: Stoichiometric factors for overall reactions scheme

Components	Stoichiometric factors
Octadecane	1
Heptadecane	1/2
Methane	1/3
Water	1/3
Carbon monoxide	1
Carbon dioxide	1

Table 4.2: Stoichiometric factors for detailed reactions scheme

Components	Stoichiometric factors
Methyl stearate	1
Stearic acid	1
Octadecane	1
Heptadecane	1/2
Methane	1
Water	1/3
Carbon monoxide	1
Carbon dioxide	1

### **Selectivity towards formation of main products**

On the other hands, selectivity is the measure of the favourability of reactions towards the formation of main products. In the case of methyl oleate conversion to green diesel, the desired products are octadecane and heptadecane. Thus, the analysis on the temperature and pressure effects towards the selectivity of these two components is discussed here. The selectivity is calculated using formula below. Graph is plotted in terms of selectivity towards main product (ratio) versus temperature (220, 250, 270, 300 °C) in different initial hydrogen pressures (20, 30, 40, 50 bar).

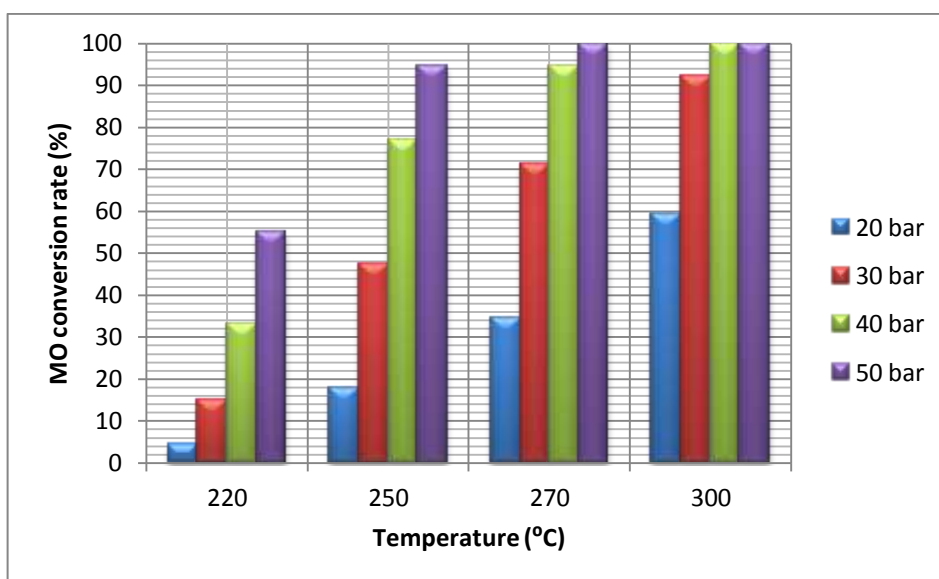
$$selectivity = \frac{yield\ of\ desired\ product}{conversion\ of\ reactant} \quad \text{—————(Eq. 4.4)}$$

Where,

Both the conversion of reactant (methyl oleate) and yield of desired products are taken from 4.1 and 4.2 respectively.

## 4.1 Overall reactions scheme

### 4.1.1 Methyl oleate conversion

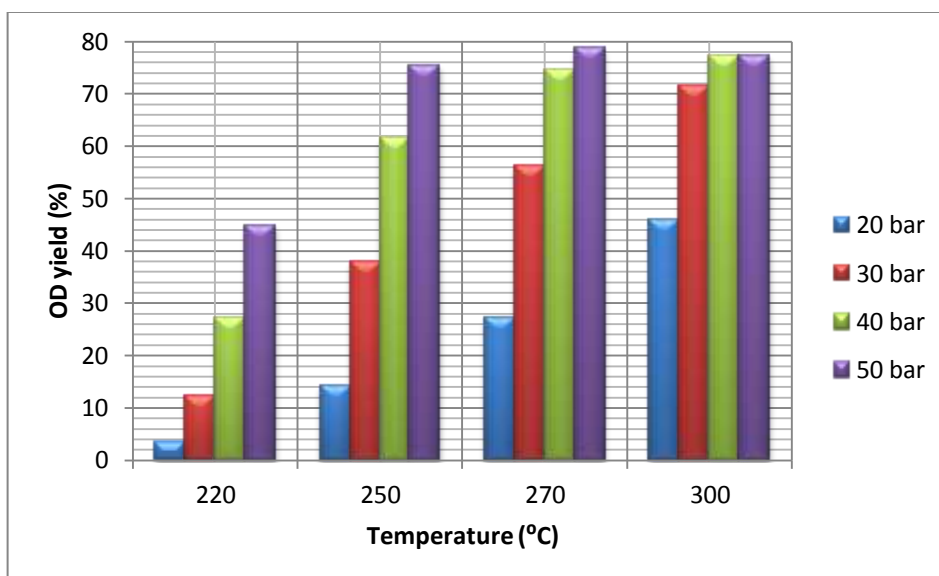


*Figure 4.1: Methyl oleate conversion vs. temperature*

Discussion:

- As the temperature is increased from 220 °C to 300 °C, the rate of methyl oleate conversion is also increased. This is because, high temperature enhanced the rate of reaction as it provides more energy for the methyl oleate molecules to react.
- As the initial hydrogen pressure is increased, the rate of methyl oleate conversion is also increased because higher initial hydrogen pressure favours HDO reaction, causing more methyl oleate to be converted to octadecane.
- Methyl oleate conversion rate is fastest at initial hydrogen pressure of 50 bar. However, at this pressure, maximum temperature for full conversion is limited at 270 °C.
- Overall, complete methyl oleate conversion after 2 hours is achieved at initial hydrogen pressure of 50 bar and operating temperature of 270 °C.

