



Catalytic Hydro-cracking of Bio-oil to Bio-fuel

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Abstract

Over the last hundred years, the fossil fuels consumption is increasing dramatically and this lead to a significant increase in greenhouse gas emissions, the depletion of natural reserves of fossil fuels and increase the fuel production cost. Consequently, renewable and sustainable fuel sources such as bio-oil are receiving increased attention. In bio-based oil such as micro-algae oil, triglycerides and fatty acids are sustainable resources with high energy densities that can be converted into liquid hydrocarbon fuels, efficiently. One of the efficient ways for bio-oil conversion to applicable fuels is hydro-cracking. Hydro-cracking with acidic catalysts is a single step and energy efficient process for bio-oil upgrading towards bio-fuels. Zeolitic structures such as ZSM-5 and beta-zeolite are prevalent acidic catalysts in hydro-treating processes due to their strong acidity, their crystalline porous structure and their high hydrothermal stability. The aim of this research is checking the feasibility of hydro-cracking synthesis towards the light (LC) and middle (MC) range of hydrocarbons over the zeolite based catalysts. Two different types of zeolite catalysts, ZSM-5 and beta-zeolite, were chosen and they were impregnated with $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and calcined at 500 °C. The prepared catalysts were tested with oleic acid which is the main component of plant-derived oil. The catalysts were injected in a lab-scale trickle bed reactor in certain operating conditions. The oleic acid conversion over beta-zeolite was greater than ZSM-5 due to higher pore size distribution and acidity of beta-zeolite compared with ZSM-5. Also the reaction rate constant and Arrhenius equations for beta-zeolite and ZSM-5 were identified. The second step

of this research is investigating the hydro-cracking performance with performing a mathematical modelling. The model predictions showed reasonable correlation with experimental data and conversion rates. The total conversion for the hydro-cracking reactor model was 82.54 % for 4 major classes of hydrocarbons (light [LC], middle [MC], heavy [HC] and oligomerised [OC]). In addition, the concentration distribution and temperature profile along the reactor were investigated. At the end, a comprehensive sensitivity analysis was performed to analyse the hydro-cracking reactor performance.

Declaration

I certify that this work contains no material which has been accepted for the award of any other degree or diploma in my name, in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text. In addition, I certify that no part of this work will, in the future, be used in a submission in my name, for any other degree or diploma in any university or other tertiary institution without the prior approval of the University of Adelaide and where applicable, any partner institution responsible for the joint-award of this degree.

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CHAPTER 1

INTRODUCTION

1.1. Background

Recently, dramatic increases in the atmospheric concentration of greenhouse gases and carbon dioxide, lead to worldwide concern about global warming [1, 2]. The most abundant greenhouse gases in the Earth's atmosphere are: vapour of water (H₂O), carbon dioxide, methane, oxides of nitrogen and ozone (O₃) and Chlorofluorocarbons (CFCs) [3]. However, CO₂ has the major contribution to the global warming, due to its high concentration in the atmosphere [4, 5]. The concentration of CO₂ in the atmosphere has been raised significantly in 2013 due to industrialisation [6], which is mainly because of our significant dependency on the fossil fuel for energy production [3, 4]. For instance, fossil fuels account for more than 80% of global energy demand which was 16 TersWatts (TW) in 2009. [4]. Furthermore, a research was performed by the Energy Information Administration (EIA) within the U.S. Department of Energy (DOE), which has been confirmed that the consumption of fossil fuels will grow about 27% over the next 20 years [2]. However, if no action or pollicises is taken, the world could be warmer around 4 °C by the end of this century than it was at the beginning of industrial revolution [7]. This temperature raise would have serious impacts on sea level rise, water supplies security and agriculture industry.

The technologies for fossil fuels production are nearly matured. They are cheap, high available and reliable [1] but because of global warming, the urgent attention is required to decrease CO₂ emission. Therefore, there is need to develop novel technologies that enable reduction in CO₂ emissions into the atmosphere, while also mitigating the significant economic and political advantages that favour the business-as-usual technologies. There are three options to reduce total CO₂

emissions, to reduce the energy consumption (including increasing the efficiency of the energy conversion and/or utilization systems), to switch to non-fossil fuel energy sources such bio-oil and biomass and finally Carbon Capture and Storage (CCS) [8].

During the last decades significant global attempts has been allocated to developing new technologies that enables preventing CO₂ emission. Among these technologies, alternative energy production ones through bio-fuel has gained more interest. This is mainly due to the synergy between the available power generation systems and the fuels produced from bio sources. Also, these days biofuels contributes about 2.7% of the global energy consumption special in transport sector [9] and this is the evidence of high attention to bio-fuel technologies. Various resources are existed for biofuel production which are categorised to edible and non-edible feedstocks [3, 10]. Non-edible feedstock such as Jatropha oil and micro-algae oil is one of the major feed sources for the economical biofuel production [11, 12]. Several factors promote micro-algae feedstock in comparison with Jatropha oil: potentially low aromatics and sulfur content of produced fuel; lower air pollution on burning compared with fossil fuels; the potential abundance of micro-algae; their relatively low cost of nourishment; and their overall environmental compatibility [12-14]. Also, micro-algae feedstock can capture about 3-8% of solar energy and contains around 60% oil content by weight of dry biomass depend on the micro-algae species [12, 15, 16]. The bio-oil from micro-algae can be used directly in diesel engines, but the direct engine combustion causes carbon deposits and coking on the injectors and also due to high viscosity of bio-oil the engine can't operate properly [17, 18]. The aforementioned

problems prove that the bio-oil required to be upgraded. Recently, bio-oil upgrading to applicable fuels becomes more highlighted due to low heating value, high viscosity and poor stability of crude bio-oil [19-21]. The overall aim of this research is investigating on bio-oil upgrading towards biofuels.

Esterification (solvent addition), Hydro-treating and hydro-cracking are three major existing processes for bio-oil upgrading to fuels [22]. Catalytic hydro-cracking of bio-oil has been reported as a promising alternative in biofuel preparation. Different bio-oil feedstocks were employed to produce biofuels such as gasoline and bio-diesel with zeolitic catalysts [21, 23-27]. Zeolitic catalysts are emerging as effective materials for efficient catalytic cracking of bio-oil due to their high heating stability and strong acidity [11, 14, 27].

The main advantage of using zeolitic structures as catalyst in catalytic conversion of bio-oil is performing the conversion process in one single step process which can consume less energy than other upgrading processes [13, 14, 27]. Also some studies have been performed to show the influence of the impregnated metal oxides with zeolite basis in bio-oil conversion [27-31]. The selectivity of hydrocarbon fuels was improved with the application of metal oxides on zeolite but the problem is most of the applied metal oxides are expensive to commercialise. Therefore, in this thesis, the application of cheap metal oxides such as nickel over zeolite was investigated to convert the catalyst and conversion process very cost effective.

As mentioned above, in the recent decade, numerous experimental researches have been performed on the different aspects of catalytic conversion of bio-oil. In order to optimise and commercialise the bio-oil conversion reactions, numerous

costly experimental measurements are required at high pressure and temperature which are expensive and time consuming. Therefore, the numerical analysis provides an appropriate and complementary alternative to investigate the reaction kinetics and optimise the total yield and conversion efficiency. However, in the open literature, the operational performance of bio-oil has not been reported and all of the related studies focused on experimental aspect of crude oil upgrading. This thesis is focused on modelling and optimisation of the bio-oil conversion reactor and the effect of some significant operational parameters were investigated in this research.

1.2. Aims

The specific aims of the thesis were outlined as follows:

- To explore the application of nickel on two types of zeolite such as ZSM-5 and Zeolite β to produce cost effective catalyst for catalytic cracking of bio-oil.
- To investigate the performance of prepared catalyst samples in catalytic cracking reactions.
- To set up a mathematical model for the catalytic cracking reactions of crude bio-oil to biofuels.
- To identify the parameters those best describe the performance of the bio-oil cracking reactor.

1.3. Thesis outline

The thesis is presented in seven chapters, the sequence of which highlights the chronology of the knowledge development and research undertakings to meet the defined aims. The first Chapter, which is the introduction, gives an overview of the subject and specifies briefly the gap in knowledge. The principle objective and the aims of the thesis are also defined in this Chapter. Chapter 2 provides a comprehensive literature review and explains the gap in knowledge as well as the importance of the research in more details. The main body of the thesis, Chapters 3 to 6, is a collection of four manuscripts that have been published, or are currently under review. These publications present the progress made in the course of this study and explain the achievements of this research. Finally, the conclusions of the research performed in addition to some basic recommendations for the future works are given in the Chapter 7. In the following paragraphs the content of each chapter and the alignment of the research with the specified aims are described.

Chapter 2 provides a critical review of three major parts of catalytic cracking of bio-oil. Firstly, the different types of bio-oil upgrading processes to biofuels are discussed. Secondly, the role of acidic catalysts and the application of different types of metal oxides over zeolite, as the cracking catalyst, were investigated. In the third part, the catalytic upgrading reactor types and advantages of process modelling was explained in order to obtain better understanding from bio-oil catalytic upgrading.

The research was begun by investigating the feasibility of mathematical modelling of bio-oil hydro-cracking synthesis for the first time. A numerical

model was set-up for the hydro-cracking reactor and the performance of the bio-oil catalytic cracking was discussed in chapter 3. The bio-oil hydro-cracking model needs to be examined in details; hence a comprehensive sensitivity analysis of the model was performed in chapter 4. In chapter 5, procedure of making and analysing an unexpensive nickel based catalysts for bio-oil hydro-cracking was explained. In this chapter, nickel was impregnated over two types of zeolite, ZSM-5 and Zeolite β and then the prepared catalyst samples were tested in a micro-scale trickle bed reactor to explore the catalysts performance in hydro-cracking reactions by measuring the conversion rate and production yields. The hydro-cracking experimental data and the established model of bio-oil upgrading have been connected in chapter 6. In this chapter, it was proved that our model is valid with the experimental data were achieved from chapter 5.

Finally Chapter 7 lists the conclusions from this research along with recommendations for further development of the concept toward commercialisation step up.

1.4. Papers arising from this thesis

The research discussed in this thesis has led to the generation of four journal papers and two conference presentations. The journals in which the papers are published or submitted are three of the best in the fields of bio-energy and chemical engineering.

Journal papers:

- **A. A. Forghani**, M. Jafarian, P. Pendleton, and D. M. Lewis, “Mathematical modelling of a hydro-cracking reactor for triglyceride conversion to biofuel: model establishment and validation”. *International Journal of Energy Research*, (2014), DOI: 10.1002/er.3244.
- **A. A. Forghani** and D. M. Lewis, “Performance investigation of a hydro-cracking reactor for triglyceride conversion to bio-fuel production”. *Energy Conversion and Management*, (2014), (Under review).
- **A. A. Forghani**, S. H. Madani, P. Pendleton, A. Tanksale, D. M. Lewis “Catalytic Conversion of Oleic Acid in Bio-oil to Liquid Hydro-carbon Fuels”. *Energy and Environmental Science*, (2014), (Under review).
- **A. A. Forghani** and D. M. Lewis, “Hydro-cracking of Oleic Acid in Bio-oil to Liquid Hydro-carbon Fuels: experimental and modelling investigation”. *Chemical Engineering Journal*, (2014), (Under review).

Conference presentations

- **A. A. Forghani**, D. M. Lewis, “Bio-fuels Production from Micro-Algae: Unlocking the potential”. APCAB conference (2012), Adelaide, Australia.
- **A. A. Forghani**, D. M. Lewis, P. Pendleton, “Application of Zeolite-based catalysts in jet-fuel production”. The 2nd International

Conference on Algal Biomass, Biofuels and Bioproducts (2012), San-Diego, USA.

1.5. Format

The thesis has been submitted as a portfolio of the publications according to the formatting requirements of The University of Adelaide. The printed and online versions of this thesis are totally identical. The online version of the thesis is available as a PDF. The PDF version can be viewed in its correct fashion with the use of Adobe Reader 9.

