

**Kinetic Modeling of Hydrodeoxygenation of Triolein to Liquid  
Hydrocarbons using Solid Acid Catalysts**

By

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**12026**

Dissertation submitted in partial fulfillment of  
the requirements for the  
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(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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(CHEMICAL ENGINEERING)

Approved by,

(Dr Periyasamy Balasubramanian)

UNIVERSITI TEKNOLOGI PETRONAS  
TRONOH, PERAK  
SEPTEMBER 2012

## CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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MOHD RAIDZ BIN OSMAN

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## **ABSTRACT**

Hydrodeoxygenation of triolein into liquid hydrocarbons using solid catalyst provides good prospects for the production of green diesel. The present work focuses on the kinetic modeling of liquid hydrocarbons from triolein using MATLAB for parametric study. The model incorporates the reaction mechanism involved in this process. The developed model is used to investigate the effect of temperature range from 250<sup>0</sup>C to 400<sup>0</sup>C, pressure range from 40 bar to 80 bar by using solid catalysts.

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# CHAPTER 1

## INTRODUCTION

### 1.1. BACKGROUND

In the past decade, the price of crude oil has continuously increased due to the limitation of oil production from refineries and high petroleum-fuel consumption. With strict environmental legislation, renewable energy has become an important energy source for many aspects, especially transportation section. Biofuel, nowadays, is a favourable alternative energy because it has less negative environmental impact on carbon dioxide emission and lower particulate matter. The blending of fatty acid mono-esters (FAME) derived from biomass (vegetable and algal oils and fats) with diesel fuel is practiced in many countries to decrease dependence on petroleum, and for environmental reasons. In spite of the attractive features of diesel– FAME blends, there are still many disadvantages, such as the need for an expensive transesterification process, lower heating value of the blends and compatibility problems with some components in the vehicle. Moreover, the transesterification process can generate wastewater of concern to the environment. A useful approach that overcomes many of these difficulties is to hydroprocess vegetable oil–gas oil blends to obtain an oxygenate-free fuel. Such hydroprocessed blends tend to possess larger cetane numbers than the parent gas oil due to an increase in concentration of n-paraffins. Generally, the production of diesel like hydrocarbons from vegetable oils can be achieved by various reactions such as pyrolysis or thermal cracking, catalytic cracking and deoxygenation. Both thermal and catalytic cracking yield high volume of hydrocarbons, but they cannot provide high yield of diesel range while deoxygenation can preserve hydrocarbons in the diesel range.

## 1.2 PROBLEM STATEMENT

Generally people have started using hydrodeoxygenation process of triolein from sunflower oil as one of the method to produce a green diesel which comprises of  $n$ -C<sub>17</sub>– $n$ -C<sub>18</sub>hydrocarbons. Already, blends of vegetable oil and petroleum oils have also been investigated by many. Sunflower oil–gas oil blends have been processed over Ni–Mo–P–alumina (Krár et al., 2010; Tóth et al., 2011)jatropa oil–gas oil blends over Co–Mo, Ni–Mo and Ni–Wcatalysts (Kumar et al., 2010), waste soya-oil–gas oil blends over Ni–Mo and Ni–W catalysts (Tiwari et al., 2010), sunflower oil–HVO (heavy vacuum oil) blends over Ni–Mo–alumina (Huberet al., 2007; Bezergianni et al., 2009). However kinetic modelling of hydrodeoxygenation process of triolein is not available in the literature. Therefore in the author’s work, he would like to consider triolein to be model compound in the hydrodeoxygenation process by considering the reaction stoichiometric, reaction mechanism and reactor modeling.

## 1.3 OBJECTIVES

- 1) To elucidate the reaction mechanisms involved in the hydrodeoxygenation of triolein into liquid hydrocarbons.
- 2) To develop the kinetic model for this process from the first principles
- 3) To perform the simulation by using MATLAB from this hydrodeoxygenation process.

## 1.4 SCOPE OF STUDY

This research focuses on thehydrodeoxygenation oftriolein oil into  $n$ -C<sub>17</sub> – $n$ -C<sub>18</sub> hydrocarbons. There are a few factors that need to be consider throughout the process such as reaction mechanism, type of catalyst used, type of reactors and the undesired product of this process.Addition parameters that need to be check during the research are temperature, pressure and feed rate on the conversion of the vegetable oil in the blend are presented in the process.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 THEORY

Basically, triolein can be obtained from vegetable oils. Vegetable oil can be directly mixed with diesel fuel and may be used for an alternative fuels. The blending of vegetable oil with diesel fuel were experimented successfully by various researchers. A diesel fleet was powered with a blend of 95% filtered used cooking oil and 5% diesel in 1982. A blend of 20% oil and 80% diesel was found to be successful (A.S. Ramadhas et al, 2004). In the present study, hydroprocessing of blends of vegetable oil and straight run gas oil over sulfided Ni–Mo–BEA–c-alumina catalysts at moderate pressure and temperature ranges was carried out.

#### 2.2 EXPERIMENTAL ANALYSIS

Mixtures of sunflower oil and a straight run gas oil in the diesel fuel range were hydroprocessed over sulfided NiO(3%)–MoO<sub>3</sub> (12%)–c-Al<sub>2</sub>O<sub>3</sub> incorporating 0, 15 or 30 wt. % zeolite beta (BEA). The hydroprocessing of the gas oil–sunflower oil blends was carried out at different process conditions in a stainless steel high pressure fixed bed reactor (100 ml volume; 15 mmid) using 30 g of broken catalyst particles (1–2 mm diameter)The studies were carried out at 320–350<sup>0</sup>C; 30–60 bars, and weight hourly space velocities (WHSV), 1–4 h<sup>-1</sup>. Catalyst containing 30% BEA achieved nearly 100 % conversion of the vegetable oil into hydrocarbons at 330<sup>0</sup>C, 60bars and a WHSV of 2 h<sup>-1</sup> compared to 95.5% by the Ni–Mo–c-alumina catalyst without BEA. The composition of sunflower oil is ;(C<sub>16</sub> acids, 6.53 wt.% and C<sub>18</sub> acids, 93.47 wt.% (stearic,0.54 wt.%; oleic, 22.38 wt.% and linoleic, 70.54 wt.%(T.M. Sankaranarayanan, 2011). The reaction procedure was summarized in the table below:

Temperature	Pressure	H <sub>2</sub> /Oil ratio	WHSV	Types of Reactor	Catalyst
320-360 <sup>0</sup> C	30-60bars	500 STP	1-4h <sup>-1</sup>	Fixed Bed Reactor	Ni-Mo-Al-zeolite beta composites

**Table 1: Kinetics Parameter Value for experimental analysis**

The results of the hydroprocessing of 20 wt.% vegetable oil–80 wt.% gas oil blend over Ni–Mo supported on alumina, alumina+ BEA (15 wt.%) and alumina + BEA (30 wt.%) are discussed in this section. Many of the studies have been carried out using the 20% vegetable oil–gas oil blend because B-20 is a commonly used blend of biodiesel and diesel fuel. Limited studies were also carried out with a 40% vegetable oil–gas oil blend to check the effectiveness of the formulations at a higher loading of vegetable oil and also to study catalyst limitations in converting feeds that are rich in oxygenates. It is most likely that the unsaturation present in the sunflower oil (in oleic and linoleic acids) was saturated quickly to produce the idealized triglyceride molecule (glyceryl tri-stearate) (T.M. Sankaranarayanan, 2011).