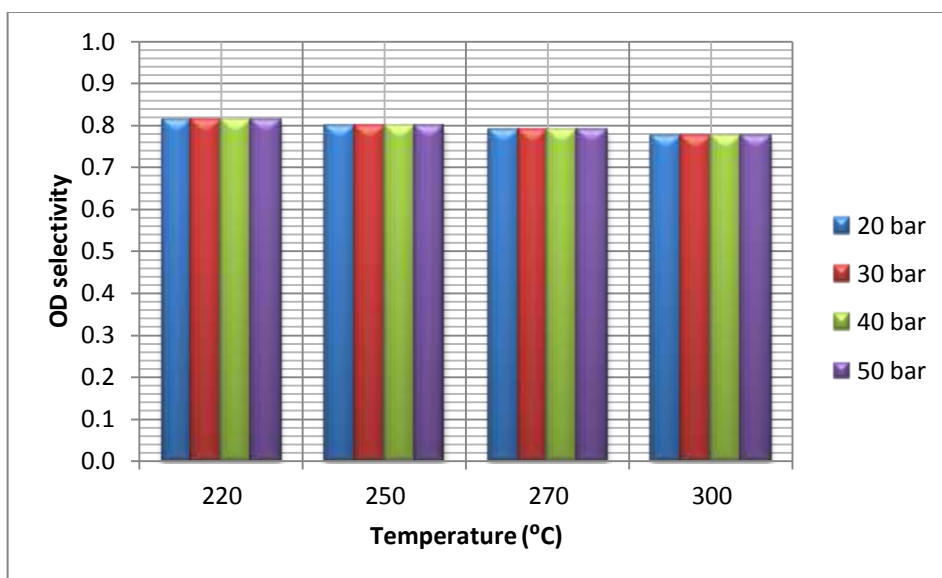
#### 4.1.2 Yield of octadecane



*Figure 4.2: Yield of octadecane vs. temperature*

- As the operating temperature is increased, the octadecane yield is also increased shows that, the applied operating temperature and pressure ranges capable to maximize the HDO reaction yield, forming octadecane rather than heptadecane.
- At initial hydrogen pressure of 50 bar, the maximum octadecane yield of 79% is achieved at 270°C. Beyond this temperature, the octadecane yield is decreasing showing that the selectivity shifted towards heptadecane formation.
- This trend is verified by a study showing that, the decarboxylation reaction forming heptadecane is favoured at higher temperature. The heptadecane formation suppressed the yield of octadecane.

### 4.1.3 Selectivity of octadecane

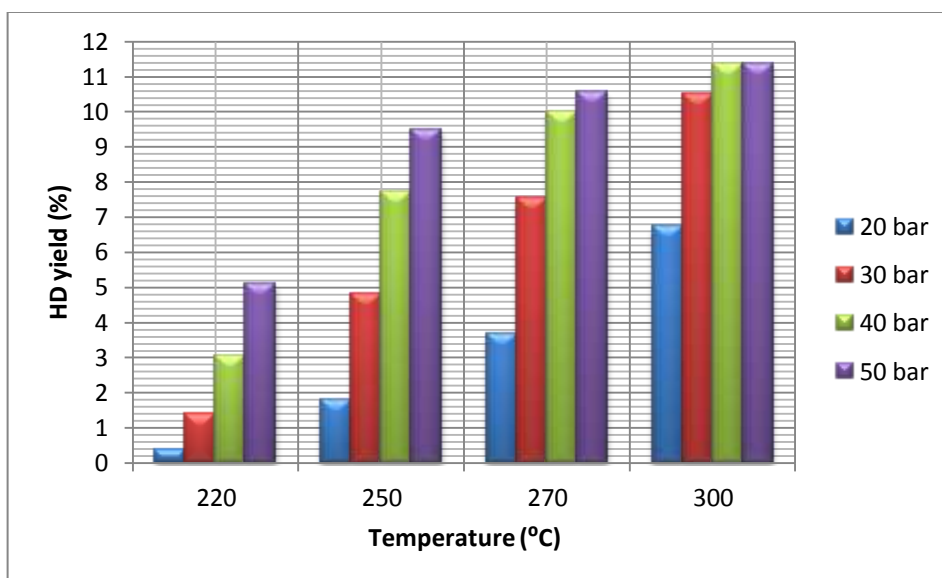


*Figure 4.3: Selectivity of octadecane vs. temperature*

Discussion:

- As the temperature is increased, the selectivity towards formation of octadecane is decreased. This is because the decarboxylation route is favoured at higher temperature, suppressing the hydrodeoxygenation route. This statement is verified by the trend shows by the increasing heptadecane selectivity as temperature is increased.
- As the pressure is increased, the selectivity towards formation of octadecane remains constant, indicates that initial hydrogen pressure has no effect on the selectivity of octadecane. It can be deduced that, monoglyceride structure is simpler compared to triglycerides structure. Thus, change in pressure at each temperature interval could not be observed.
- At applied temperature and initial hydrogen pressure range, selectivity towards octadecane formation is quite high with 0.78-0.82 by ratio approximately.