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CHAPTER 2

LITERATURE REVIEW

2.1. Bio-oil upgrading processes and applied catalysts

Recently, bio-oil upgrading to applicable fuels becomes more highlighted due to low heating value, high viscosity and poor stability of crude bio-oil [1-3]. Bio-oil upgrading has been begun with vegetable oil conversion over acidic and basic catalysts in the 1920s [4]. Al_2O_3 and AlCl_3 were the early cracking acidic catalysts which were operated in batch reactor between temperature of 450-500 °C [4, 5]. Esterification (solvent addition), Hydro-treating and hydro-cracking are three major existing processes for bio-oil conversion to fuels [6]. Esterification is the catalytic reaction between bio-oil and short chain alcohol as solvent such as methanol and ethanol and it is very popular in bio-diesel production but it needs a large amount of solvent [6, 7]. Hydro-treating is simple hydrogenation which has been applied in refineries to convert aromatics to naphthenes at temperatures above 500°C and atmospheric pressure but recently it is applied for bio-crude conversion over sulfide Co & Mo/ Al_2O_3 , Ni & Mo/ Al_2O in order to remove oxygen from triglyceride [8, 9]. Hydro-treating yield is low and due to sulfide catalyst application, it produces a lot of char and coke in the process which can result reactor clogging and catalyst deactivation [6]. Hydro-cracking is combination of different cracking reactions with hydrogenation in high temperatures (above 350°C) and high pressures (above 7 Bar) [10, 11] over dual-function catalysts. Dual-function catalysts have a zeolite or silica alumina base which is provide the cracking function and metal oxides such as nickel, molybdenum which are catalysing the reactions towards light hydrocarbons [6-8, 11-14]. The bio-oil conversion processes were summarised in table 1.

CHAPTER 2

Table 1. Bio-oil conversion processes to hydrocarbons

Upgrading Process	Process Details	Disadvantage
Esterification	It is a catalytic reaction between bio-oil and short chain alcohol as solvent such as methanol and ethanol.	<ul style="list-style-type: none"> - High amount of solvent - Non- economic
Hydro-treating	Simple hydrogenation over sulfide Co & Mo/Al ₂ O ₃ , Ni & Mo/Al ₂ O in order to remove oxygen from triglyceride.	<ul style="list-style-type: none"> - High amount of coke production - Catalyst deactivation
Hydro-cracking	Single step process with combination of different cracking reactions with hydrogenation in temperatures above 350°C and pressures above 7 Bar. It can be perform over sulfide and non-sulfide catalyst.	<ul style="list-style-type: none"> - Catalyst deactivation if sulfide catalysts were applied

One of the recent upgrading methods is catalytic cracking of bio-oil to liquid hydrocarbon fuels [15-20]. The main advantage of using catalytic bio-oil cracking process is performing this process in one single step process which can consume less energy than other upgrading processes [7, 14, 21]. Catalytic upgrading of bio-oil is consisting of several complex reactions such as cracking, decarbonylation, decarboxylation, hydro-cracking, hydro-deoxygenation and hydrogenation. An example of bio-oil upgrading is shown in figure 1.

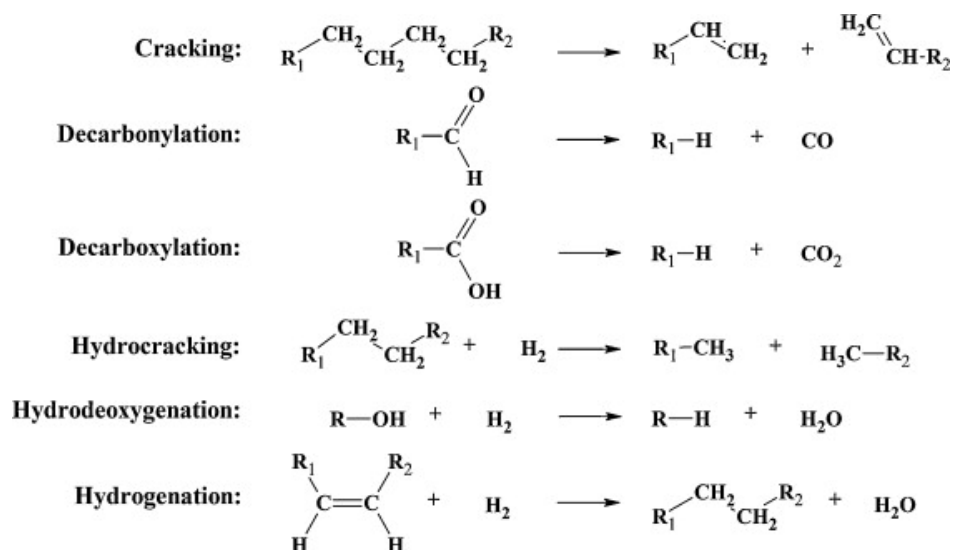


Figure 1. All associated reactions with catalytic upgrading of bio-oil from refs. [22, 23]

These complex reactions have been reported to take place on zeolitic catalyst structures [22-24]. Hence, bio-oil catalytic upgrading over zeolite catalysts became an alternative method in bio-oil and triglyceride conversion to usable fuels [25]. Zeolitic catalysts are emerging as effective materials for efficient bio-oil cracking due to their high heating stability and strong acidity [7, 14, 26]. In 1995 and 1999, three types of zeolites such as HZSM-5, HBEA and USY zeolites were applied in a fixed bed reactor for the cracking of palm oil [25, 27]. These three types of zeolite catalysts were operated in the temperature range of 350-450 °C and they yielded 99%, 82% and 53% conversions with gasoline selectivity of 28%, 22% and 7% respectively [25, 27]. Also HZSM-5 led to produce aromatic hydrocarbons especially benzene and toluene, USY favouring the formation of diesel range of hydrocarbons while BEA formed fewer diesel [4, 25, 27]. The main disadvantage of HBEA and USY catalysts in catalytic cracking of bio-oil is coke formation. The rate of coke formation for these two catalysts are higher than HZSM-5 and this issue corresponds with the pore diameter increment. With increasing the pore diameters, the coke formation inside the catalyst is growing as well [27, 28] but ZSM-5 and HZSM-5 catalysts have a great potential to produce gasoline and jet fuel range of hydrocarbons with less coke formation [26, 27, 14]. For instance, the application of ZSM-5, HZSM-5 and MCM-41 were investigated as catalysts for fatty acids and bio-oil conversion [29, 30]. The gasoline selectivity with aforementioned catalysts increased to the range of 38-47% [29, 30]. The most important section in bio-oil upgrading to biofuels is oxygen extraction from bio-oil. Recent investigations shown that oxygen removal can be performed with a number of parallel reactions such as hydrodeoxygenation

which is producing water molecule, decarboxylation which is producing carbon dioxide and decarbonylation which is generating carbon monoxide molecule [31]. Based on this approach, several researchers developed single step process with different ranges of zeolitic catalysts to convert bio-oil to paraffinic fuels. Another procedure which has a great attention recently is hydrotreating of bio-oil over the metal based catalysts. In the next part the metal based catalysts has been discussed in details.

2.2. Application of metal based catalysts in bio-oil conversion

2.2.1. Application of supported metal sulfide catalysts

Metal based catalysts for bio-oil and triglyceride conversion can be categorised to two main types which are named metal sulfide catalysts and sulfur free metal catalysts. The common sulfide catalysts for bio-oil conversion are conventional Ni-Mo and Co-Mo sulfide catalysts over zeolites. They are used in petroleum refineries to produce straight-chain alkanes ranging from C₁₂ to C₁₈ at temperature of 350-450°C in the presence of hydrogen with pressure of 40-150 bar [32, 33]. The sulfided catalysts were analysed widely in hydro-treating of bio-oil to produce diesel and middle range of hydrocarbons. For example, Bezrgianni et al analysed catalytic hydrocracking of waste cooking oil with sulfided Ni-Mo/ γ -Al₂O₃ to produce white diesel. Hydrocracking increases the H/C ratio, and removes heteroatoms S, N, O, and metals from the bio-oil feedstock [34, 35]. In their studies, temperature increase from 330 to 398 °C led to increase the fraction of iso-paraffins from 5% to 38%, and also the lighter alkanes (C₈-C₁₄) increased to

22% at 398 °C but a main disadvantage of this liquid fuel is the poor flow properties at lower temperatures [34, 35]. Gusmao *et al* investigated hydrocracking of soy bean and babassu oils in a batch reactor at the temperature range of 350-400 °C and at H₂ partial pressure of 10 to 200 bar. They applied sulfided Ni–Mo/ γ -Al₂O₃ and reduced Ni/SiO₂ catalysts, and found that only double bonds were hydrogenated in soy bean oil at the reaction temperatures less than 200°C. The decomposition of triglycerides accompanied by hydrogenation of the decomposition products was detected above temperature of 290 °C. Compared to reduced Ni catalyst, sulfide Ni-Mo catalysts required higher reaction temperatures (230-280 °C) to hydrogenate double bonds. On the other hand, transformation of the carboxylate groups was achieved at around temperature of 300 °C on both catalysts [36].

Kubička *et al* researched hydroprocessing of rapeseed oil for the production of components in the diesel fuel range [37-39]. Rapeseed oil was hydroprocessed at 260-340°C under a hydrogen pressure of 70 Bar in a continuous trickle bed reactor. Three Ni-Mo/Al₂O₃ sulfide hydrotreating catalysts were evaluated. Reaction products included water, H₂-rich gas, and organic liquid product. The main components of organic liquid product were C₁₇ and C₁₈ n-alkanes. At low reaction temperature, organic liquid components contained also free fatty acids and unconverted triglycerides. At reaction temperatures higher than 310°C, organic liquid components contained only green hydrocarbons similar to diesel range of hydrocarbons [37-39]. Furthermore, Ni/Mo-based catalysts were applied in hydroprocessing of Jatropha oil, Palm oil, Canola oil and sunflower oil [40-42]. Corma *et al* analysed the hydroprocessing of pure sunflower oil over

sulfide Ni-MO/Al₂O₃ at 350°C and they resulted complete oil conversion with 71% yield of C₁₅-C₁₈ alkanes [42]. Also Jatropha, Palm and Canola oil were tested over Ni/Mo based catalysts in a high pressure fixed bed flow reactor at temperature of 350°C and hydrogen pressure of 40 bar [40, 41]. Among the Ni/Mo based catalysts, Ni-Mo/H-Y and Ni-Mo/H-ZSM-5 formed a high yield of gasoline-range of hydrocarbons due to the strong acid sites of zeolites [41]. Although sulfided metal support catalysts can improve the yields of fuel productivity and bio-oil conversion, but they contaminate products via sulfur leaching, and deactivate the catalysts due to S removal from the surface by a reverse Mars van Krevelen mechanism [40].

2.2.2. Application of supported sulfured-free metal catalysts

Supported noble metal catalysts such as Pd/C are frequently analysed for decarboxylation and decarbonylation of fatty acids in different bio-oil feedstocks [43-52]. For instance, 5 wt% Pd/C can yield 100% C₁₇ and C₁₈ from stearic acid at temperature of 300°C [52]. Noble metal catalysts showed high activities and selectivities for fatty acid conversion when their activity and selectivity were analysed comprehensively by Murzin et al [53-59]. However, they showed much lower activities and selectivities to the targeted alkanes for triglycerides conversion [60, 61]. The high price of noble metal limits their industrial applications as catalyst.

Furthermore, Peng et al. used base metal catalysts such as Ni supported on zeolites for hydrodeoxygenation of fatty acids [62]. Ni/HZSM-5 (10 wt%)

catalysed complete conversion of stearic acid in dodecane at temperature of 260°C for 6 hour in the presence of 40 bar hydrogen pressure. Zhang et al prepared Ni based catalysts over γ -Al₂O₃ and HZSM-5 (Si/Al=38) for hydrotreatment of bio-oil [63]. Their catalysts were analysed with the temperature range of 160-240°C and the conversion of 91.8% was achieved [63].

In conclusion, the upgrading of bio-oil is expected to be commercialised, so the application of noble metal catalysts over zeolite could significantly raise biofuel production costs. On the other hand, sulfide metal based zeolitic catalysts led to product contamination with sulfur and deactivates the catalyst by S removal. Consequently, application of non sulfur metal based catalyst over zeolite is the cost effective option for bio-oil upgrading which is investigated in this research. In this thesis two types of inexpensive non-sulfide Ni-based bifunctional catalysts are introduced characterised and then analysed in bio-oil upgrading process.