### 2.2.1 REACTION MECHANISM

The mechanism of the transformation of triglycerides into hydrocarbons in the presence of H<sub>2</sub> over Ni–Mo–Al<sub>2</sub>O<sub>3</sub> has been discussed by many authors (Huber et al., 2007; Donniss et al., 2009; Gusmão et al., 1989). The general belief is that the double bonds present in the triglycerides are rapidly hydrogenated and the saturated triglyceride then breaks up mainly into the carboxylic acids, which undergo either hydrodeoxygenation to produce n-paraffins with the same carbon number as the parent acid or decarboxylation/decarbonylation to produce n-paraffins with one carbon atom less. These reactions can also occur directly through multiple cracking of the triglyceride molecule (Donniss et al., 2009).

## 2.2.2 RESULTS

The major products of the conversion of the oil and FFA were *n*-C<sub>18</sub> paraffin (formed from hydrodeoxygenation, HDO) and *n*-C<sub>17</sub> paraffin (formed from decarboxylation and decarbonylation; DCO<sub>2</sub>) (Fig. 1)

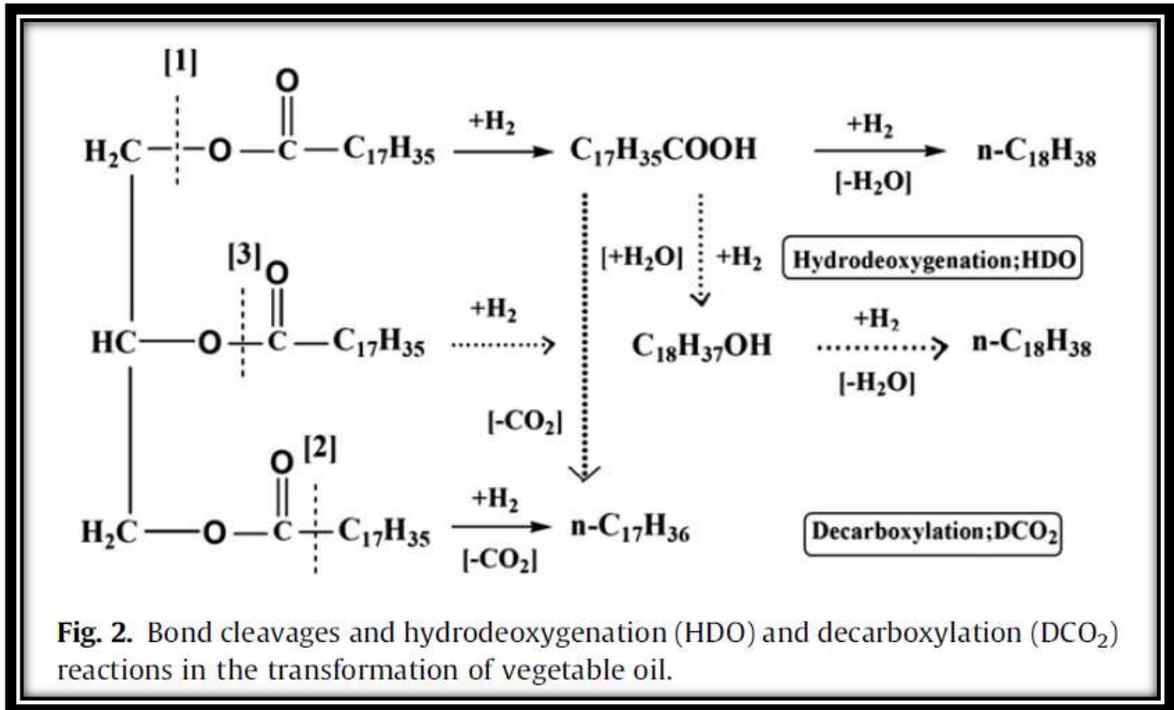


Figure 1: Example of Hydrodeoxygenation Process

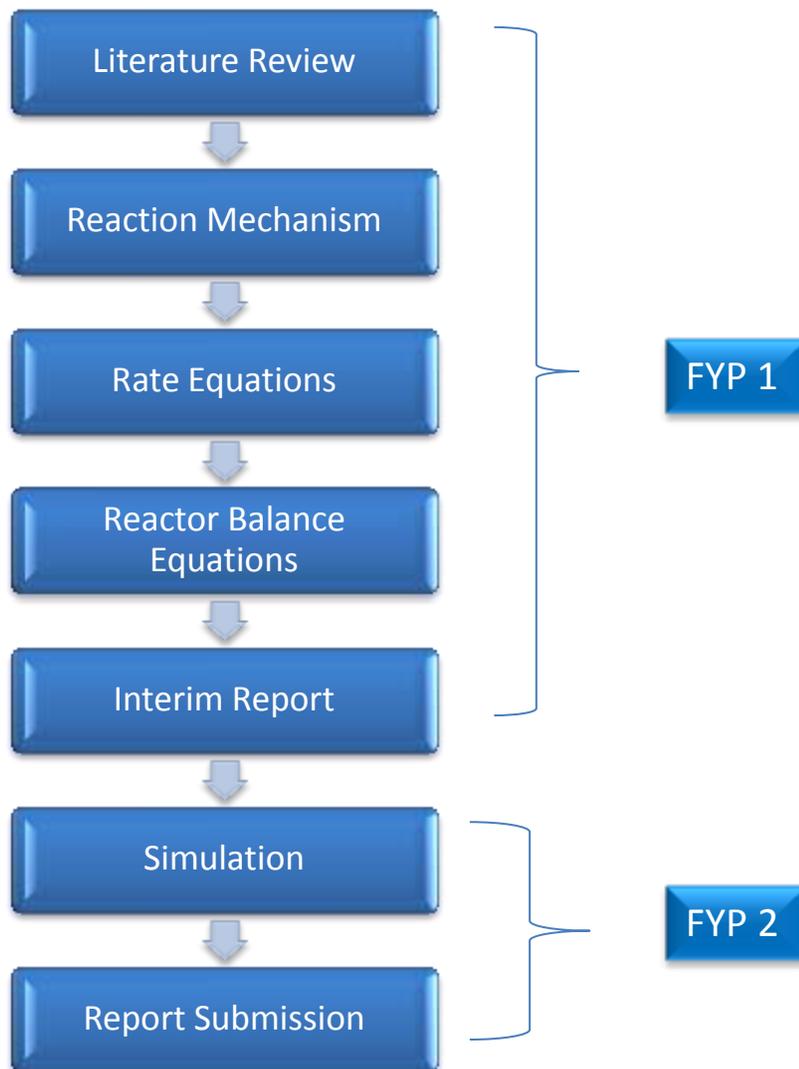
### 2.2.3 INFLUENCE OF PROCESS PARAMETERS

The influences of temperature, pressure and feed rate on the conversion of the vegetable oil in the blend are presented in Fig. 3. At the temperatures between 320 and 350°C, greater than 96% conversion was achieved over all the catalysts, the conversion being the largest over Ni–Mo–30BEA; a near quantitative conversion was observed even at the lowest temperature (320 °C, WHSV, 2 h<sup>-1</sup>) over this sample. Over all the catalysts, an increase in pressure (30–60 bars) increased conversion. This is expected as the conversion of the oil occurs through hydrocracking and hydrogenolysis reactions that involve hydrogen. Ni–Mo–30BEA is more active than the others, a conversion of nearly 93% being obtained at a pressure of 30 bars (at 320°C; WHSV, 2 h<sup>-1</sup>). Conversion decreased with increasing feed rate and this decrease was again dependent on the BEA content of the samples. Though the conversions were in the range of 97–100% at a WHSV (h<sup>-1</sup>) of 1 for the three catalysts, the differences become large at higher space velocities; the conversions for Ni–Mo–Al, Ni–Mo–15BEA and Ni–Mo–30BEA were, respectively, 64%, 81% and 90% at a WHSV (h<sup>-1</sup>) of 4 (T.M. Sankaranarayanan, 2011).