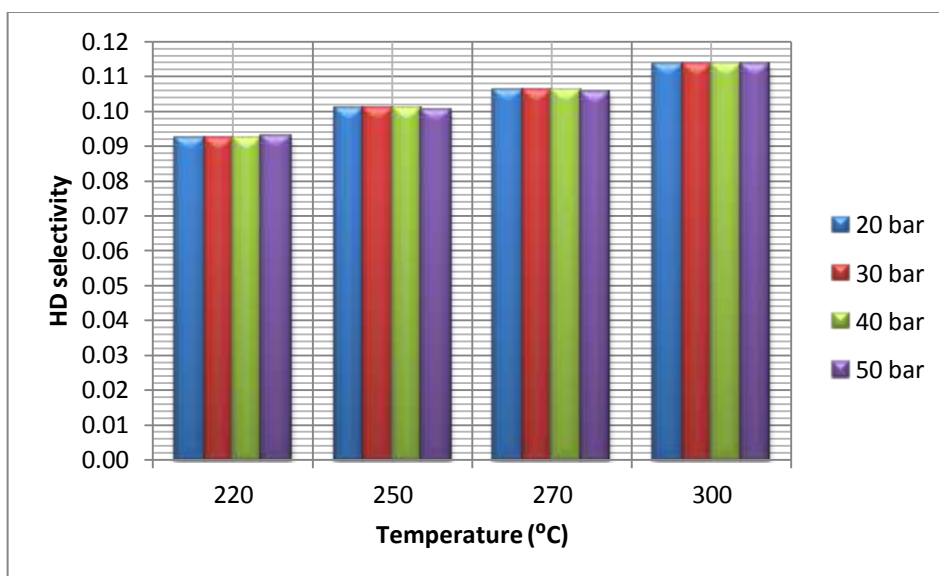
#### 4.1.4 Yield heptadecane



*Figure 4.4: Yield of heptadecane vs. temperature*

- Overall, heptadecane yield is very low compared to octadecane yield with maximum yield of only 11.4%. This trend indicates that for methyl oleate conversion to green diesel, hydrodeoxygenation is the prevailing route at the applied temperature and initial hydrogen pressure.

#### 4.1.5 Heptadecane selectivity

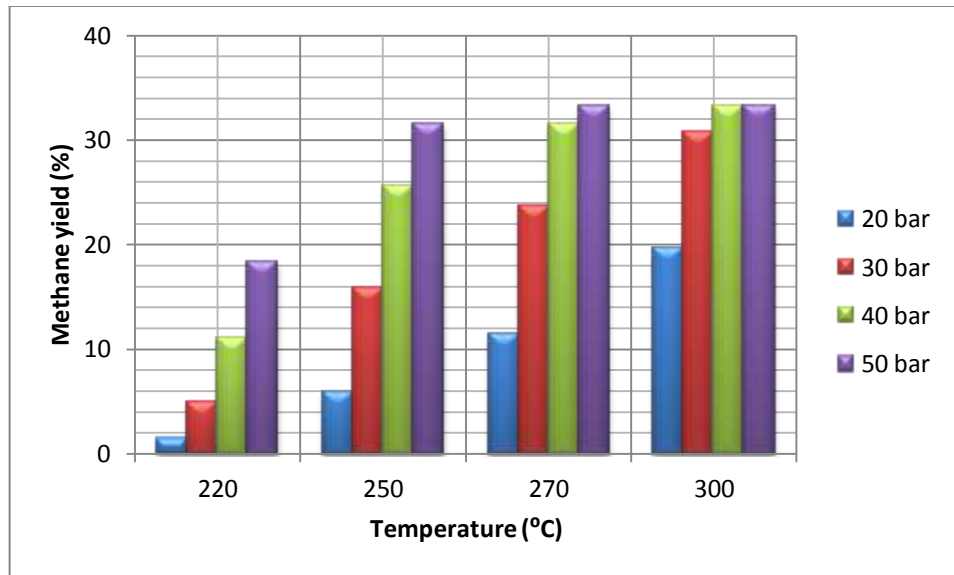


*Figure 4.5: Selectivity of heptadecane vs. temperature*

Discussion:

- The trend for heptadecane selectivity is opposite of octadecane selectivity. As the temperature is increased, the selectivity towards heptadecane formation is increased. This is due to carboxylation reaction is favoured at higher temperature.
- The heptadecane selectivity is indifferent of pressure. This condition is exactly the same as what happened on octadecane's selectivity, due to monoglyceride structure which is too simple..
- Reaction temperature of 300°C showed highest selectivity towards heptadecane formation with 0.14 by ratio. Overall, the selectivity of heptadecane formation is lower as compared to the selectivity of octadecane.

#### 4.1.6 Yield methane



*Figure 4.6: Yield of methane vs. temperature*

Discussion:

- The undesired side reaction for the methyl oleate conversion to green diesel is methanation reaction, producing methane as by-product. Methane formation increases hydrogen consumption thus decreasing hydrocarbon yield.
- Methane maximum yield is 33% and is achieved at 300°C for both initial hydrogen pressure of 40 and 50 bar.



#### 4.1.7 Yield of water

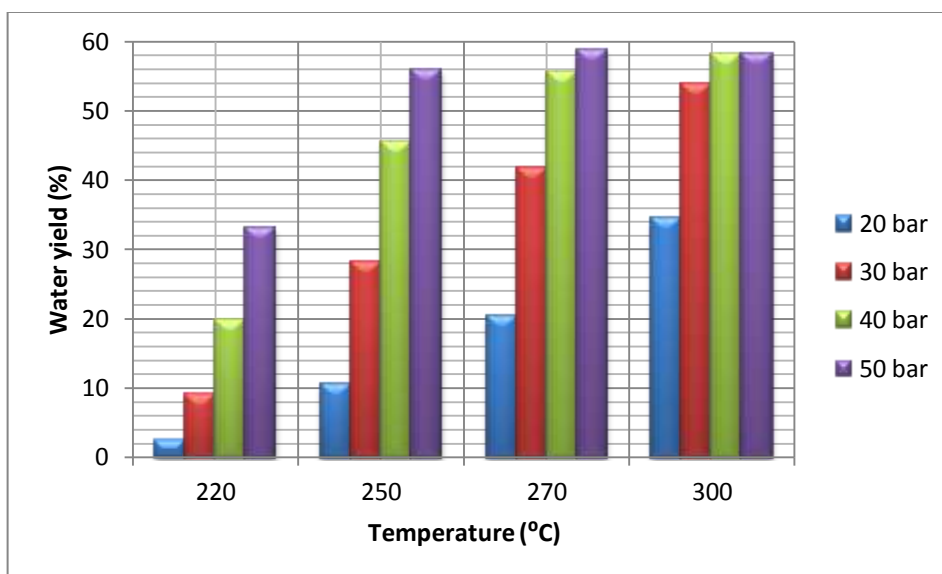
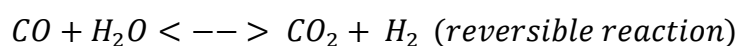