2.3. Mathematical modelling of the Catalytic bio-oil upgrading reactors

There is increasing interest in the different aspects of catalytic hydro-reforming of bio- oil [15, 16, 19, 64, 65]. To optimise the conversion reforming reactions, localised experimental measurements are required at high pressure and temperature in different types of reactors. The large numbers of reaction design options render empirical optimisation both time consuming and costly. Alternatively, numerical analysis provides an appropriate and complementary methodology to investigate reaction kinetics and identify how to improve the total

conversion efficiency. Of the recent numerical modelling methods, Bhaskar *et al.* (2004) presented a three phase heterogeneous model that was applied to simulate the performance of a trickle-bed reactor for hydro-desulfurisation of diesel fractions of crude oil [66]. They investigated the influence of temperature and feed-rates on the hydro-treating reactions and products and analysed the performance of the reactor under various operating conditions [66]. A mathematical model of a heterogeneous trickle-bed reactor for the hydro-treatment of vacuum gas oil was presented by Korsten and Hoffmann in 1996. In this model, the two film-theory was applied to assess the performance of the reactor in terms of temperature, pressure, space velocity and the gas/oil ratio [67]. Also they found from their model that incomplete catalyst wetting and low feed velocity lead to poor conversion of crude oil hydro-treating reactions in the pilot-plant reactor. Larachi *et al.* (2014) proposed a 1-D model of a trickle-bed reactor to investigate the feasibility of scaling up from lab-scale to a pilot scale reactor system. Alvarez and Ancheyta (2008) developed a heterogeneous plug-flow model for a hydro-processing fixed bed reactor to describe the behaviour of the crude oil residue. In their model, the gas-liquid and liquid-solid mass transfer and experimental kinetic data were considered for validation of their model using pilot-plant data. Their model results showed appropriate agreement with the experimental data, and a higher (8-18%) performance could be achieved by the scaling up their pilot plant reactors. No operational performance of a hydrocracking trickle-bed reactor for micro-algal bio-oil has been reported in the literature. Therefore, a clear aim of the reported research is to present a

heterogeneous plug-flow model of a trickle-bed reactor for hydrocracking of bio-oil.

The major section in setting up a reliable trickle-bed reactor model is defining a reliable reaction kinetic. Several studies investigated the reaction pathway of hydro-cracking of triglyceride, which is the major component of bio-oil. For instance, Benson and Kloprogge (2009) studied the reaction pathways of triglyceride cracking and upgrading over acidic zeolitic structures [64, 68]. The mechanism of hydrocracking of Jathropha oil at different temperatures was discussed by Anand and Sinha (2012). They proposed 7 different reaction mechanisms to model triglyceride hydrocracking over alumina supported Co-Mo mixed catalysts. In their study, they grouped reactants and products into various assortments, referred to as lumps, e.g. the reactant triglyceride was identified as a lump consisting of four major components as stearic acid, palmitic acid, linoleic acid and oleic acid. They also used four product lumps: light hydrocarbons (LC); middle hydrocarbons (MC); heavy hydrocarbon (HC); and, oligomerised products (OC). The rate of reaction as a function of both temperature and concentrations for each lump were identified [15]. However, they proposed that each reaction kinetics model is appropriate for a specific range of temperature.

In conclusion, despite the large numbers of experiment were performed on bio-oil upgrading but the modelling of the bio-oil upgrading reactor hasn't been reported yet in the open literature. Another significant aim of this thesis is investigation of the upgrading reactor performance by mathematical modelling and then the reactor is optimised with a comprehensive sensitivity analysis.

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CHAPTER 3

**Mathematical modelling of a hydrocracking
reactor for triglyceride conversion to biofuel:
model establishment and validation**

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Name of Co-Author	Mehdi Jafarian
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CHAPTER 4

Performance investigation of a hydro-cracking reactor for triglyceride conversion to bio-fuel production

CHAPTER 4

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Performance investigation of a hydro-cracking reactor for triglyceride conversion to bio-fuel production

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Abstract

The performance analysis of triglyceride conversion is reported for a hydro-cracking reactor (HCR). A two-dimensional, non-isothermal, heterogeneous model of a triglyceride hydro-cracking reactor is established and then the film theory is applied in the model incorporating the internal heat and mass transfer within the phases in the reactor. The modelling was completed with consideration of an appropriate hydro-cracking kinetic model. After the reactor model establishment, a sensitivity analysis based on reactor inlet feed temperature, reactor heat flow and reaction bed length was performed. The hydrocarbon products are considered in the reactor model with two products, namely the light hydrocarbons (LC) and the middle hydrocarbons (MC), are targeted in the HCR performance analysis. The results show that triglyceride conversion, LC and MC production were increased with increased inlet feed temperature but the heavy hydrocarbon (HC) production decreased. The reactor heat flow variations affected the liquid, gas and reactor wall temperature profiles; but triglyceride conversion, LC and MC production rates were not affected. The effects of varying the reaction bed length showed that with higher reactor bed lengths, triglyceride conversion and hydrocarbon lump yields (LC and MC) increased.

Keywords: Triglyceride hydro-cracking, Reactor Modeling, Bio-fuel production, Sensitivity analysis.

CHAPTER 4

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Nomenclature

a	specific surface area of catalyst (m^2/m^3)
C_i^L	Liquid concentration of each lump (mol/m^3)
C_p^l	Liquid specific heat capacity ($\text{J}/\text{kg}\cdot\text{K}$)
h_G	Gas heat transfer coefficient ($\text{W}/\text{m}^2\cdot\text{K}$)
h_l	Liquid heat transfer coefficient ($\text{W}/\text{m}^2\cdot\text{K}$)
k_i	Rate constant of major reactions ($1/\text{s}$)
K_i^g	mass transfer coefficients in gas phase (m/s)
k'_i	Rate constant of internal reactions ($1/\text{s}$)
L_0	Reactor length (m)
$LHSV$	Liquid hourly space velocity ($1/\text{h}$)
m_g	Gas mass flow-rate (kg/s)
P_i^g	Partial pressure (Pa)
P_i^*	saturation pressure in the liquid-gas phase interface (Pa)
r_i	Rate of reaction ($\text{mol}/\text{m}^3\cdot\text{s}$)
R	Universal gas constant ($\text{J}/\text{mol}\cdot\text{K}$)
Re	Reynolds number
Sc	Schmidt number
Sh	Sherwood number
T_L	Liquid phase temperature (K)
T_g	Gas phase temperature (K)
T_w	Reactor wall temperature (Tube) (K)
X	Each point along the reactor length (m)
$Y(i)$	Yield of each lump
ΔH_i	Enthalpy of reaction for each lump (kJ/mol)
\square	Bed porosity

Superscripts and subscripts

<i>amb</i>	Ambient
<i>g</i>	Gas phase
H_2	Hydrogen
<i>HC</i>	Heavy hydrocarbons
<i>i</i>	Each lump index
<i>in</i>	Inside
<i>L, l</i>	Liquid
<i>LC</i>	Light hydrocarbons
<i>MC</i>	Middle hydrocarbons
<i>OC</i>	Oligomerised products
<i>out</i>	Outside
<i>Tg</i>	Triglyceride
<i>w</i>	Wall

1. Introduction

According to the BP statistical report in 2008, the world energy consumption has surged in the past 20 years [1] and fossil fuels are the largest contributors in the global energy consumption [2], especially in the transportation and manufacturing sectors. The limitation in fossil fuel reservoirs their contribution to greenhouse gases emissions [3] and their additive prices, a significant research motivation is continuing on developing sustainable processes to produce renewable fuels [4]. Among the various options for renewable fuels, biofuels from micro-algae are being considered as commercially attractive [2] because of their potential for fast growth rates, high oil yields (1000 – 6500 gal acre⁻¹ yr⁻¹ vs. soybean 48 gal acre⁻¹ yr⁻¹), high triglyceride and fatty acid content, and the potential to use non-arable land for mass cultivation, ability to grow in a variety of water sources and the potential benefits associated with large-scale CO₂ mitigation [5, 6]. In bio-based oil such as micro-algae oil, triglycerides and fatty acids are potentially sustainable resources with high energy densities that can be converted into liquid fuels. One of the efficient ways for triglyceride conversion is through hydro-treatment [4]. Hydro-treating is currently used in petroleum refineries to remove sulfur, nitrogen, and metals from petroleum-derived feedstock such as heavy or vacuum gas oil [7, 8]. Recently, significant attempts have been undertaken for the application of the hydro-treating processes on conversion of plant derived triglyceride to hydrocarbon fuels [4, 9-17].

The main advantage of using hydro-treating processes is being able to perform triglyceride upgrading in a single step process, reducing energy consumption [17-19]. The aim of the reported work was to quantify the hydro-treatment of triglycerides to produce bio-fuels.

In the last decade, numerous experimental work has been focused on the different aspects of catalytic hydro-treating of micro-algae oil [9, 10, 15, 20, 21]. To optimise the triglyceride conversion reaction, localised and costly experimental measurements are required at high pressure and temperature, which is expensive and time consuming. Numerical analysis provides an appropriate and complementary alternative for the investigation of the reaction kinetics and provides the ability to optimise the total yield and conversion efficiencies. Numerous mathematical models are reported in the literature on the hydro-cracking process. In 2004, Bhaskar *et al.* presented a three phase heterogeneous model that was applied to simulate the performance of a trickle bed reactor for hydro-desulfurisation of diesel fractions of crude oil [22]. They investigated the influence of temperature and feed-rates on the hydro-treating reactions [22]. A mathematical model of a heterogeneous trickle bed reactor for the hydro-treatment of vacuum gas oil was presented by Korsten and Hoffmann [23]. In their model, the two film-theory was applied to assess the performance of the reactor in terms of temperature, pressure, space velocity and the gas/oil ratio [23]. Alvarez and Ancheyta (2008) developed a heterogeneous plug-flow model for a hydro-processing fixed bed reactor to describe the behavior of the crude oil residue [24]. In their model, the gas-liquid and liquid-solid mass

transfer and experimental kinetic data were considered for validation of their model using pilot-plant data. Their model results showed good agreement with the experimental data, and also the feasibility of scaling up that demonstrated that a higher 8-18% performance could be achieved in comparison to their pilot plant reactors [24]. However, according to open literature resources, the operational performance of a hydro-cracking trickle bed reactor for micro-algal bio-oil has not been reported and all of the related studies focused on crude oil upgrading. Therefore, the main aim of this study is to present a heterogeneous plug flow model of a trickle-bed reactor for hydro-treating of micro-algal triglyceride as one of the renewable resources for fuel production.

A few scientific papers report the reaction kinetics of bio-oil conversion to bio-fuels [9, 20, 25]. Benson and Kloprogge (2009) studied the reaction pathways of triglyceride cracking and upgrading over acidic zeolitic structures [20, 25]. The mechanism of hydro-cracking of jathropha oil at different temperatures has been recently studied by Anand and Sinha (2012) [9]. They proposed 7 different reaction mechanisms to model the hydrocracking of triglyceride over Co-Mo/Alumina catalyst. In their study, they grouped reactants and also products into various assortments named lump. For instance, triglyceride was identified as a separate lump consists of four major components of stearic acid, palmitic acid, linoleic acid and oleic acid. They also used four lumps, namely light hydrocarbons (LC), middle hydrocarbons (MC), heavy hydrocarbon (HC) and oligomerized products (OC) as products. The rate of reaction as a function of both

temperature and concentrations for each lump were identified [9]. They proposed that each reaction kinetics model is more appropriate when used with a specific range of temperature. The effect of two individual kinetics models were investigated previously [26] and it was found that the proposed A7 kinetic model has a better agreement with the experimental data, with an average error of less than 12.53%.

Hence, in the reported work, the recently proposed kinetic model was investigated using a simulation of a trickle-bed reactor (A7-model). The main aim of this study in particular, was to optimise the performance of the hydrocracking reactor by performing a sensitivity analysis on feed input temperature, reactor length and reactor heat flow.

2. Methodology

2.1. Model description

A schematic representation of a trickle-bed reactor is shown in Figure 1 (a). The process consists of a catalyst bed in a trickle-bed reactor. The triglyceride as a rich feed and high-pressure hydrogen enters the reactor from the top and bottom of the reactor, respectively. Through the reactor, shown in Figure 1 (b), hydrogen from the gas phase is transferred to the liquid-solid inter-phase for the hydrocracking reactions. The produced species such as LC, MC, HC and OC disperse through the gas and liquid phases depending on the operating temperature and pressure within the reactor. As shown in Figure 1 (c), an element of the reactor with

length of Δz is considered to derive the mass and energy balance equations for the model.