## CHAPTER 3

### METHODOLOGY

#### 3.1 PROJECT FLOW CHART



### 3.2 GANTT CHART

No	Detail / Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14	
1	Selection of Project Topic	■	■						Mid Semester Break								
2	Literature review and survey		■	■													
3	To understand the reaction mechanisms				■	■	■										
4	Submission of extended proposal						■	■									
5	Proposal Defense						■	■			■	■					
6	Rate Equations						■	■			■	■					
7	Reactor Balance Equations												■	■	■	■	
9	Submission of Interim Draft Report																■
10	Submission of Interim Report																■



Expected Completion

### 3.3 REACTION MECHANISM

The pathway of the reaction of triolein into liquid hydrocarbon will be as below:

1) Conversion of triolein into tristearin.

Based on the diagram below, the saturation of double bond into single bond by three mole of hydrogen will convert triolein into tristearin.

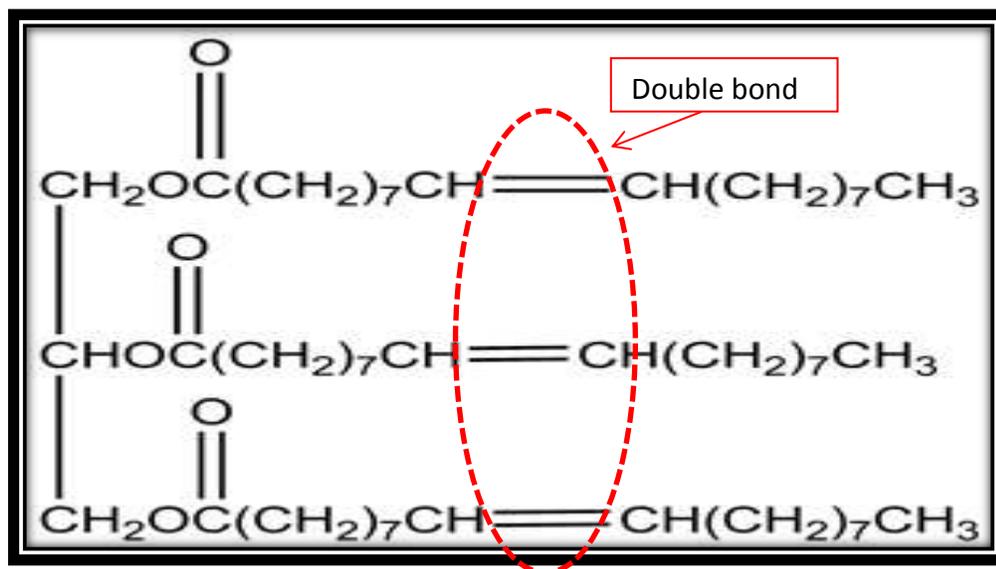


Figure 2: Structural Formula for Triolein

2) Conversion of tristearin into stearic acid.

The cracking/braking bond between carbon-carbon bonds will attract hydrogen into the oxygen. Thus this will result in the formation of three mole of stearic acid.

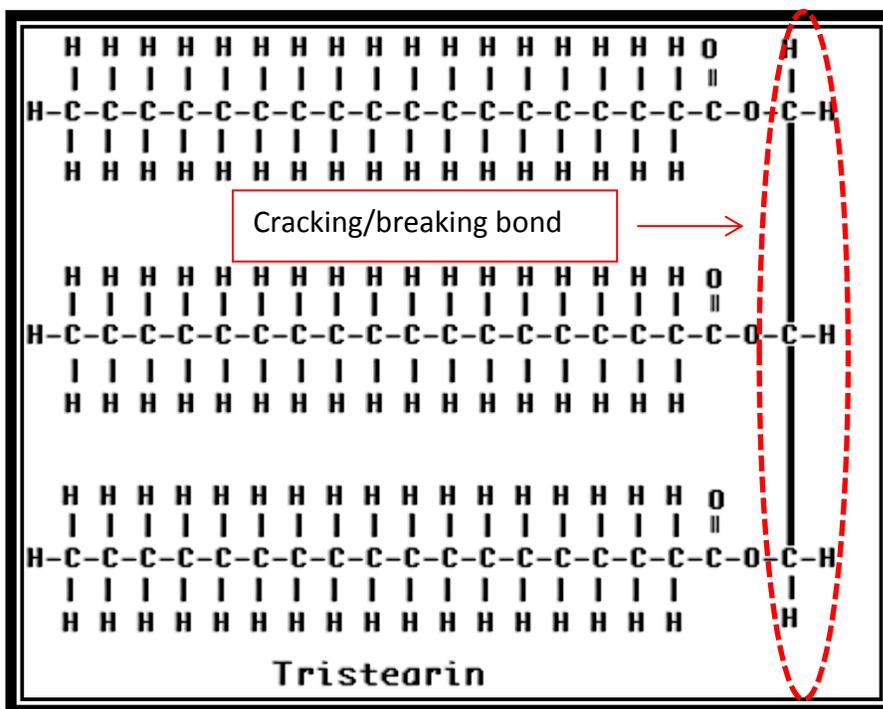


Figure 3: Structural Formula for Tristearin

3) Conversion of stearic acid into  $n\text{-C}_{18}$  hydrocarbons.

In the next reaction, stearic acid will once again undergo cracking or bond breaking to remove oxygen. By removing oxygen from the component, stearic acid will convert into  $n\text{-C}_{18}$  hydrocarbons.

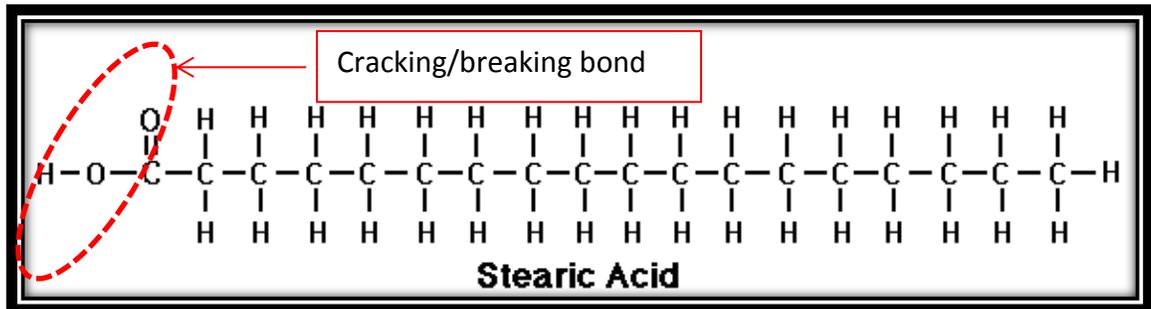


Figure 4: Structural Formula for Stearic Acid

4) Final product of hydrodeoxygenation process of triolein will be  $n\text{-C}_{18}$  hydrocarbons.