Figure 4.7: Yield of water vs. temperature

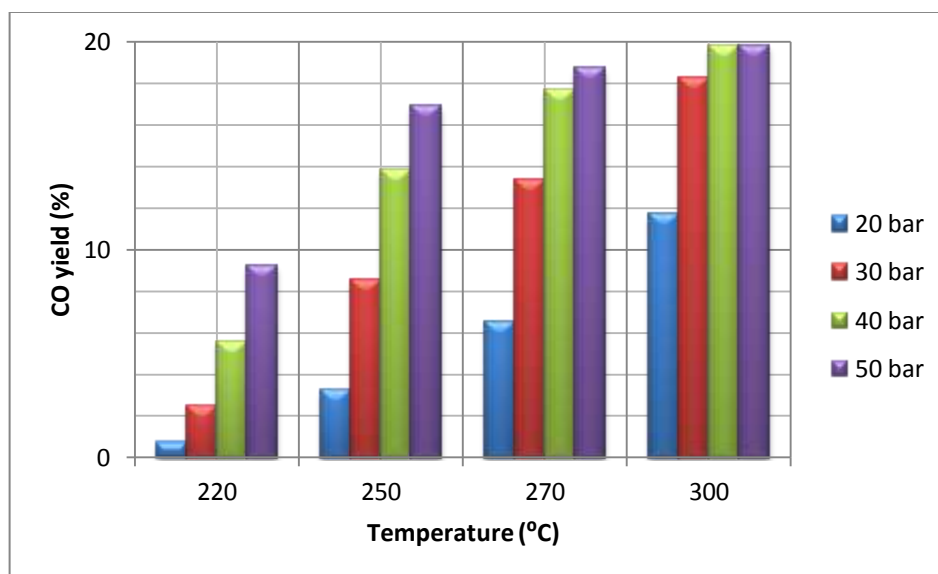
Discussion:

- The yield of water formation is highest among other by-products. Even at low temperature of 220°C, the water yield is already as high as 33%. Because of the use of a few assumptions in kinetic equations development, the yield can be reduced by using actual kinetic constant. This high yield percent is due to hydrodeoxygenation reaction that prevailed at low temperature and high pressure condition.

- At high initial hydrogen pressure of 50 bar, there is slight decreased in water yield from 59% to 58%. Theoretically, this is due to water-gas shift reaction that uses water to form carbon dioxide [4]. The reaction of the side-reaction is as follow:



#### 4.1.8 Yield of carbon monoxide

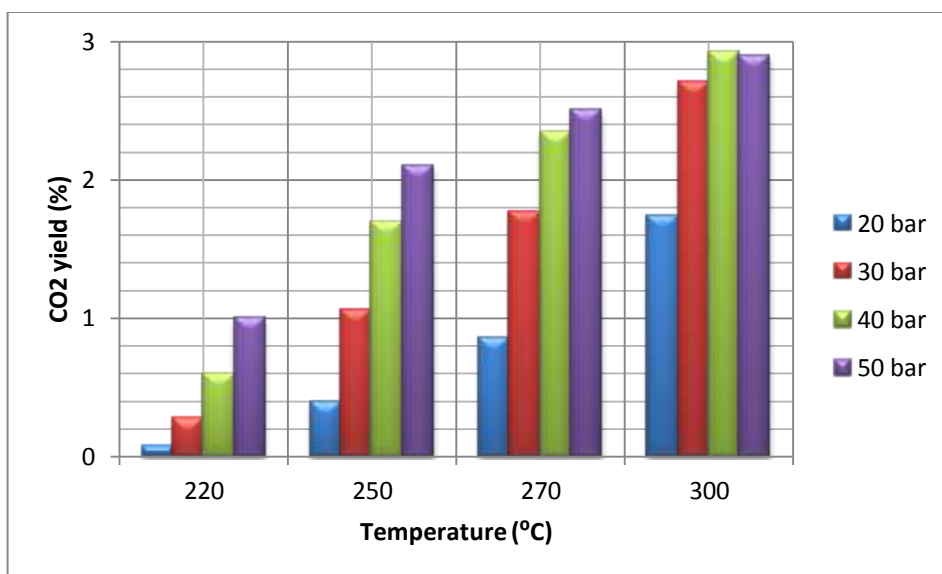


*Figure 4.8: Yield of carbon monoxide vs. temperature*

Discussion:

- As the temperature is increased, the formation of carbon monoxide is also increased. Overall, the carbonylation reaction (producing carbon monoxide) has the same trend as decarboxylation reaction. Both reactions favoured at high temperature and low pressure.

#### 4.1.9 Yield of carbon dioxide



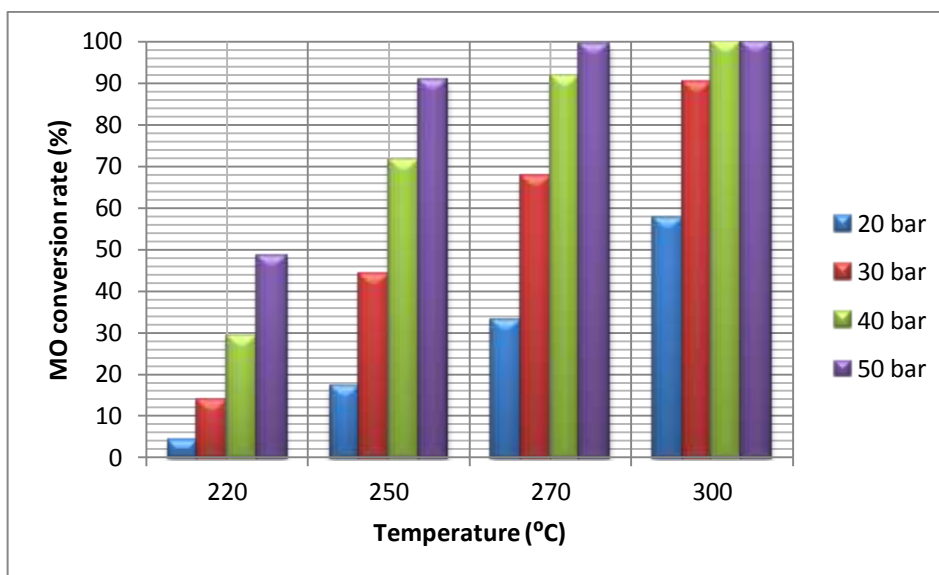
*Figure 4.9: Yield of carbon dioxide vs. temperature*