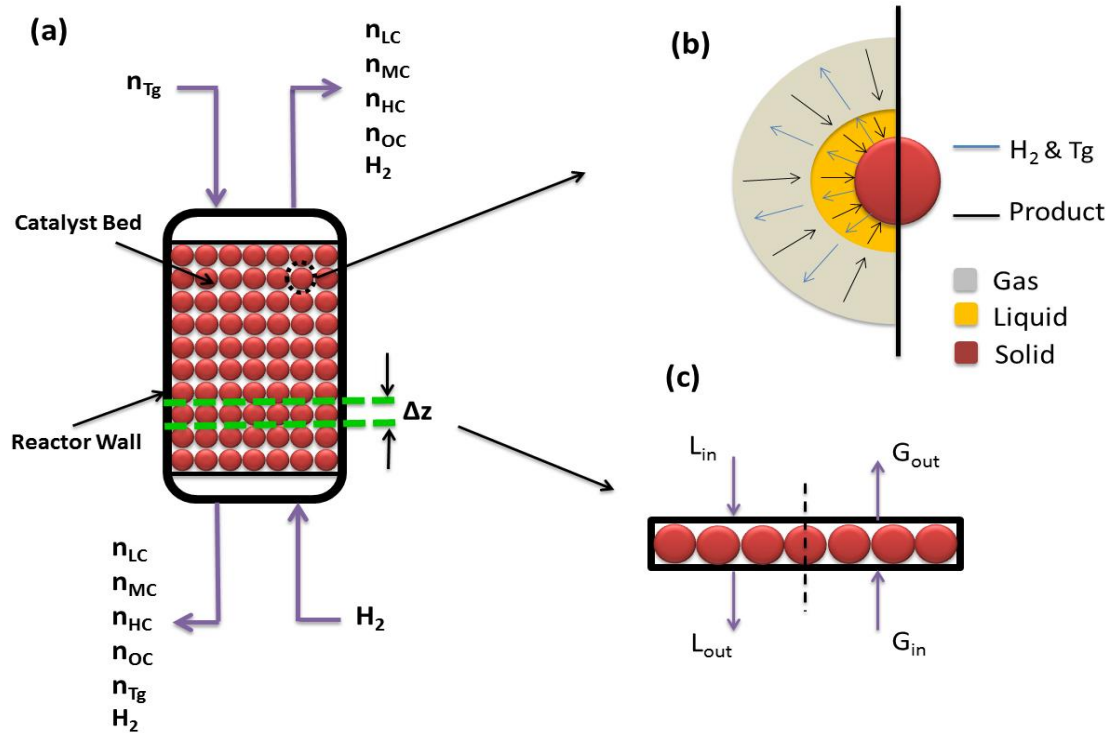


Figure 1. (a) Schematic representation of the trickle-bed reactor, (b) Film theory over the catalyst and (c) The selected element of the trickle-bed reactor for development of the governing equations

2.2. Mathematical model of the hydro-cracking trickle bed reactor

To set up a hydro-processing plant, a comprehensive evaluation should be done to check the performance of the plant, which is time consuming, too risky and too expensive when using a full-scale system to evaluate the plant performances. Modeling is one of the most efficient ways to evaluate plant performance. Recently, models were employed to optimise the impact of changes in design variables. The first step to make an

efficient model is the formation of the appropriate mass and energy balance equations. To this set of equations, suitable kinetic equations that represent the rate of reaction/s are added [27].

In this study, a three-phase heterogeneous reactor model was developed for hydrocracking of triglyceride. The model considers two-film theory, which incorporates mass transfer at the gas-liquid and liquid-solid interfaces and employs correlations which were presented in the literature [7, 8, 22-24]. In the present model, the catalyst is represented as the solid phase; hydrogen, as a reactant, is the gas phase and triglyceride is the liquid phase. The following assumptions were made for the three-phase heterogeneous reactor model:

- 1) Plug flow was considered along the reactor and there was no radial concentration gradient.
- 2) The trickle bed reactor was operated at steady state conditions.
- 3) The developed reaction rates by Anand and Sinha were applied in the model.
- 4) For model validation, the reactor was operated isothermally.
- 5) Axial dispersion of heat was neglected.
- 6) The phase change of light components is negligible.
- 7) All reactions according to Anand and Sinha (2012) were assumed to be performed in the liquid phase [9].

All the assumptions were valid and they are reasonable to apply in the mathematical model. For example, because length per diameter ratio of

trickle-bed reactor (diameter is 1.3 cm and length is 30 cm) has a large number, therefore the first and fifth assumption are justified. The experimental data was collected at the steady-state condition with a lab-scale trickle-bed reactor. Also the lab-scale trickle bed reactor was operated isothermally to obtain experimental data for validation. So, the fourth section is justified. For justification the 7th section, according to temperature and pressure of hydrocracking reactions in the trickle-bed reactor, all components such as triglyceride and all products remain in the liquid phase thermodynamically.

2.3. Model Equation

Due to the large number of components produced within hydrocracking synthesis in a trickle bed reactor, five lumps of components were considered in the reaction kinetics model. Anand and Sinha (2012) proposed a kinetics reaction model named A7 model for triglyceride hydrocracking conversion reactions above 360 °C. The triglyceride lump (Tg) consisted of 4 components: Stearic acid, Oleic acid, Palmitic acid and Linoleic acid. The light (LC), middle (MC), high (HC) and oligomerized (OC) hydrocarbon components are shown in the Fig. 2 [9]. In the model A7, as shown in Fig. 2, the triglyceride is converted directly to LC, MC, HC and OC by 4 major reactions and two side reactions convert HC to MC and MC to LC respectively. All reactions are identified by the specific rate of reactions and reaction constants. According to our previous study, the

A7 kinetics model was considered in the modeling due to its low deviation from the experimental data [26]. So A7 kinetic model was selected to simulate the hydro-cracking reactor and performing the sensitivity analysis.

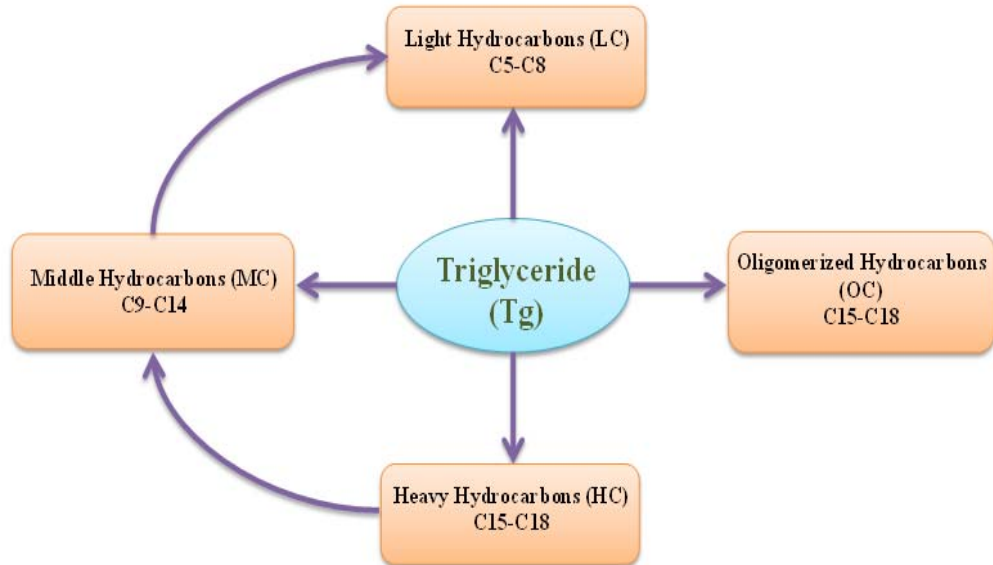


Figure 2. A7 reaction kinetics model which is proposed by Anand and Sinha for triglyceride conversion [9].

Using the stated assumptions the following mass balances and energy balances equations were obtained. The mass distribution along the reactor in both, gas and liquid, phases for different considered lumps is given by:

For lipid and triglyceride as the feedstock (Tg):

$$u_g \cdot A \cdot \frac{\partial P_{Tg}^g}{\partial z} = - \frac{K_{Tg}^l \cdot a \cdot A_c}{R \cdot T_g} (x_{Tg} P_{Tg}^* - P_{Tg}^g), \quad (1)$$

For light hydrocarbon (LC):

$$u_g \cdot A \cdot \frac{\partial P_{LC}^g}{\partial z} = -\frac{K_{LC}^l \cdot a \cdot A_c}{R \cdot T_g} (x_{LC} P_{LC}^* - P_{LC}^g), \quad (2)$$

For middle hydrocarbon (MC):

$$u_g \cdot A \cdot \frac{\partial P_{MC}^g}{\partial z} = -\frac{K_{MC}^l \cdot a \cdot A_c}{R \cdot T_g} (x_{MC} P_{MC}^* - P_{MC}^g), \quad (3)$$

For heavy hydrocarbon (HC):

$$u_g \cdot A \cdot \frac{\partial P_{HC}^g}{\partial z} = -\frac{K_{HC}^l \cdot a \cdot A_c}{R \cdot T_g} (x_{HC} P_{HC}^* - P_{HC}^g), \quad (4)$$

For oligomerized hydrocarbon (OC):

$$u_g \cdot A \cdot \frac{\partial P_{OC}^g}{\partial z} = -\frac{K_{OC}^l \cdot a \cdot A_c}{R \cdot T_g} (x_{OC} P_{OC}^* - P_{OC}^g), \quad (5)$$

For hydrogen (H₂):

$$\frac{\partial P_{H_2}^g}{\partial z} = -\frac{K_{H_2}^l \cdot a \cdot A_c \cdot R \cdot T_g}{u_g} \left(\frac{P_{H_2}^g}{h_{H_2}} - C_{H_2}^l \right), \quad (6)$$

where, u_g, x_i, P_i^g and K_i^g are the gas velocity, i 'th lump, $i = LC, MC, HC$ and OC , liquid mole fraction in the gas and liquid interface, partial pressure, and mass transfer coefficients in gas phase, respectively.

The stated equations represent the mass transfer of each lump and the hydrogen from the liquid-gas interface to the bulk of the gas. For each lump, the evaporation term was considered.

Mass balance equations in liquid phase

The differential equations of mass balance for the concentrations of hydrogen and light, middle, heavy and oligomerised hydrocarbon in the liquid phase can be written by equating the concentration gradients for the mass transfer of Tg, LC, MC, HC, OC and H₂ across the gas-liquid interface as follows:

For lipid and triglyceride as the feedstock (Tg):

$$u_L \cdot A \cdot \frac{\partial C_{Tg}^L}{\partial z} = -r_{LL} + \frac{K_{Tg}^g \cdot a \cdot A_c}{R \cdot T_g} (x_{Tg} P_{Tg}^* - P_{Tg}^g), \quad (7)$$

For light hydrocarbons (LC):

$$u_L \cdot A \cdot \frac{\partial C_{LC}^L}{\partial z} = r_{LC} + \frac{K_{LC}^l \cdot a \cdot A_c}{R \cdot T_g} (x_{LC} P_{LC}^* - P_{LC}^g), \quad (8)$$

For heavy hydrocarbon (HC):

$$u_L \cdot A \cdot \frac{\partial C_{HC}^L}{\partial z} = r_{HC} + \frac{K_{HC}^l \cdot a \cdot A_c}{R \cdot T_g} (x_{HC} P_{HC}^* - P_{HC}^g), \quad (9)$$

For oligomerized hydrocarbon (OC):

$$u_L \cdot A \cdot \frac{\partial C_{OC}^L}{\partial z} = r_{OC} + \frac{K_{OC}^l \cdot a \cdot A_c}{R \cdot T_g} (x_{OC} P_{OC}^* - P_{OC}^g), \quad (10)$$

Where u_L , C_i^L , r_i , P_i^g and P_i^* are the liquid velocity, i 'th lump, $i = LC, MC, HC$ and OC , liquid concentration, rate of reaction for each lump,

partial pressure in the gas phase, and saturation pressure in the liquid-gas phase interface, respectively.