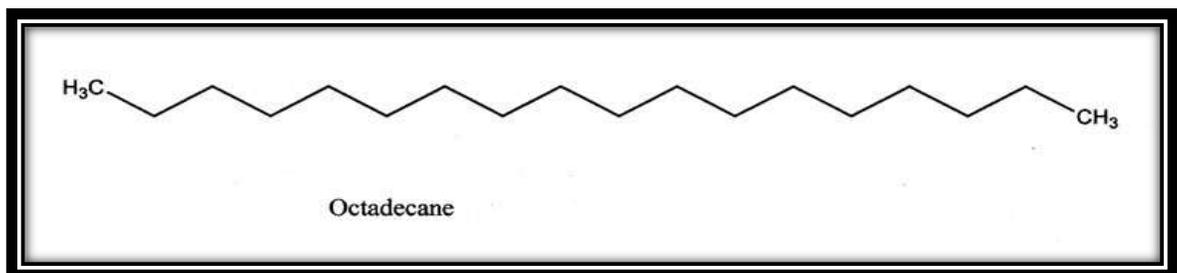
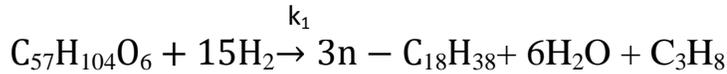


Figure 5: Structural Formula  $n\text{-C}_{18}$  hydrocarbons

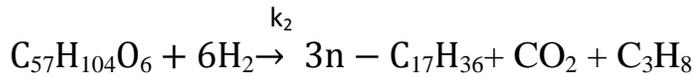
### 3.4 REACTION STOICHIOMETRIC

The stoichiometries of hydrodeoxygenation of conversion of triolein into hydrocarbon are summarized as below:

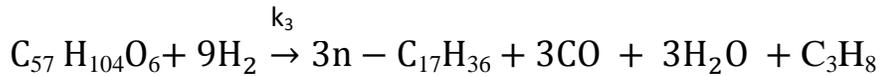
#### Main Reaction [HYDRODEOXYGENATION]



#### Side Reaction 1 [DECARBOXYLATION]



#### Side Reaction 2 [DECARBONYLATION]



The rate equations for the above mentioned stoichiometry are given by:

$$r_{TRIOLEIN} = -(k_1 C_{HYDROGEN}^{\alpha_1} + k_2 C_{HYDROGEN}^{\alpha_2} + k_3 C_{HYDROGEN}^{\alpha_3}) C_{TRIOLEIN}$$

$$r_{OCTADECANE} = 3k_1 C_{HYDROGEN}^{\alpha_1} C_{TRIOLEIN}$$

$$r_{PROPANE} = (k_1 C_{HYDROGEN}^{\alpha_1} + k_2 C_{HYDROGEN}^{\alpha_2} + k_3 C_{HYDROGEN}^{\alpha_3}) C_{TRIOLEIN}$$

$$r_{HEPTADECANE} = (3k_2 C_{HYDROGEN}^{\alpha_2} + k_3 C_{HYDROGEN}^{\alpha_3}) C_{TRIOLEIN}$$

$$r_{CO_2} = k_2 C_{HYDROGEN}^{\alpha_2} C_{TRIOLEIN}$$

$$r_{CO} = 3k_3 C_{HYDROGEN}^{\alpha_3} C_{TRIOLEIN}$$

$$r_{WATER} = (6k_1 C_{HYDROGEN}^{\alpha_1} + 3k_3 C_{HYDROGEN}^{\alpha_3}) C_{TRIOLEIN}$$

The batch reactor balance equations for the reacting species in significant amount of hydrogen are:

$$\frac{dC_{TRIOLEIN}}{dt} = -(k_1 C_{HYDROGEN}^{\alpha_1} + k_2 C_{HYDROGEN}^{\alpha_2} + k_3 C_{HYDROGEN}^{\alpha_3}) C_{TRIOLEIN}$$

$$\frac{dC_{OCTADECANE}}{dt} = 3k_1 C_{HYDROGEN}^{\alpha_1} C_{TRIOLEIN}$$

$$\frac{dC_{PROPANE}}{dt} = (k_1 C_{HYDROGEN}^{\alpha_1} + k_2 C_{HYDROGEN}^{\alpha_2} + k_3 C_{HYDROGEN}^{\alpha_3}) C_{TRIOLEIN}$$

$$\frac{dC_{HEPTADECANE}}{dt} = (3k_2 C_{HYDROGEN}^{\alpha_2} + k_3 C_{HYDROGEN}^{\alpha_3}) C_{TRIOLEIN}$$

$$\frac{dC_{CO_2}}{dt} = k_2 C_{HYDROGEN}^{\alpha_2} C_{TRIOLEIN}$$

$$\frac{dC_{CO}}{dt} = 3k_3 C_{HYDROGEN}^{\alpha_3} C_{TRIOLEIN}$$

$$\frac{dC_{WATER}}{dt} = (6k_1 C_{HYDROGEN}^{\alpha_1} + 3k_3 C_{HYDROGEN}^{\alpha_3}) C_{TRIOLEIN}$$

In this reaction it was consider  $k = A \exp\left(-\frac{Ea}{RT}\right) \left(\frac{P}{P_{Preference}}\right)^\beta$

## CHAPTER 4

### RESULTS AND DISCUSSION

As mention in the reaction stoichiometric where in this reaction was consider;

$$k = A \exp\left(-\frac{Ea}{RT}\right) \left(\frac{P}{P_{reference}}\right)^\beta$$

#### 4.1 KINETICS PARAMETER

$[A_1 A_2 A_3] (s^{-1})$	[3.26e6, 4.9e6, 1.21e6]
$[Ea_1 Ea_2 Ea_3] (kJ)$	[136500, 143200, 156000]
Temperature ( $^{\circ}C$ )	[250, 270,300, 350 ,400]
Pressure (bar)	[40 , 60 , 80 ]

Table 2: Kinetics Parameter Value for simulation

#### 4.2 REACTIONS IN EXCESS HYDROGEN

In the first simulation, it was assumed the reaction to be in excess hydrogen. Therefore the batch reactor balance equation will have a slight difference where the concentration of hydrogen will be neglected as shown below. The result is shown in the next page.

$$\frac{dC_{TRIOLEIN}}{dt} = -(k_1 + k_2 + k_3)C_{TRIOLEIN}$$

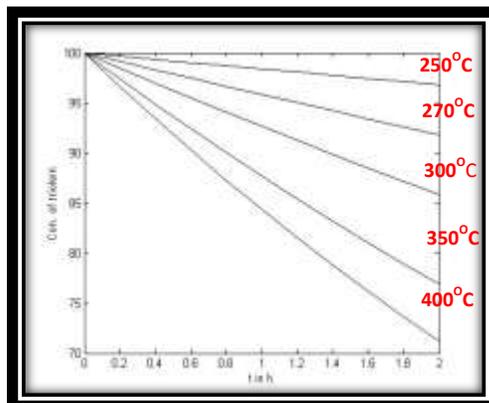
$$\frac{dC_{OCTADECANE}}{dt} = 3k_1C_{TRIOLEIN}$$

$$\frac{dC_{HEPTADECANE}}{dt} = 3(k_2 + k_3) C_{TRIOLEIN}$$

**PRESSURE = 40 BAR**

**1) FEEDSTOCK**

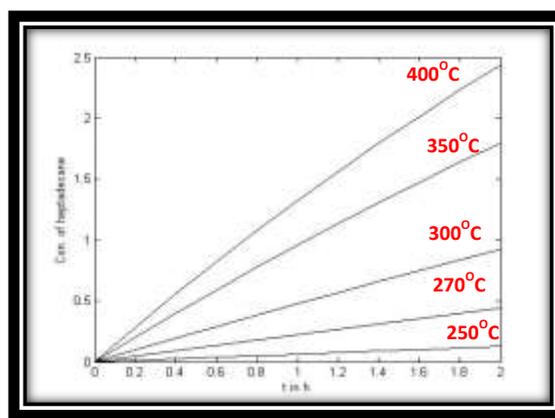
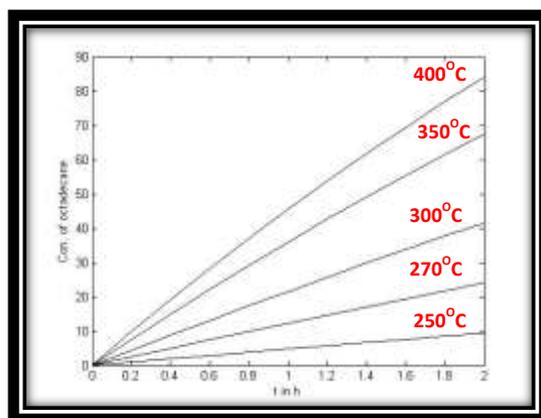
➤ *TRIOLEIN*