Discussion:

- At higher temperature, decarboxylation is favoured. The yield of carbon dioxide is increased at higher temperature and higher pressure conditions.

## 4.2 Detailed reactions scheme

### 4.2.1 Methyl oleate conversion

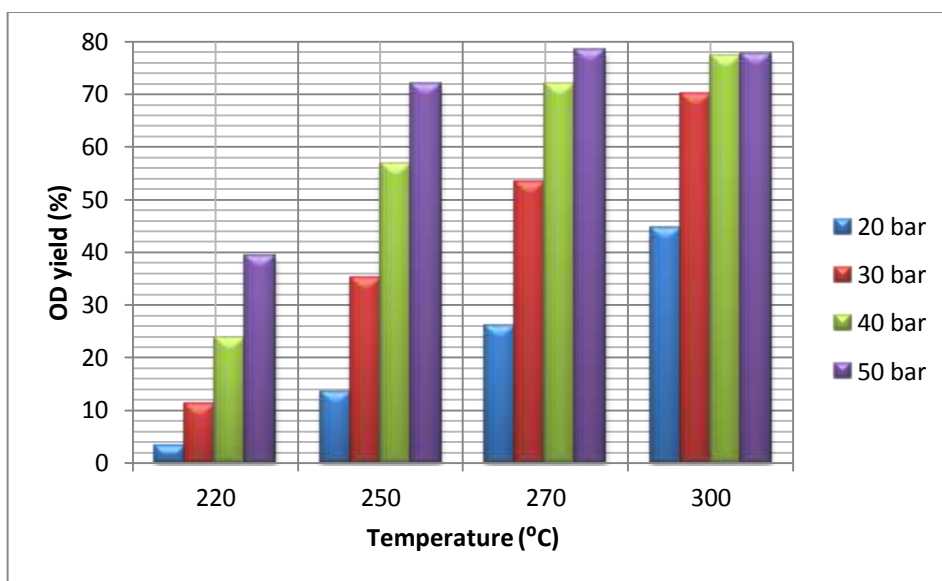


*Figure 4.10: Methyl oleate conversion vs. temperature*

Discussion:

- The conversion of methyl oleate is increased as the temperature is increased from 220°C to 270°C for initial hydrogen pressure of 20, 30 and 40 bar. However, for 50 bar hydrogen pressure, maximum conversion of 100% is achieved at 270°C.
- Overall, complete methyl oleate conversion after 2 hours is achieved at initial hydrogen pressure of 50 bar and operating temperature of 270 °C.
- The trend is the same as the trend for methyl oleate conversion for overall reaction scheme and has been discussed at page 36.

#### 4.2.2 Yield of octadecane

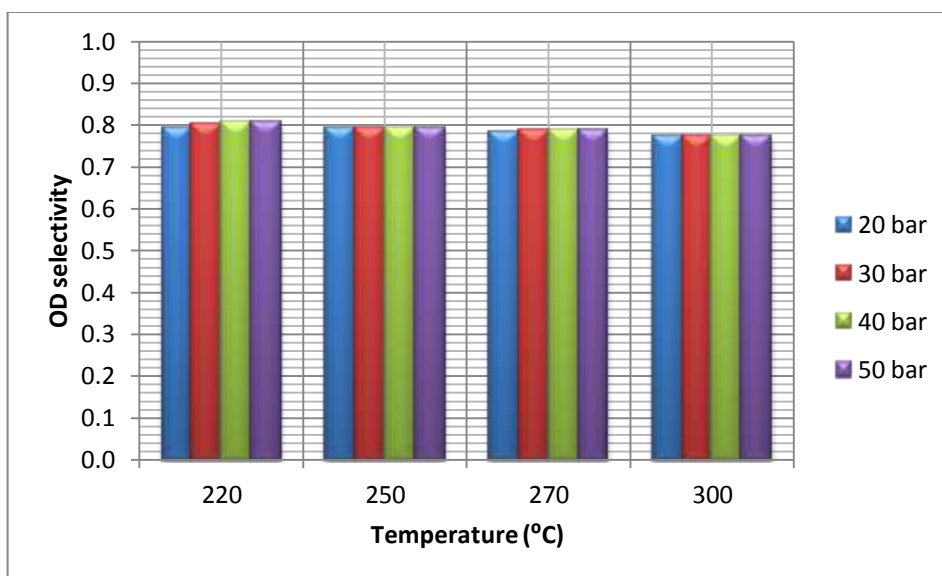


*Figure 4.11: Yield of octadecane vs. temperature*

Discussion:

- As the operating temperature is increased, the yield of octadecane is also increased.
- The trend is the same as the trend for yield of octadecane for overall reaction scheme and has been discussed at page 37.