Chemical Reaction Model

Developing the kinetic models for the triglyceride hydrocracking reactions was not straightforward due to the complexity of the triglyceride composition. Several attempts have been performed to investigate the hydro-cracking reaction pathways [9, 20, 25] but only Anand and Sinha (2012) found the rate of hydro-cracking reactions [9]. Their proposed rates of reactions are expressed as follows for the A7 kinetic model:

$$-r_{LL} = (k_1 + k_2 + k_3 + k_4)C_{Tg}, \quad (11)$$

$$r_{LC} = k_1 C_{Tg}, \quad (12)$$

$$r_{MC} = k_2 C_{Tg}, \quad (13)$$

$$r_{HC} = k_3 C_{Tg}, \quad (14)$$

$$r_{OC} = k_4 C_{Tg}. \quad (15)$$

Two internal cracking reactions between heavy (HC) and middle (MC) hydrocarbons were considered. The first reaction cracks HC to MC and the second one for converting MC to LC. The internal rates of reaction are expressed as follows:

$$r_{HC-MC} = k_5 C_{HC}, \quad (16)$$

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$$r_{MC-LC} = k_6 C_{MC}, \quad (17)$$

Where k_i and C_i , i th lump, $i = LC, MC, HC$ and OC ; are rate constants and liquid concentration respectively. The reaction constant for all lumps can be estimated from the Arrhenius equation as follows:

$$k_i = A_i \exp\left(\frac{-Ea_i}{RT}\right), \quad (18)$$

Where k_i is the lump reaction constant and Ea_i is the activation energy for each lump and the values which were reported in Table 1.

Table 1. Lump reaction constants and activation energy values for various lumped products and reactants [9]

Reactant and Product Lumps	Lump reaction constant (hr ⁻¹)	Activation energy (KJ/mol)
Triglycerides (Tg)	31.97 * 10 ²	26
Lighter Hydrocarbons (LC)	62.62 * 10 ⁵	83
Middle Hydrocarbons (MC)	4.2 * 10 ¹⁰	127
Heavy Hydrocarbons (HC)	13.73 * 10 ⁴	47
Oligomerized Hydrocarbon (OC)	14.58 * 10 ⁴	47

In addition, the production yield of each lump during hydro-cracking is calculated according to the following formula:

$$\text{Yield} = \frac{\text{Mass Of Each Lump}}{\text{Mass Of Triglycerides}} * 100\% \quad (19)$$

Energy balance equation for the reaction bed

For liquid phase:

$$m_g C_p^l \frac{\partial T_L}{\partial z} = \sum r_i \Delta H_i A_c - h_G a A (T_g - T_l) - 2\pi r_{in} \varepsilon h_l (T_w - T_l), \quad (20)$$

For gas phase:

$$m_g C_p^g \frac{\partial T_g}{\partial z} = h_G a A (T_g - T_l) - 2\pi r_{in} (1 - \varepsilon) h_l (T_w - T_g), \quad (21)$$

Where m_g , C_p^l , T_L , T_g , T_w , h_G , ε , h_l and ΔH_i are mass flow-rate, specific heat of liquid phase, liquid temperature, gas temperature, reactor wall temperature, gas heat transfer coefficient, bed porosity, liquid heat transfer coefficient and enthalpy of reaction for each lump, respectively. Also the calculation of the enthalpy of each lump reaction is shown:

$$\Delta H_i = \sum_{\text{Pr oducts}} \Delta H_p - \sum_{\text{Re ac tan ts}} \Delta H_r, \quad (22)$$

Here ΔH_p and ΔH_r are the enthalpy of all products and reactants respectively, which are triglyceride and hydrogen.

Energy balance equation for the tube of the reactor

$$K \frac{\partial^2 T}{\partial z^2} + K \cdot \frac{1}{r} \frac{\partial}{\partial r} \left(\frac{\partial T}{\partial r} \right) = 0, \quad (23)$$

Boundary conditions:

$$\text{At } r = r_{out} \quad -K \frac{\partial T}{\partial r} = h_{out} (T - T_{amb}), \quad (24)$$

$$\text{At } r = r_{in} \quad -K \frac{\partial T}{\partial r} = h_{in} (T - T_f), \quad (25)$$

$$\text{At } z = 0 \text{ \& } z = L \quad \frac{\partial T}{\partial z} = 0, \quad (26)$$

Where T_{amb} and T_f are the ambient and fluid temperature respectively and h_{in} and h_{out} are the heat transfer coefficients inside and outside of the reaction side of the reactor.

Gas-liquid mass transfer coefficient

The correlation for the estimation of the gas-liquid mass transfer coefficients are [23]:

$$\epsilon j_D = \frac{0.765}{\text{Re}^{0.82}} + \frac{0.365}{\text{Re}^{0.386}} \quad (27)$$

$$j_D = \frac{Sh}{\text{Re} \cdot \text{Sc}^{1/3}} \quad (28)$$

$$Sh = \frac{K \cdot d_p}{D_{AB}} \quad (29)$$

Here ϵ , D_{AB} , Sh , Re and Sc are porosity, molecular diffusion, Sherwood, Reynolds and Schmidt numbers respectively.

Molecular Diffusivity

In order to determine the gas-liquid mass transfer coefficient, it is essential to calculate the molecular diffusivity of each lump and hydrogen in the liquid and gas. The diffusivity was determined by the Fuller correlation [28].

$$D_{AB} = \frac{1 \times 10^{-8} \cdot T^{1.75} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{0.5}}{P \left[\left(\sum_A v_i \right)^{1/3} + \left(\sum_B v_i \right)^{1/3} \right]^2}, \quad (30)$$

Where P , M_i and v_i are the total pressure, molecular weight of each lump and the specific volume of each lump respectively.

2.4. Numerical Solution

To solve these sets of partial differential equations, the mass and energy balance equations were discretised and solved simultaneously using the Gauss-Seidel iteration technique [29, 30]. The numerical algorithm is illustrated in Figure 3. According to the algorithm, the input parameters such as feed temperature, pressure, flow-rate and H₂/feed ratio are specified. Initially, distribution of temperature and lump concentrations assumed along the reactor. Conservation equations for energy and mass balances were discretised and solved simultaneously using modified Gauss-Seidel iteration method to determine the temperature and concentration distribution along the reactor. This process continued until convergence was reached. The output of the model provides the lump concentration and temperature distribution along the reactor. The catalyst specifications and

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operating conditions that were applied in the model are listed in Table 2. Three major lumps of LC, MC and HC were the targets as products for the model validation and optimisation. The model sensitivity analysis were performed and reported after model validation.

Table 2. The operating condition and catalyst specifications chosen for the simulation of the hydro-cracking reactor [9]

Catalyst	4% CoO, 16%MoO₃, 1%P₂O₅ on γ-Al₂O₃
Catalyst mass	2 g
Catalyst volume	2.4 ml
Catalyst shape	Powdered
Feed inlet temperature	380°C
Reactor pressure	80 bar
LHSV	8 hr ⁻¹
H₂/Feed ratio	1500
Reactor heat load	1000 W/m ²

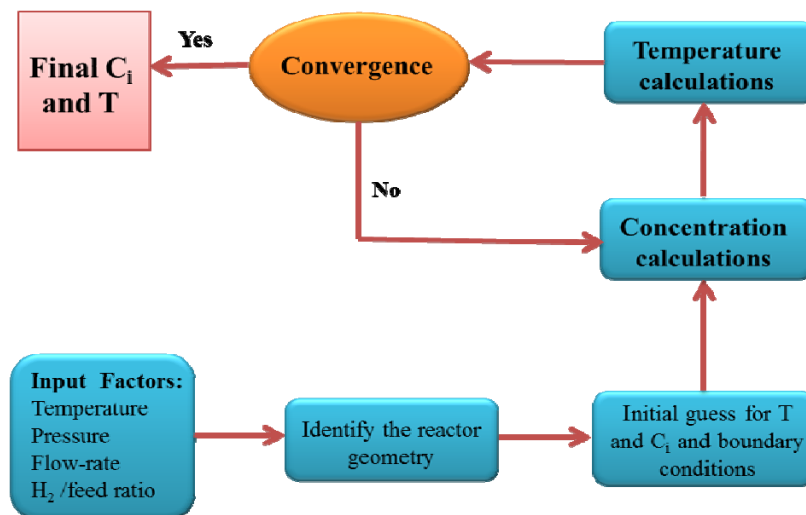


Figure 3. Numerical algorithm which was applied in the hydro-cracking reactor model

3. Model Validation

Validation was required to evaluate the accuracy and validity of the mathematical model. Validation of the model was performed using the experimental data reported by Anand and Sinha (2012) [9]. For validation, the model was run with A7 reaction kinetic model at different temperatures. The product lumps of LC, MC, HC and OC were considered as major products. The reactor model based on A7 kinetic model was compared to the experimental data in terms of yields versus temperature (Table 3). To obtain the validation results, the reactor model was run with a fixed temperature. For all major product lumps, the kinetic model has a good agreement with experimental data in term of the average deviation from experimental data. The average errors of the applied kinetic model in the reactor model was 26.6% for the LC lump, 8.2% for the MC lump, and 2.8% the for HC lump. According to previously reported literature for reactor modelling [29-32], the aforementioned error values show good agreement of the kinetic model to reality.

Table3. Experimental products yield of LC, MC and HC Vs. A7 kinetic model

Temperature	Experimental data	A7 kinetic model
Low Hydrocarbon production yield (LC)		
300	0.081	0.172
340	0.572	0.5856
360	0.873	0.9218
380	1.715	1.461
Middle Hydrocarbon production yield (MC)		
300	0.083	0.112
320	0.473	0.7026
340	2.092	1.5006
360	3.994	2.8758
Heavy Hydrocarbon production yield (HC)		
320.00	50.23	49.8936
340.00	37.07	40.8451
360.00	72.47	71.8153

4. Results and Discussion

The hydrocracking reactor was situated in a furnace to control the reactor temperature by a constant heat-flow. A constant heat flux along the reactor surface was assumed in the model and hydrogen with a specific ratio, which is reported in Table 2, was injected to the reactor. The applied parameter of X/L_0 is the dimensionless form of the reactor length. In this section, the performance of the reactor is investigated with sensitivity analysis on feed inlet temperature, reactor length and reactor heating load.

4.1. Effect of feed inlet temperature

Temperature profile of components in liquid phase and gas phase and the reactor wall temperature along the reactor are shown in Figure 1. The gas phase (Hydrogen) enters the reactor at the bottom of the reactor and in counter current mode with liquid (Triglyceride) flow. So the gas phase temperature, at the various feed inlet temperatures, increases linearly along the reaction bed. The gas phase temperature also increased linearly along the reactor because the gas physical properties remain constant between 380 °C and 520°C. At the inlet temperature of 450°C, the highest heat was absorbed in the gas phase and this lead to highest temperature increment, 66.6°C, from the entrance to the end of the reactor. In the liquid phase (Triglyceride and Lump products), for all inlet temperatures, a rapid increase occurred for all feed inlet temperatures because of low liquid flow-rate and quick heat absorption at the beginning of the hydro-cracking endothermic reactions but after that the liquid temperature is decreasing linearly along the reactor due to decrease in triglyceride concentration along the reaction bed. The absorbed heat in 380°C is higher than other feed inlet temperatures' demonstrating that at inlet temperature of 380°C, more energy is needed for activation of hydrocracking reactions than other inlet temperatures. The reactor wall transfers the heat flow to the reaction bed, so the temperature range is larger than the liquid and gas phase temperature profile due to the difference in the heat transfer coefficients of reactor wall, liquid and gas phase. In the section 'c' of Figure 4, the temperature variations of reactor wall temperature for all feed input temperatures are the same.