**2) PRIMARY PRODUCT**

A) *OCTADECANE*

B) *HEPTADECANE*



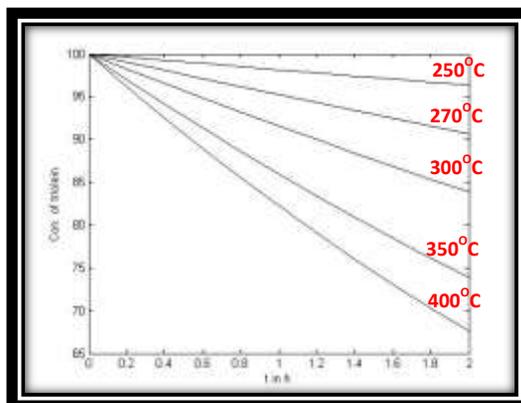
**Figure 6: Conversion of Triolein and yield of liquid hydrocarbons at different T and P of 40 bar**

Based on the figure above, the conversion of triolein is getting higher with an increase in temperature where the concentration of triolein is getting lower. Meanwhile for the formation of liquid hydrocarbons it can be stated that high temperature will yield more liquid hydrocarbons.

**PRESSURE = 60 BAR**

**1) FEEDSTOCK**

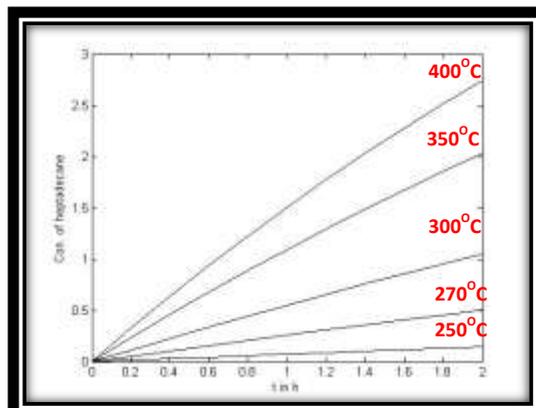
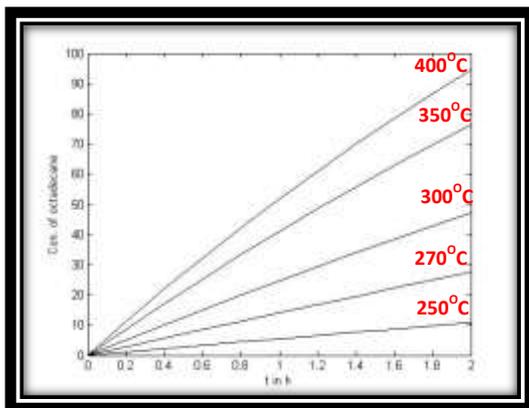
➤ *TRIOLEIN*



**2) PRIMARY PRODUCT**

A) *OCTADECANE*

B) *HEPTADECANE*



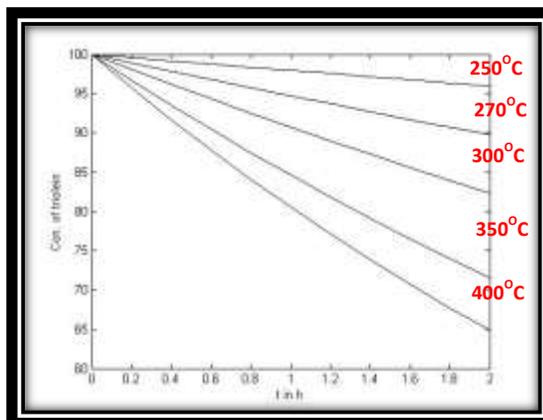
**Figure 7: Conversion of Triolein and yield of liquid hydrocarbons at different T and P of 60 bar**

Based on the figure above, the conversion of triolein is getting higher with an increase in temperature where the concentration of triolein is getting lower. Meanwhile for the formation of liquid hydrocarbons it can be stated that high temperature will yield more liquid hydrocarbons. The difference between the reaction at 40 bar and 60 bar is that the yield of liquid hydrocarbons is getting higher with an increase in pressure.

## PRESSURE = 80 BAR

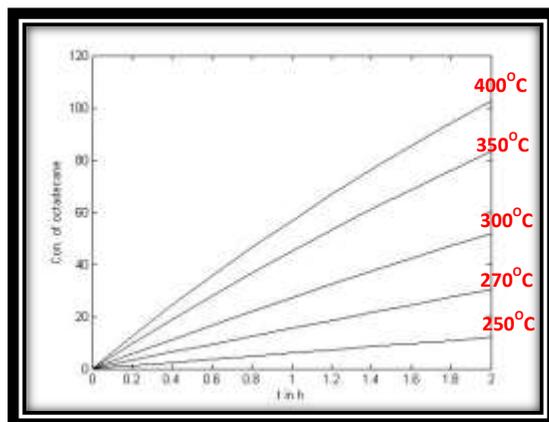
### 1) FEEDSTOCK

➤ *TRIOLEIN*



### 2) PRIMARY PRODUCT

➤ *OCTADECANE*



B) *HEPTADECANE*

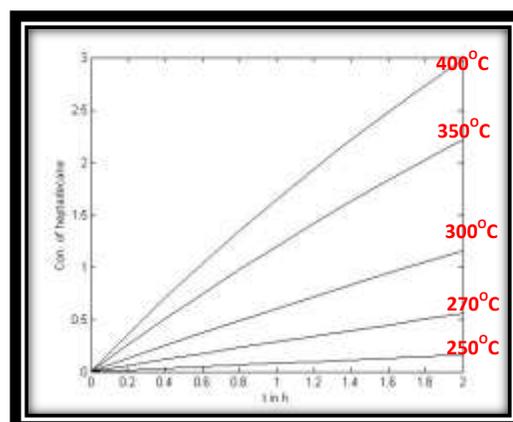


Figure 8: Conversion of Triolein and yield of liquid hydrocarbons at different T and P of 80 bar

Based on the figure above, the conversion of triolein is getting higher with an increase in temperature where the concentration of triolein is getting lower. Meanwhile for the formation of liquid hydrocarbons it can be stated that high temperature will yield more liquid hydrocarbons. The difference between the reaction at 40 bar, 60 bar and 80 bar is that the yield of liquid hydrocarbons is the highest at P=80 bar and T=400°C.

#### 4.3 DISCUSSION FOR THE REACTION OF TRIOLEIN IN EXCESS HYDROGEN

After performing the first simulation for the reaction in excess hydrogen, it was found that the result does not complement as what has been done in this reaction by many researchers throughout experiment. In the experimental analysis the conversion of triolein to liquid hydrocarbons should be the highest at temperature of 330<sup>0</sup>C and pressure of 40 bar. Meanwhile in the simulation the result shown that an increase in pressure and temperature will yield more formation of liquid hydrocarbons. The weakness of the first simulation is that by not considering the concentration of hydrogen into the batch reactor balance equation, the reaction will neglect the side reaction of this process which is decarboxylation and decarbonylation process. Thus, for the second simulation the concentration of hydrogen will be included into the reaction.