### 4.2.3 Selectivity of octadecane

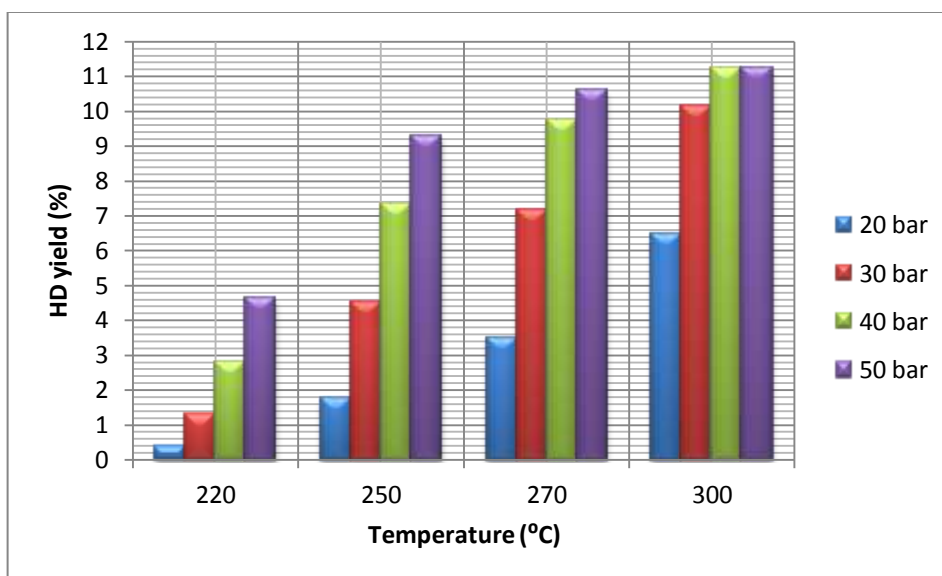


*Figure 4.12: Octadecane selectivity vs. temperature*

Discussion:

- As the temperature is increased, the selectivity towards formation of octadecane is decreased and as the pressure is increased, the selectivity towards formation of octadecane remains constant.
- The trend is the same as the trend for selectivity of octadecane for overall reaction scheme and has been discussed at page 38.

#### 4.2.4 Yield heptadecane

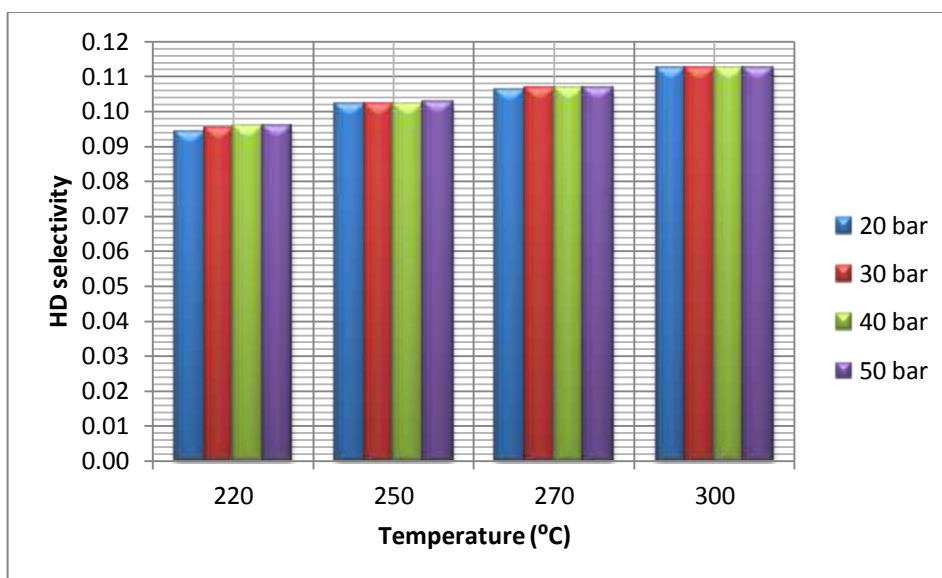


*Figure 4.13: Heptadecane yield vs. temperature*

Discussion:

- Overall, heptadecane yield is very low compared to octadecane yield with maximum yield of only 11.4%.
- The trend is the same as the trend for yield of heptadecane for overall reaction scheme and has been discussed at page 39.

#### 4.2.5 Heptadecane selectivity



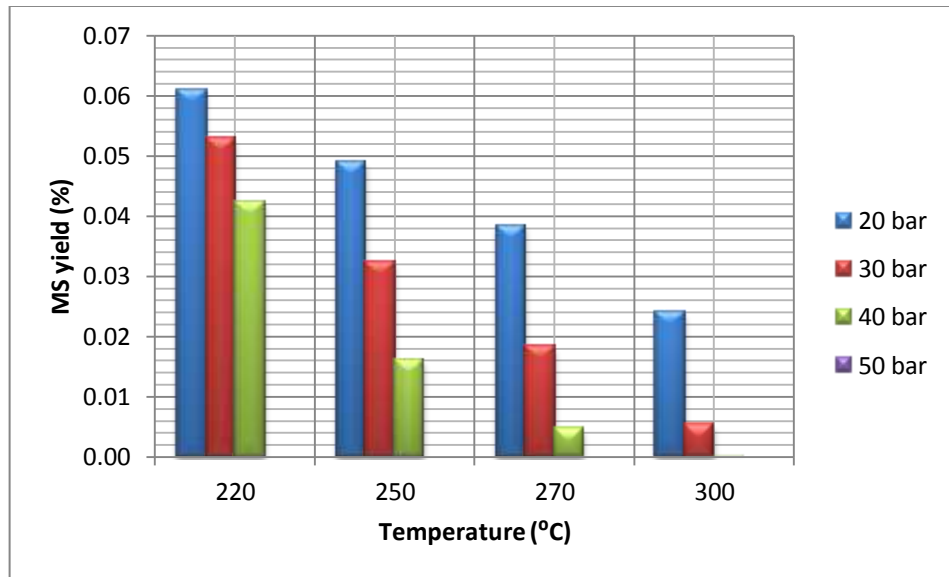
*Figure 4.14: Heptadecane selectivity vs. temperature*

Discussion:

- The trend for heptadecane selectivity is opposite of octadecane selectivity. As the temperature is increased, the selectivity towards heptadecane formation is increased.
- Overall, the selectivity of heptadecane formation is lower as compared to the selectivity of octadecane.
- The trend is the same as the trend for selectivity of heptadecane for overall reaction scheme and has been discussed at page 40.