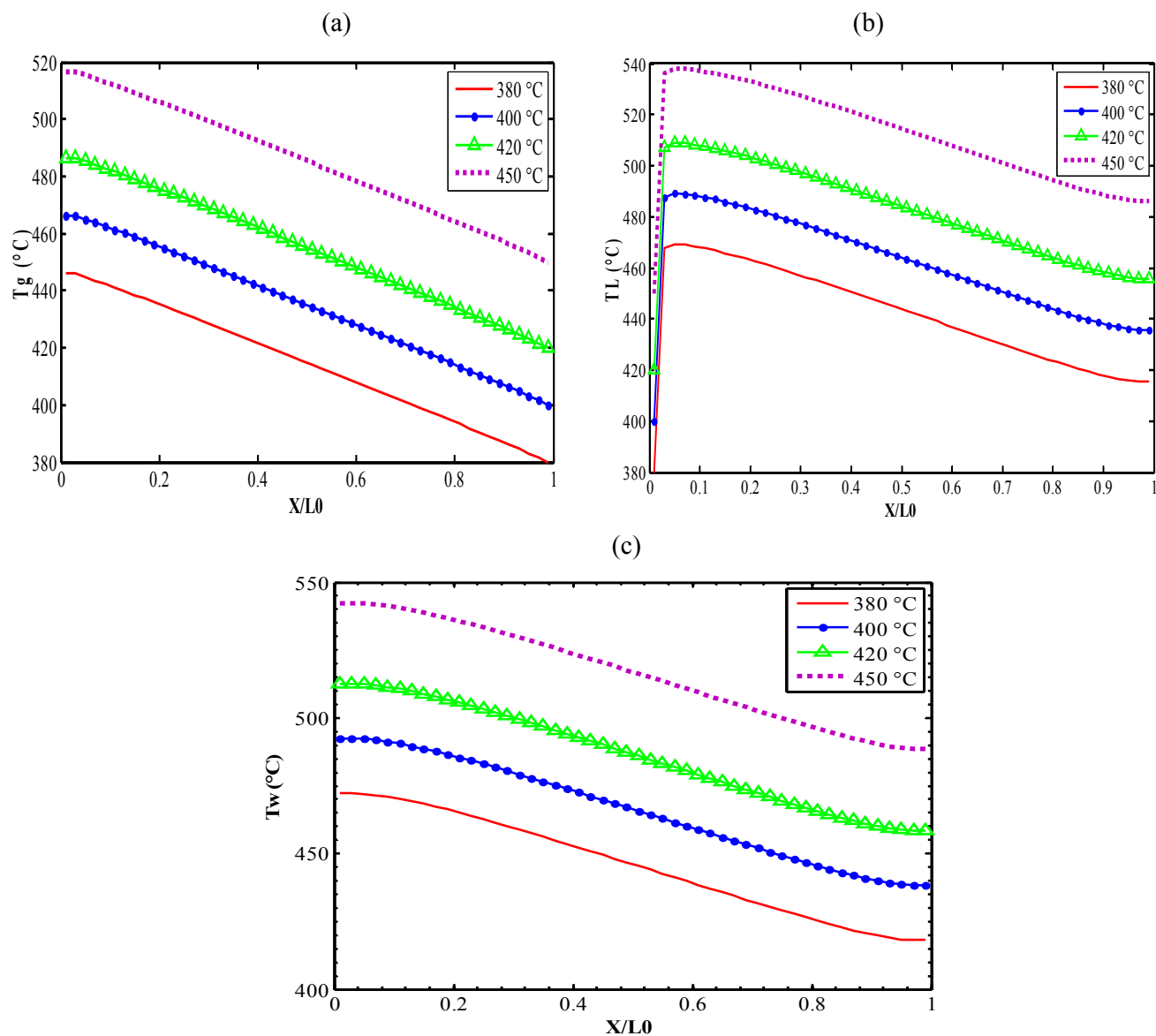


Figure 4. The liquid (a), gas (b) and reactor wall (c) temperature profile along the reactor in various feed inlet temperatures

The triglyceride, light hydrocarbons (LC) and heavy hydrocarbons (HC) mole fractions along the reactor with different feed input temperatures are shown in Figure 5. At input feed temperature of 450°C, more than 97% of triglyceride was converted in the hydrocracking reactor; and with increasing the inlet feed temperature, the conversion of triglyceride to

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products increased. As shown in section (a) and (b) of Figure 4, changing feed input temperature from 380°C to 450°C increased the triglyceride conversion about 8%. The mole fraction of light (LC) and middle (MC) hydrocarbons, as target products of hydro-cracking reactions towards light and middle hydrocarbon fuels such as gasoline and jet fuel, show that in higher feed inlet temperatures more light and middle hydrocarbons are produced.

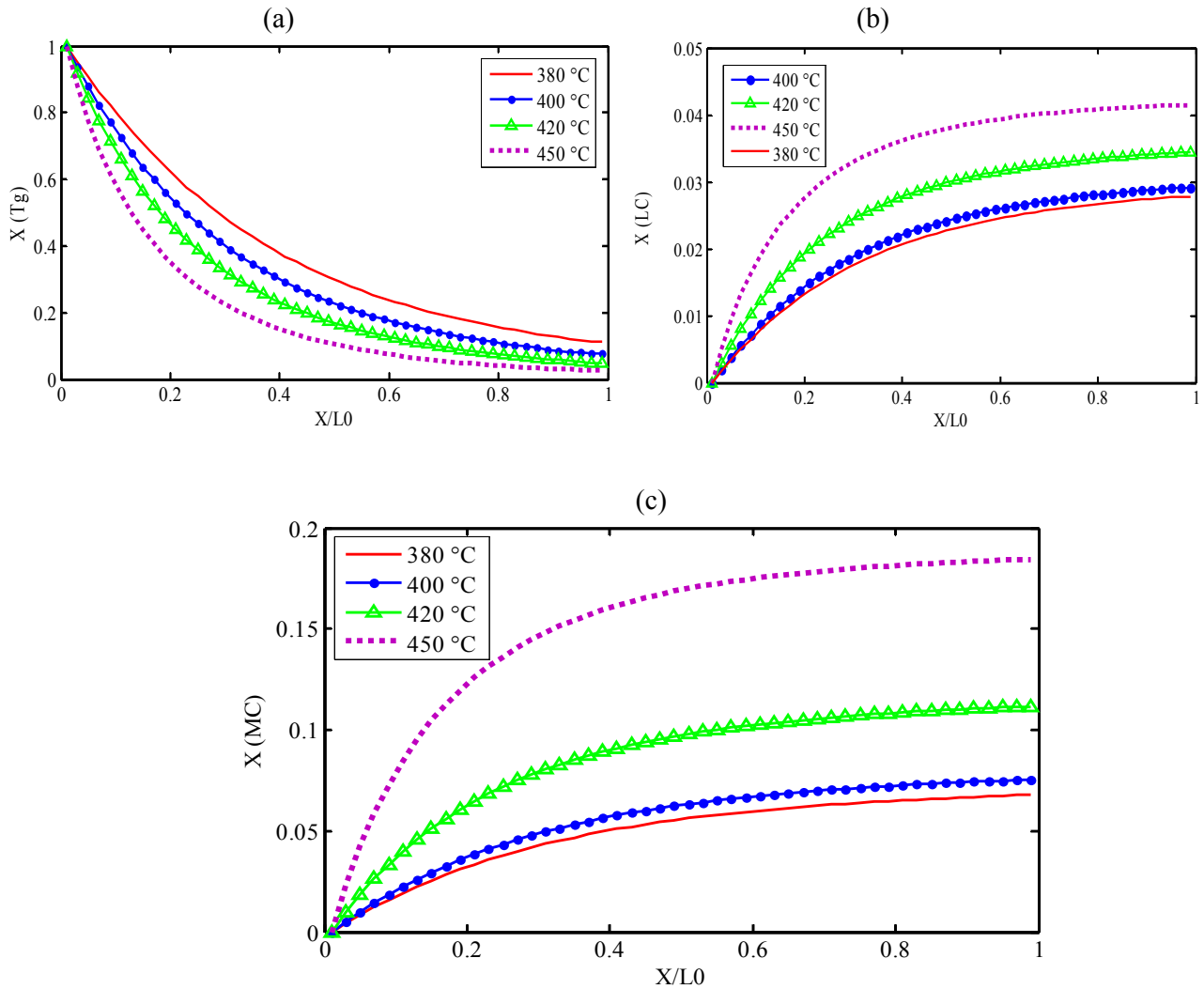
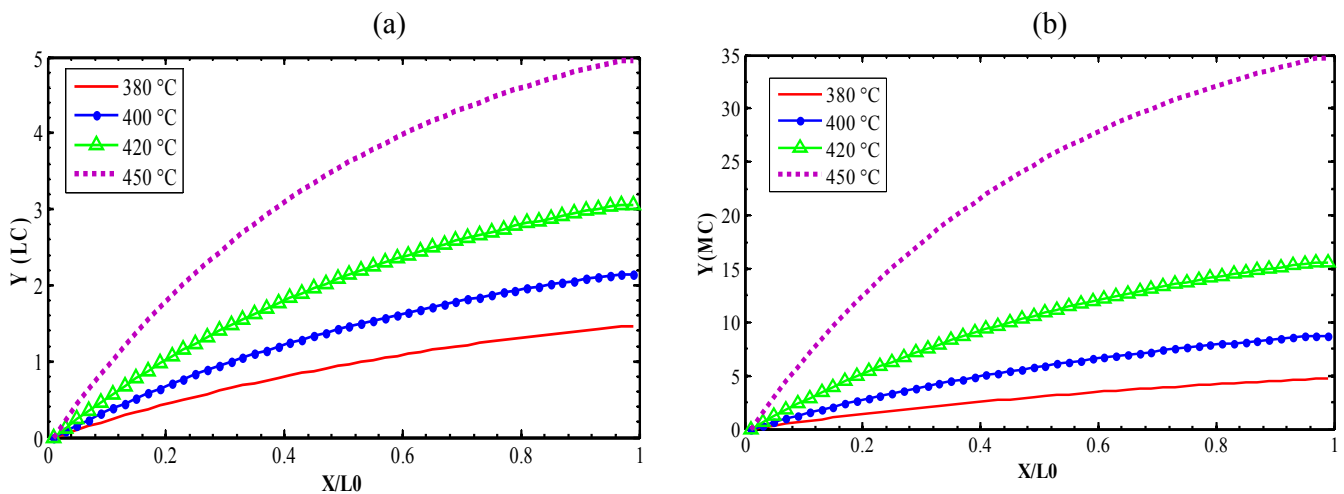


Figure 5. The Triglyceride (TG) (a), Light Hydrocarbons (LC) (b), and Middle Hydrocarbons (MC) (c) mole fraction along the reaction bed

The major lumps production yields are reported and shown in Figure 6. The production yield of light hydrocarbons (LC) and middle hydrocarbons (MC) increased with higher feed inlet temperatures; for example between temperatures 420°C and 450 °C, the increase in LC and MC yields of production were 38.3% and 55.04% respectively, but for heavy hydrocarbons (HC) lump, the story is different. The HC lump product yield decreased with higher inlet feed temperatures demonstrating that in the first 3 cm of the reactor ($X/L0 = 0.1$) the production yield of HC for all inlet feed temperatures were the same (Figure 6, section ‘C’) but after that point, HC is converted to LC and MC because of the higher temperature profiles along the reaction bed (Figure 4) and this led to more activation in hydro-cracking reactions along the reactor. The HC yield production is decreased 29.7% from temperature of 380°C to 450°C.



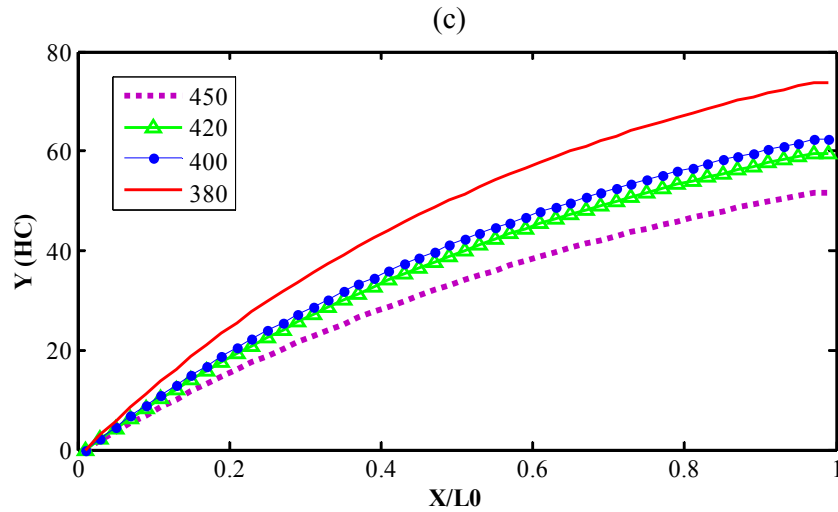


Figure 6. The Light Hydrocarbons (LC) (a), Middle Hydrocarbons (MC) (b), and Heavy Hydrocarbons (HC) (c) yields along the reaction bed

The inlet feed temperature of 450°C is the optimal inlet temperature to maximise the major lump products, which were LC (gasoline range of hydrocarbon) and MC (jet-fuel range of hydrocarbons) and minimise the HC lump product (diesel range of hydrocarbons).