#### 4.4 REACTION OF TRIOLEIN IN SIGNIFICANT AMOUNT OF HYDROGEN

In the second simulation, it was assumed the reaction to be in significant amount of hydrogen. Therefore the batch reactor balance equation will include the concentration of hydrogen in the reaction as shown below. The result is shown in the next page.

$$\frac{dC_{TRIOLEIN}}{dt} = -(k_1 C_{HYDROGEN}^{\alpha_1} + k_2 C_{HYDROGEN}^{\alpha_2} + k_3 C_{HYDROGEN}^{\alpha_3}) C_{TRIOLEIN}$$

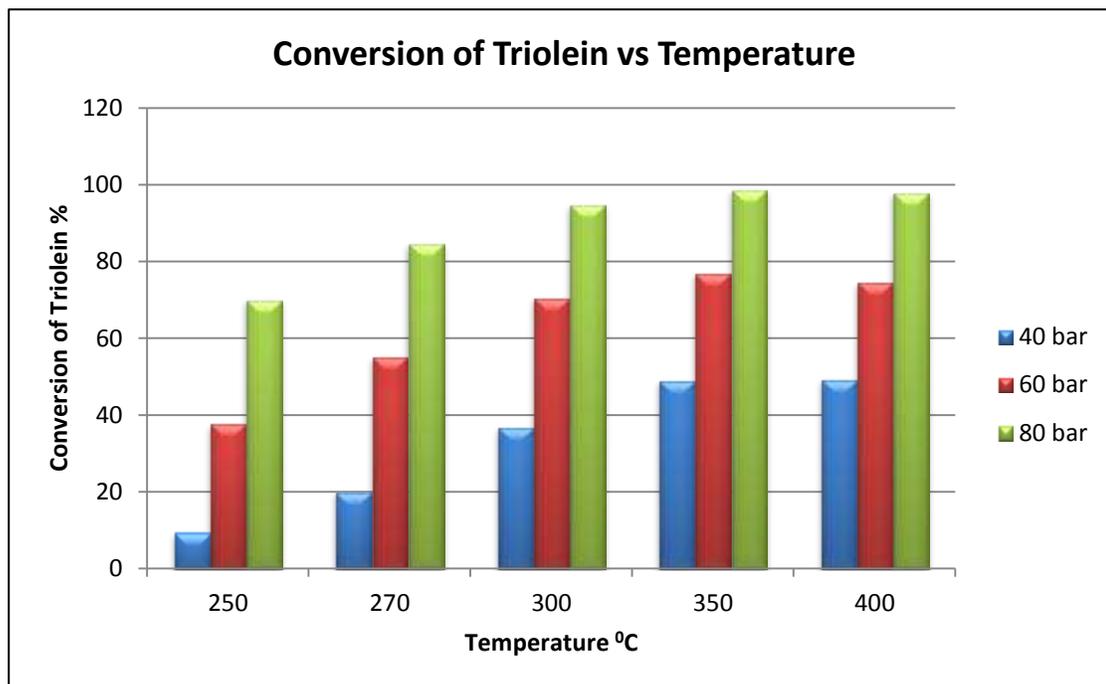
$$\frac{dC_{OCTADECANE}}{dt} = 3k_1 C_{HYDROGEN}^{\alpha_1} C_{TRIOLEIN}$$

$$\frac{dC_{HEPTADECANE}}{dt} = (3k_2 C_{HYDROGEN}^{\alpha_2} + k_3 C_{HYDROGEN}^{\alpha_3}) C_{TRIOLEIN}$$

$$\frac{dC_{HYDROGEN}}{dt} = -(15k_1 C_{HYDROGEN}^{\alpha_1} + 6k_2 C_{HYDROGEN}^{\alpha_2} + 9k_3 C_{HYDROGEN}^{\alpha_3}) C_{TRIOLEIN}$$

➤ **TRIOLEIN**

temperature (°C)	250	270	300	350	400	Pressure(bar)
Conversion of triolein (%)	9.5445	20.0873	36.9634	49.0516	49.3673	40 bar
	37.7783	55.1499	70.5592	77.018	74.5692	60 bar
	70.1087	84.7365	94.904	98.8649	97.9945	80 bar

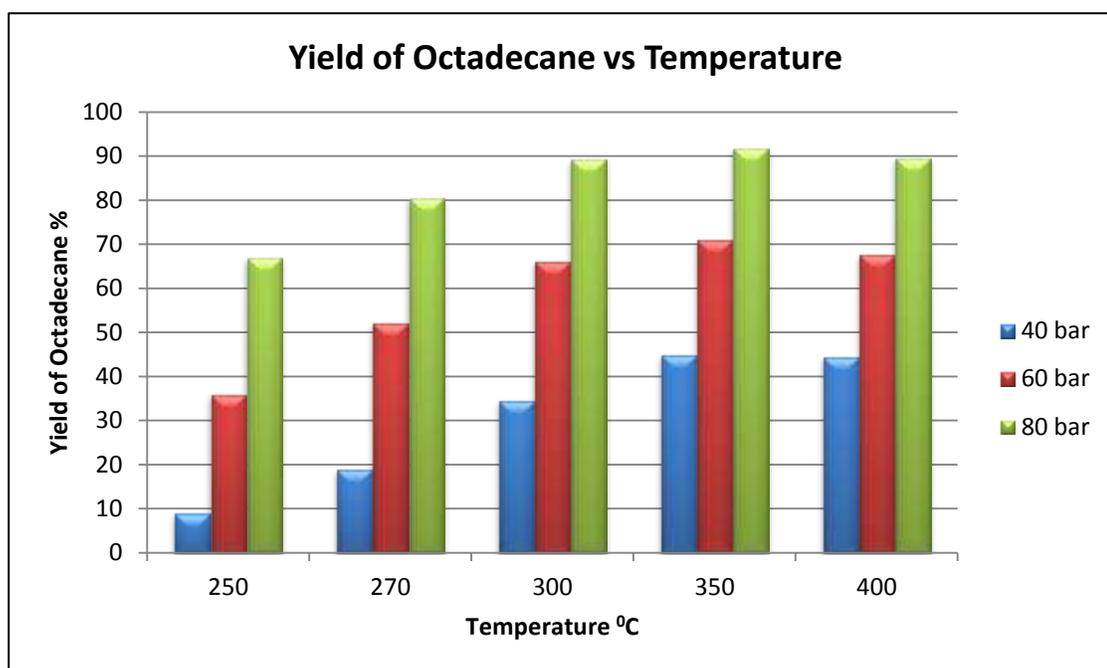


**Figure 9: Percentage of conversion of Triolein at different T and P**

The highest conversion of Triolein occurs at temperature of 350°C and pressure equal 80 bar. This happened because the highest yield of octadecane occurs during this period. At temperature of 400°C, the conversion of triolein started to decrease as shown in the figure above. This happened because decarboxylation and decarbonylation process started to take place over the hydrodeoxygenation process.