#### 4.2.6 Yield of methyl stearate



*Figure 4.15: Methyl stearate yield vs. temperature*

Discussion:

- Methyl stearate is the intermediate for the conversion of methyl oleate to green diesel. The yield is very low and it exists in trace amount.
- From the graph above, it can be seen that as the temperature is increased, the methyl stearate yield is decreasing for operating pressure of 20, 30 and 40 bar. This is because, the the temperature increase, methyl stearate is readily converted into stearic acid thus, forming products.
- However, at 50 bar, methyl state yield is too small and is negligible because at this pressure, methyl oleate directly been converted to products without intermediate formation.

#### 4.2.7 Yield of stearic acid

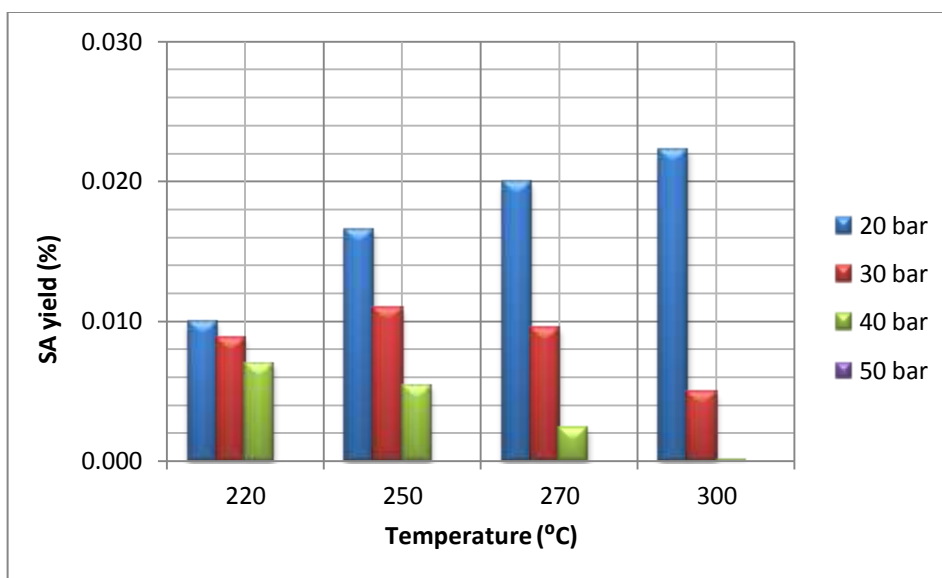
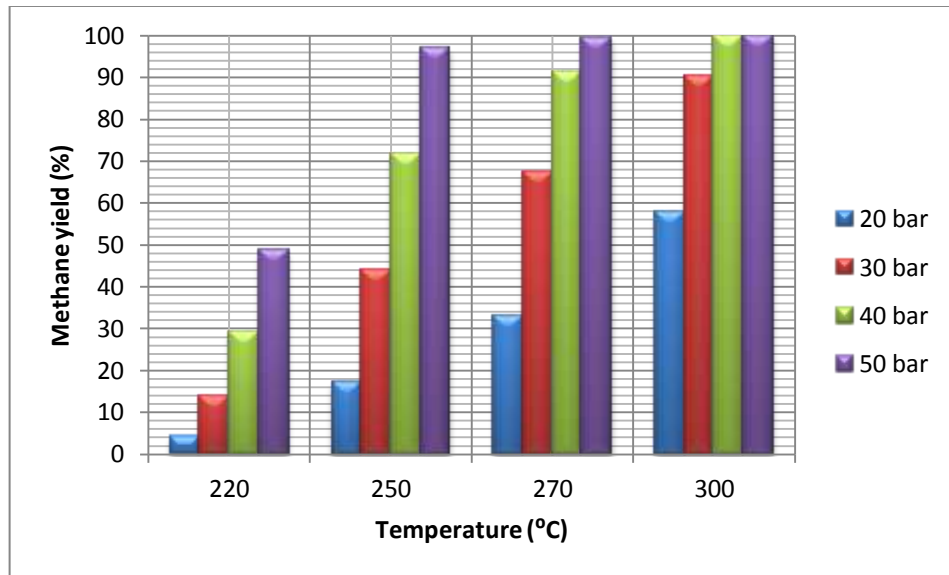


Figure 4.16: Stearic acid yield vs. temperature

#### Discussion:

- Stearic acid is the intermediate for the conversion of methyl oleate to green diesel. The yield is very low and it exists in trace amount.
- From the graph above, as the temperature is increased, the stearic acid yield is increasing at hydrogen pressure of 20 bar and is decreasing for operating pressure of 30 and 40 bar. The increasing trend at low hydrogen pressure verifies that HDO route is favoured at low pressure and high temperature. The decreasing trend for operating pressure of 30 and 40 bar shows that stearic acid is readily converted to products at increasing temperature.
- However, at 50 bar, stearic acid yield is too small and is negligible because at this pressure, methyl oleate directly been converted to products without intermediate formation.