4.2. Effect of reactor heat flow

Temperature profiles of liquid, gas and reactor wall along reaction bed in different reactor heat flows are shown in Figure 7. The reactor heat flows varied from 500-1500 W/m². The gas phase, liquid phase and reactor wall temperature profiles increased with higher reactor heat flows. The temperature variation for liquid phase which was the major part of hydrocracking reactions, was due to the gas phase and reactor wall

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temperature increasing with elevated reactor heat flow. For instance, with a heat flow of 1500 W/m^2 , the temperature variations for the gas and reactor wall were 99.6°C and 81.7°C respectively but these variations for heat flow of 500 W/m^2 are 32.6°C and 26.7°C respectively. Also for the liquid phase temperature profile, temperature increases quickly at the beginning of the reactor and then decreased slowly for all heat flow ranges. However, the temperature variations from the reactor entrance to the maximum point for heat flow of 1500 W/m^2 and 500 W/m^2 were 134.4°C and 43.4°C respectively.

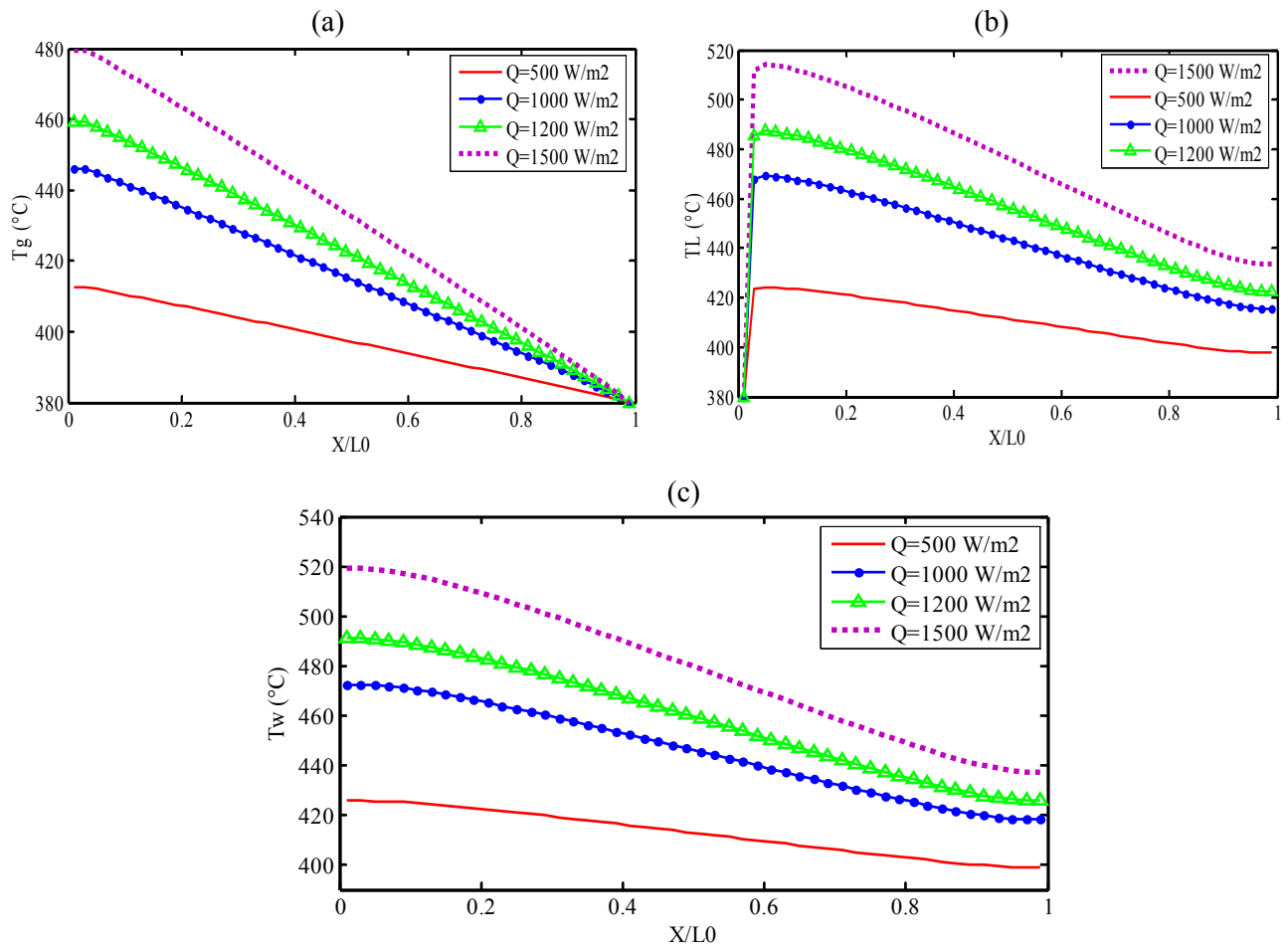


Figure 7. The liquid (a), gas (b) and reactor wall (c) temperature profile along the reactor in various reactor heat flows

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The calculated sensitivity of mole fractions of triglyceride (TG), light hydrocarbons (LC) and middle hydrocarbons (MC) to the variations in Q along the reactor are shown in Figure 8. The mole fraction variations for reactant and major lump products at various reactor heat flows were low. In details, more triglyceride was consumed and additional LC and MC were produced at higher reactor heat flows. The variation in major lump products LC and MC from the lowest heating value, 500 W/m^2 , to the highest heating value, 1500 W/m^2 , was low and the increase with LC and MC production were 7.35% and 7.33% respectively.

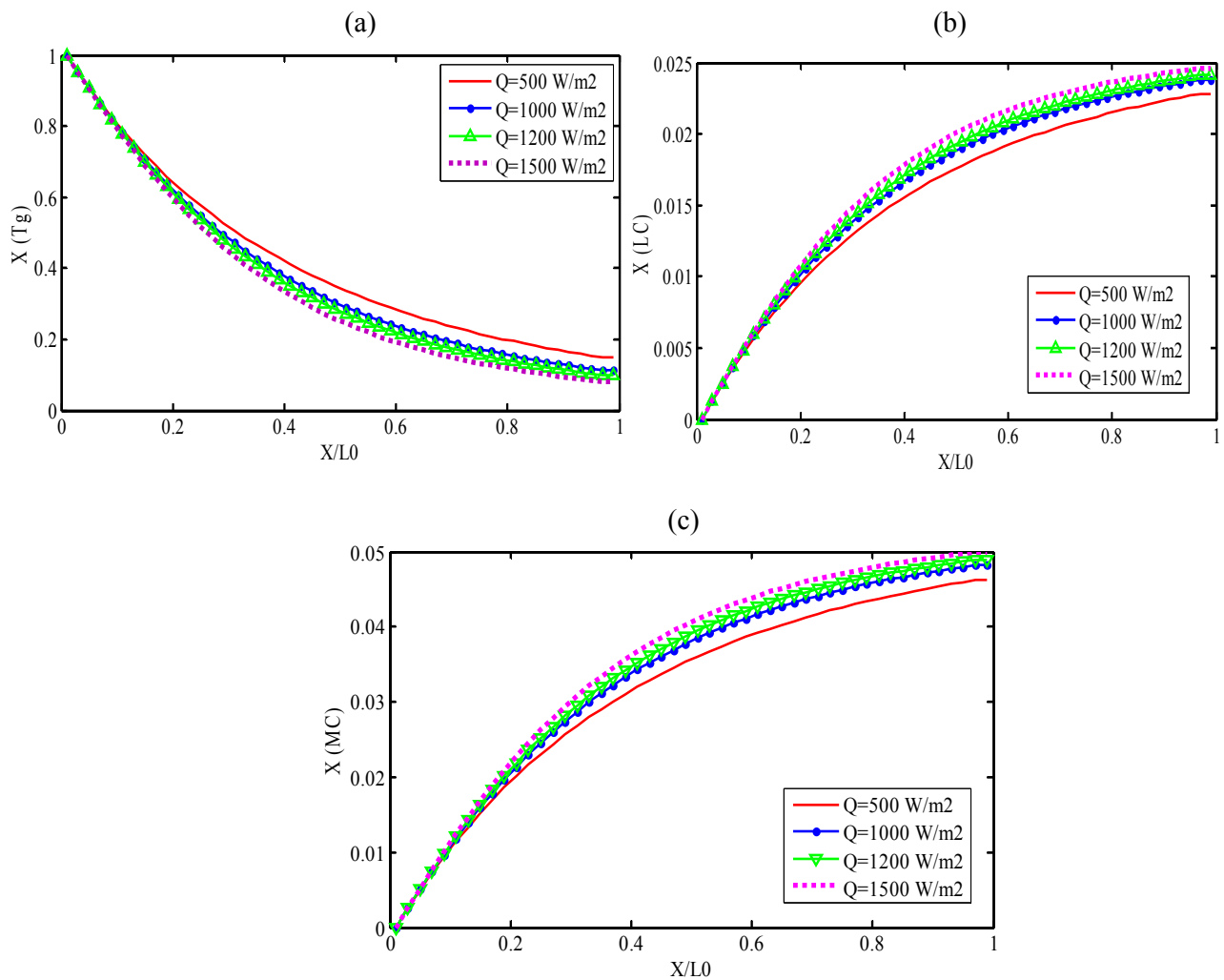


Figure 8. The Triglyceride (TG) (a), Light Hydrocarbons (LC) (b), and Middle Hydrocarbons (MC) (c) mole fraction along the reaction bed in various reactor heat flows

Therefore, applying higher heating values lead to about 7% increase in major lump productions which was negligible. Applying a minimum heating value of $\sim 500 \text{ W/m}^2$, a significant amount of LC and MC could be produced providing energy savings as consumption for hydro-cracking reactions would be reduced.

4.3. Effect of reactor length

The effect of the hydrocracking reactor length on liquid and gas was investigated, shown in Figure 9. The gas and liquid temperature profiles varied increasingly with higher reaction bed lengths because with longer reaction beds, hydrocracking reactions continue along the reactor until exhausting the reactants. Moreover, because of the endothermic nature of hydrocracking reactions, more energy and heat should be absorbed to activate the hydrocracking reactions and more reactions take place inside the reaction bed with higher reaction bed lengths, so that temperature variation of the gas phase was growing with larger reactor length values. In the liquid phase (the reaction phase) the temperature profile procedure is the same with gas phase temperature profile. The maximum liquid phase temperature increased with the reactor length enhancement. The increase of

the maximum temperature amount from the reactor length of 20 cm to 35 cm is 6.9% and it is increased from 447.2 °C to 480.4 °C.

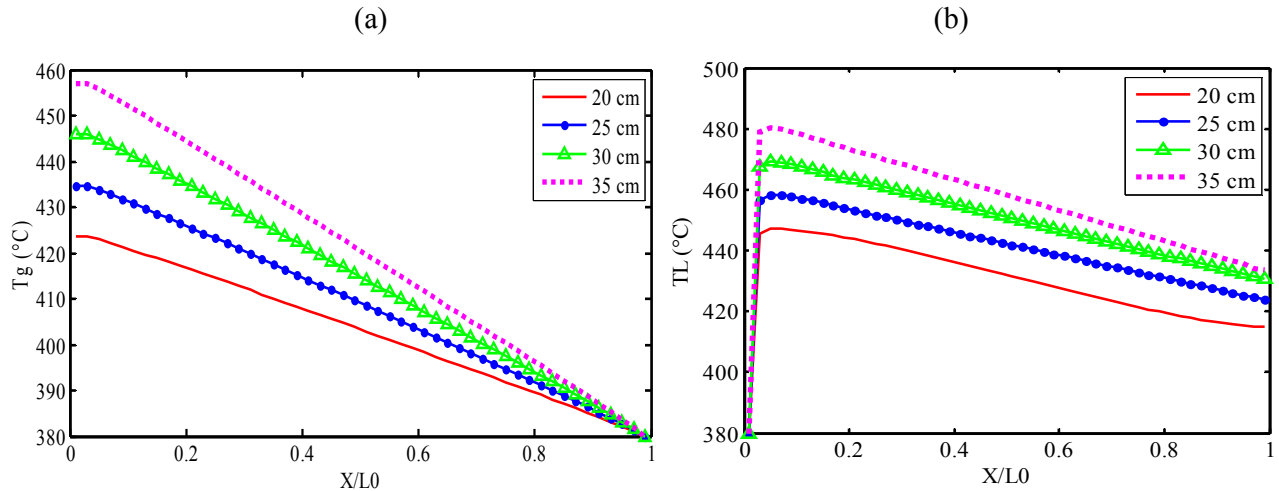


Figure 9. The liquid (a) and gas (b) temperature profile along the reactor in various reactor lengths

The mole fraction variations of triglyceride and main product lumps (LC and MC) in various reactor lengths are shown in Figure 10. With a longer reaction bed, the conversion of triglyceride was improved and more triglyceride was converted to products. The 15 cm increase in reaction bed length decreased the triglyceride mole fraction from 0.2378 to 0.07601. It means that increasing the reaction bed about 87.5% can lead to 68.03% improvement in triglyceride conversion and more hydrocracking reactions occur along the reactor. Also the 15 cm increase in reaction bed had a significant influence on LC and MC productions. The main LC and MC product lumps increased by 22.9% and 22.3% respectively by changing the

reaction bed length from 20 cm to 35 cm (87.5% increase of reaction bed length).