➤ **OCTADECANE**

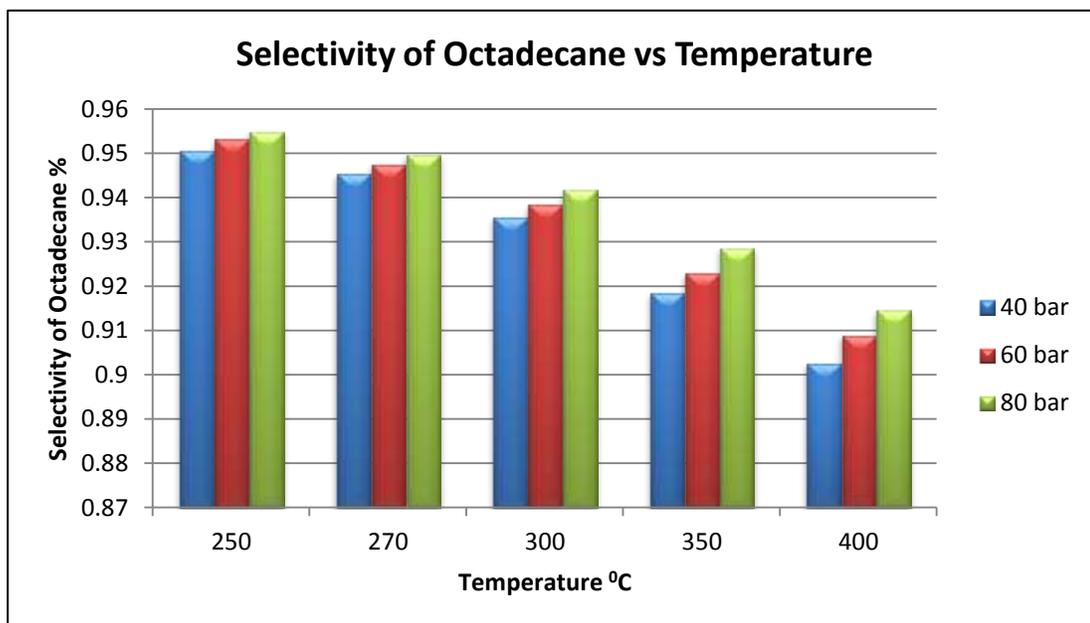
temperature (°C)	250	270	300	350	400	Pressure(bar)
Yield of octadecane(%)	9.075	18.9916	34.5918	45.0516	44.5574	40 bar
	36.0192	52.264	66.2172	71.0978	67.7862	60 bar
	66.9582	80.4813	89.3894	91.8191	89.6498	80 bar



**Figure 10: Percentage of yield of octadecane at different T and P**

Highest yield of octadecane occur at temperature of 350<sup>0</sup>C and pressure equal 80 bar and started to decrease at temperature equal 400<sup>0</sup>C due to decarboxylation and decarbonylation process takes place. Hydrodeoxygenation process takes place in the early reaction until 350<sup>0</sup>C before decarboxylation and decarbonylation process takes place.

temperature (°C)	250	270	300	350	400	Pressure(bar)
Selectivity of OD (%)	0.9508	0.9455	0.9358	0.9185	0.9026	40 bar
	0.9534	0.9477	0.9385	0.9231	0.909	60 bar
	0.9551	0.9498	0.9419	0.9287	0.9148	80 bar

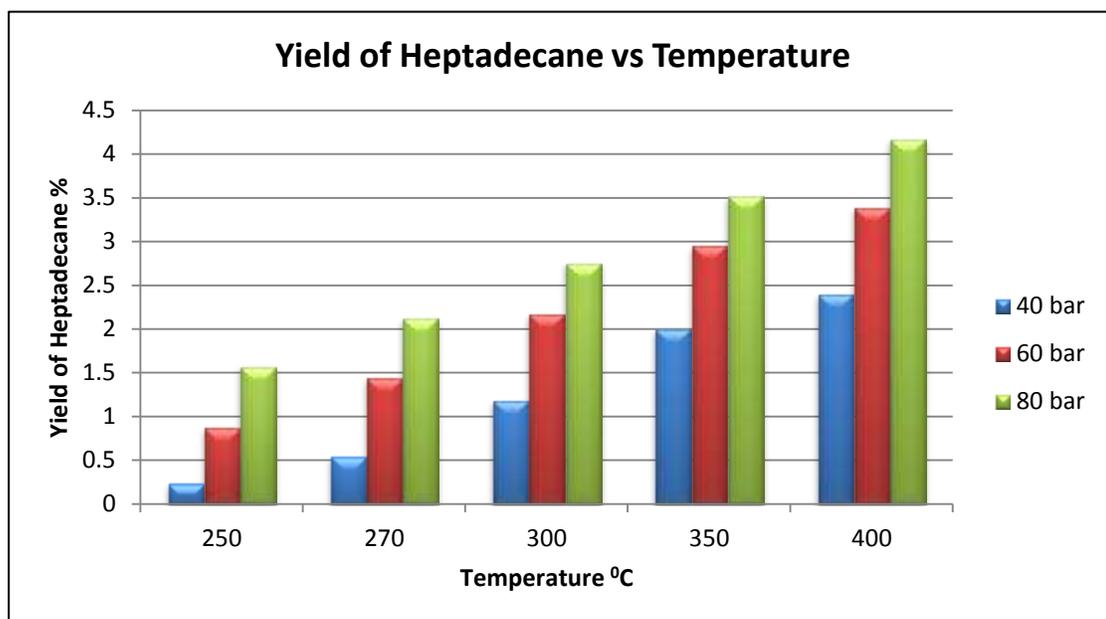


**Figure 11: Percentage of selectivity of octadecane at different T and P**

Selectivity of octadecane decrease with an increase temperature and and increase with an increase in pressure. Hydrodeoxygenation process takes place from the beginning of the reaction from 250<sup>0</sup>C to 350<sup>0</sup>C before decarboxylation and decarbonylation process started to take over the reaction until 400<sup>0</sup>C.

➤ **HEPTADECANE**

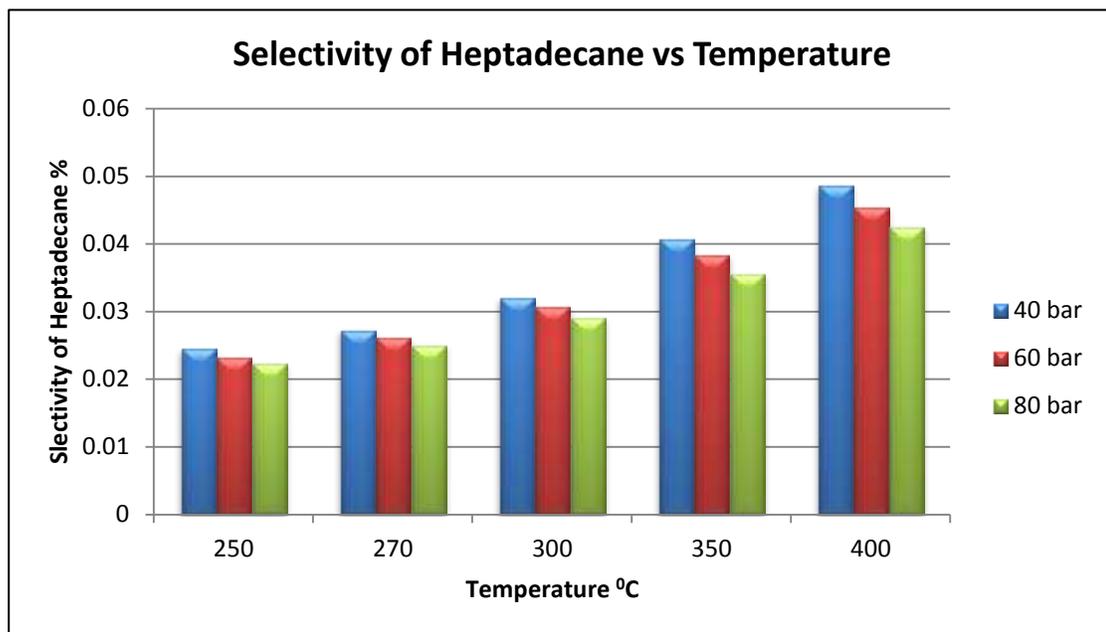
temperature (°C)	250	270	300	350	400	Pressure(bar)
Yield of heptadecane(%)	0.2348	0.5478	1.1858	2	2.405	40 bar
	0.8795	1.4429	2.171	2.9601	3.3915	60 bar
	1.5753	2.1276	2.7573	3.5229	4.1723	80 bar