#### 4.2.8 Yield of methane

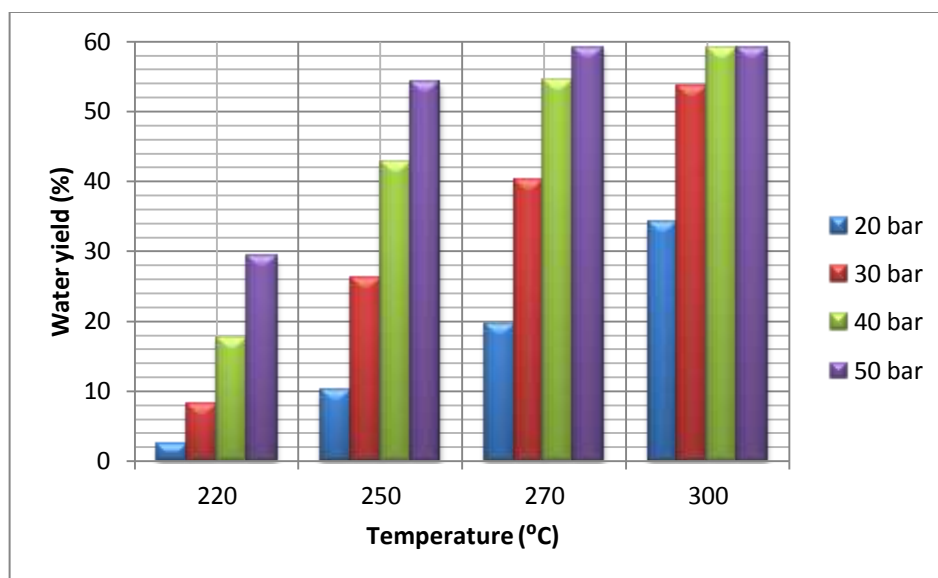


*Figure 4.17: Methane yield vs. temperature*

#### Discussion:

- The undesired side reaction for the methyl oleate conversion to green diesel is methanation reaction, producing methane as by-product. Methane formation increases hydrogen consumption thus decreasing hydrocarbon yield.
- The methane maximum yield is 100% which is too high. So, a stoichiometric equation for methane formation for detailed reactions scheme has to be revised to minimize the yield of methane. Due to time constrain, the revision will be conducted before hard copy dissertation is submitted.

#### 4.2.9 Yield of water

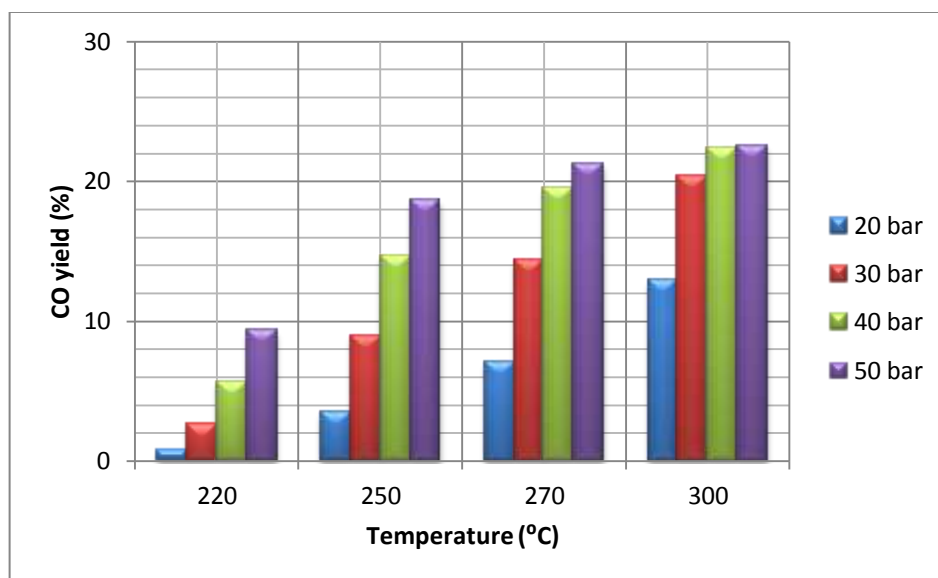


*Figure 4.18: Water yield vs. temperature*

Discussion:

- The yield of water formation is highest among other by-products. Even at low temperature of 220°C, the water yield is already as high as 29 mol%. Because of the use of a few assumptions in kinetic equations development, the yield can be reduced by using actual kinetic constant.
- At high initial hydrogen pressure of 50 bar, there is slight decreased in water yield from 59% to 58%.
- The trend is the same as the trend for yield of water for overall reaction scheme and has been discussed at page 42.

#### 4.2.10 Yield of carbon monoxide



*Figure 4.19: Carbon monoxide yield vs. temperature*

Discussion:

- As the temperature is increased, the formation of carbon monoxide is also increased. Overall, the carbonylation reaction (producing carbon monoxide) has the same trend as decarboxylation reaction. Both reactions favoured at high temperature and low pressure.

#### 4.2.11 Yield of carbon dioxide

- The carbon dioxide yield is very small of around 0.004 mol%. Thus, the formation is neglected.

## CHAPTER 5: CONCLUSION & RECOMMENDATION

This research project has successfully achieved all of the outlined objectives by managed to elucidate the reaction mechanisms involved in the hydrodeoxygenation of methyl oleate to green diesel. The kinetic models of the hydrodeoxygenation of methyl oleate to green diesel have been developed and finally, the effect of operating parameters on hydrodeoxygenation of methyl oleate to green diesel by MATLAB simulation have been identified.

From the kinetic models, author managed to observe the trend for methyl oleate conversion, selectivity towards formation of n-octadecane and n-heptadecane through hydrodeoxygenation reaction, and the yield for all of the products at varies operating temperature and initial hydrogen operating pressures.

The results is exactly as what had been reported in a few previous literature studies, where decarboxylation and decarbonylation favour high temperature and low hydrogen pressure conditions, where hydrodeoxygenation (HDO) favours high pressure and low temperature conditions.

Overall, author managed to identify the optimum operating temperature of 270 °C, pressure of 50 bar in 2 hours reaction time, for 100 % maximum methyl oleate conversion forming 79 mol% of maximum octadecane yield.

The research provides insights for future optimal operation and industrial scaling by using monoglyceride as the feedstock to produce green diesel. Recommendations for by-products; sell methane for ammonia production, steam reformed carbon monoxide to generate hydrogen needed to produce diesel and implement enhanced oil recovery (EOR) to reduce carbon dioxide impacts

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