**Figure 12: Percentage of yield of heptadecane at different T and P**

Highest yield of heptadecane occur at temperature of 400<sup>0</sup>C and pressure equal to 80 bar because decarboxylation and decarbonylation process is more favourable at this pressure and temperature. In the beginning of the reaction the process is more favourable to hydrodeoxygenation process, thus the yield of heptadecane is low until temperature of 350<sup>0</sup>C where the reaction started to favour decarboxylation and decarbonylation process. As seen from the figure above the yield of heptadecane started to increase rapidly from 350<sup>0</sup>C to 400<sup>0</sup>C.

temperature (°C)	250	270	300	350	400	Pressure(bar)
Selectivity of HD(%)	0.0246	0.0273	0.0321	0.0408	0.0487	40 bar
	0.0233	0.0262	0.0308	0.0384	0.0455	60 bar
	0.0225	0.0251	0.0291	0.0356	0.0426	80 bar

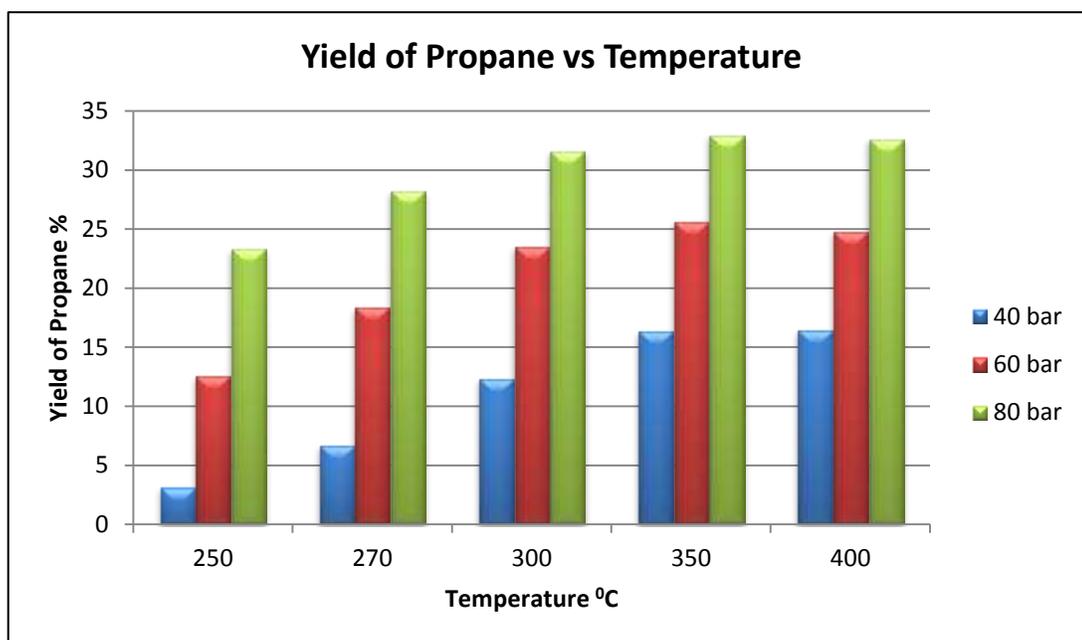


**Figure 13: Percentage of selectivity of heptadecane at different T and P**

Selectivity of heptadecane increased with an increase in temperature and pressure and decrease with a decrease in pressure. This is due to decarboxylation and decarbonylation process is started to favour in this reaction at 350°C and this is the reason it keeps increasing from 250°C.

➤ **PROPANE**

temperature (°C)	250	270	300	350	400	Pressure(bar)
yield of propane(%)	3.1815	6.6958	12.3211	16.3505	16.4558	40 bar
	12.5928	18.3833	23.5197	25.6727	24.8564	60 bar
	23.3696	28.2455	31.6347	32.955	32.6648	80 bar



**Figure 14: Percentage of yield of propane at different T and P**

As seen from the figure above the yield of propane keeps increasing from temperature of 250<sup>0</sup>C until 350<sup>0</sup>C before it started to decrease until 400<sup>0</sup>C. The yield of propane is higher than heptadecane due to their presence in all reaction which is the main reaction and side reaction.

#### 4.5 DISCUSSION OF REACTION OF TRIOLEIN IN SIGNIFICANT AMOUNT OF HYDROGEN

Based on the results that have been obtained from the second simulation, it was found that conversion of triolein is most active at temperature of 350<sup>0</sup>C and pressure of 80 bar. The yield of liquid hydrocarbons increases with respect to temperature and pressure. Meanwhile for the selectivity of liquid hydrocarbons have different pattern of result. Firstly, for octadecane the selectivity decrease with an increase in temperature and increase with an increase in pressure. For heptadecane the selectivity increased with an increase in temperature and decrease with an increase in pressure. By comparing the result with the experiment done by the researchers, the result obtained is compliment to the simulation that has been done in this project. From the experiment analysis, the highest conversion of triolein occurs at temperature of 330<sup>0</sup>C and pressure of 60 bar. The results only have a slight difference with what have been obtained in the simulation where the highest conversion of triolein occurs at 350<sup>0</sup>C and pressure of 80 bar.

## CHAPTER 5

### CONCLUSION

A kinetic model for hydrodeoxygenation of triolein to green diesel was developed in this work. The simulation of the process was carried out with the assumed kinetic parameter values. The author observed that the conversion of triolein increases with an increase in temperature and pressure and recorded the highest conversion at temperature of 350<sup>0</sup>C and pressure 80 bar. The yield of liquid hydrocarbons increases with an increase in pressure and temperature. The selectivity towards octadecane decreases with an increase in temperature and decrease in pressure. Meanwhile the selectivity towards heptadecane increases with an increase in temperature and decrease in pressure. The finalized model compound for the conversion of triolein to liquid hydrocarbons using solid acid catalyst will be shown as below:

$$\frac{dC_{TRIOLEIN}}{dt} = -(k_1 C_{HYDROGEN}^{\alpha_1} + k_2 C_{HYDROGEN}^{\alpha_2} + k_3 C_{HYDROGEN}^{\alpha_3}) C_{TRIOLEIN}$$

## REFERENCES

- T.M. Sankaranarayanan , M. Banu , A. Pandurangan , S. Sivasanker.2011, *Hydroprocessing of sunflower oil–gas oil blends over sulfided Ni–Mo–Al–zeolite beta composites*, Bioresource Technology.
- A.S. Ramadhas , S. Jayaraj, C. Muraleedharan .2004, *Use of vegetable oils as I.C. engine fuels*, Renewable Energy 29.
- MaleeSantikunapornand SawarachDanphitak.2010, *Hydrodeoxygenation of Linoleic Acid on Ni-Mo Catalyst*, Thammasat Int. J. Sc. Tech. Vol. 15 Special Edition.