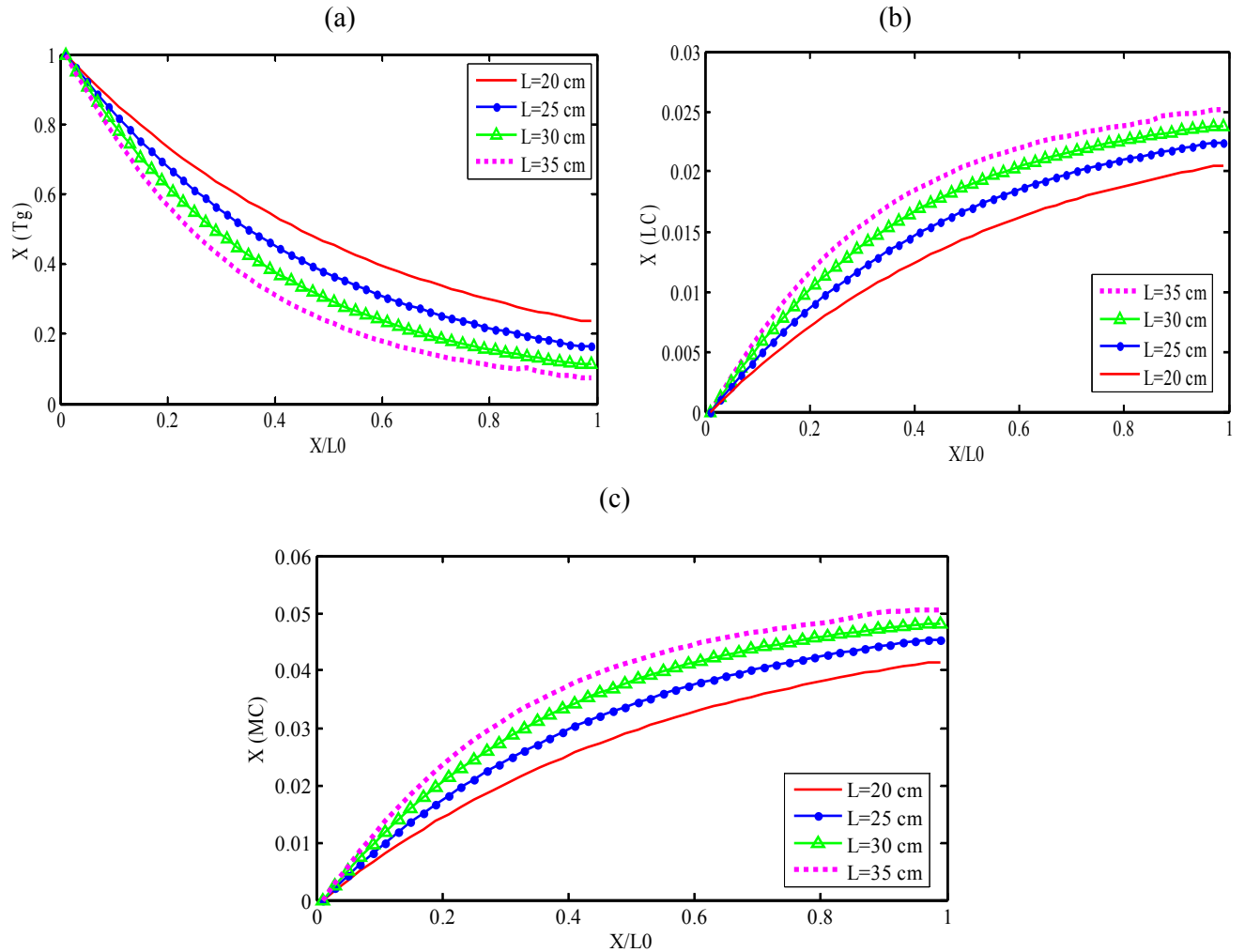


Figure 10. The Triglyceride (TG) (a), Light Hydrocarbons (LC) (b), and Middle Hydrocarbons (MC) (c) mole fraction along the reaction bed in various reaction bed lengths

The effect of reaction bed lengths on the yields of production LC, MC and HC lumps are presented in Figure 11. LC and MC lumps were the major products in the hydrocracking reactions, representing the gasoline

range of hydrocarbons and jet-fuel range of hydrocarbons respectively. LC and MC production yields were increasing with the length of reaction bed enhancement due to more hydrocracking reactions along the reactor. The increase of LC and MC production yields were 39% and 37.5% between reaction bed lengths of 20 cm to 35 cm.

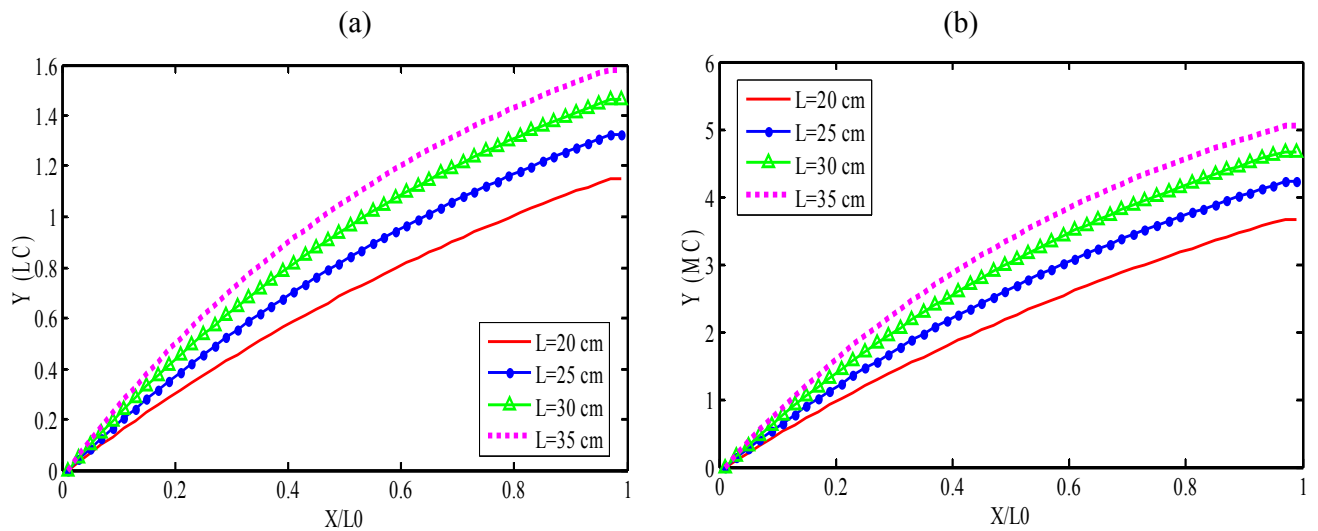
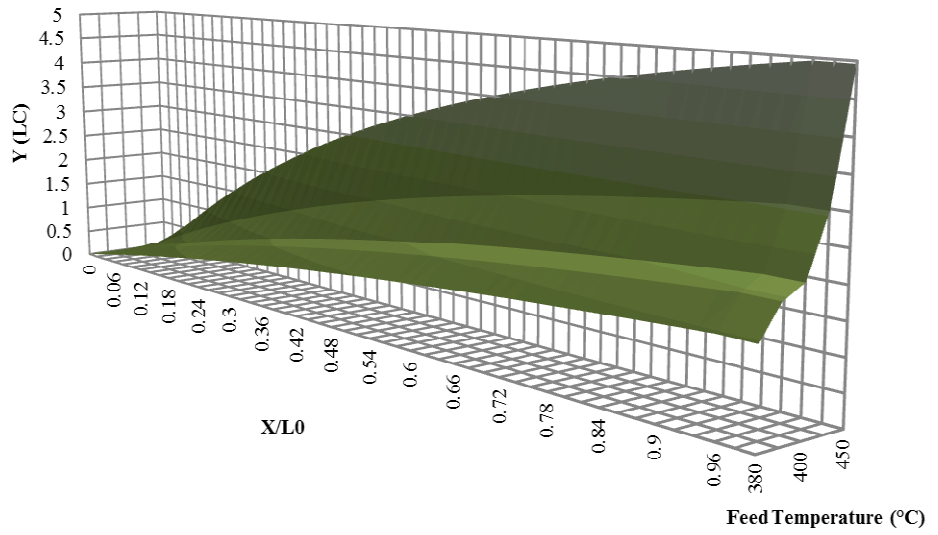


Figure 11. The yield of LC (a) and MC (b) lumps along the reaction bed in various reaction bed lengths

The yields of main product lumps that were LC and MC are plotted against feed inlet temperature and reaction bed length, as shown in Figure 12. The yields of LC and MC at the beginning of the reactor were higher with the feed inlet temperature increment supporting that with larger feed inlet temperatures, the hydro-cracking reactions were conducted to larger production rates of LC and MC lumps. Consequently, the reaction length of 35 cm was appropriate for the hydro-cracking reactions towards Tg and HC cracking to favorable lump products of LC and MC.

(a)



(b)

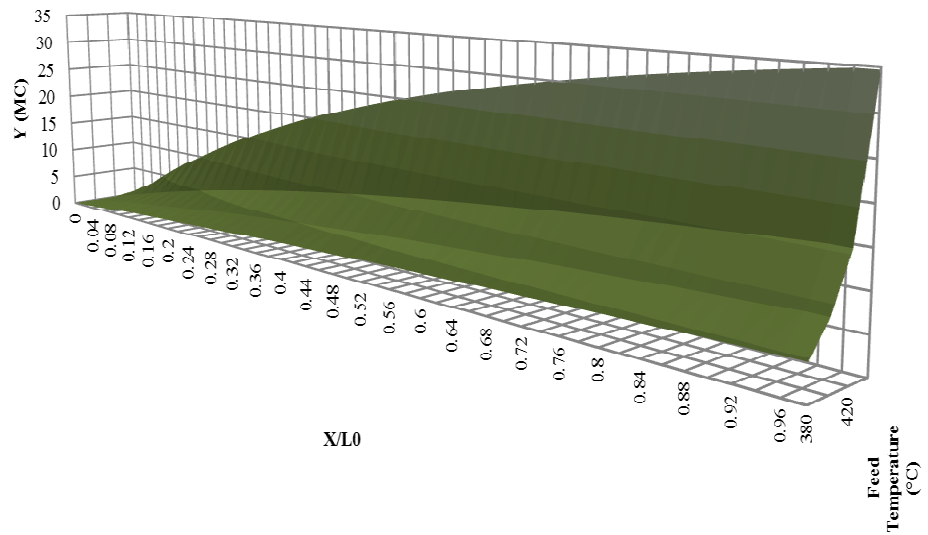


Figure 12. LC (a) and MC (b) yields of production versus reaction bed length and inlet feed temperature

5. Conclusion

In this research a non-isothermal heterogeneous model was considered to evaluate a triglyceride hydrocracking reactor. The modeled reactor was situated in a furnace with a constant heat flow to increase the reaction bed temperature. Triglyceride (Tg) and hydrogen (H_2) entered the reactor as reactants counter-currently and after reaction with the supported catalyst, three product lumps of hydrocarbons were produced, named light (LC), middle (MC) and heavy (HC) hydrocarbon product lumps. In the reported work, a model for hydro-cracking reactor was investigated and the performance of the reactor was analysed with a sensitivity analysis on the inlet feed temperature, the reactor heat flow and the reaction bed length. The result showed that 97% triglyceride conversion with increasing inlet feed temperatures from 380 °C to 450 °C was achieved. Moreover, the LC and MC production yields increased 38.3% and 55.04% respectively and HC lump yield decreased 15.19% between the input feed temperatures of 420°C and 450 °C. The input feed temperature of 450 °C was appropriate to maximise the production concentration of main lump products (LC & MC). The reactor heat flow analysis showed that high liquid, gas and reactor wall temperature variations along the reactor provided negligible increases in LC and MC production rates. Therefore, the heat flow of 500 W/m^2 was found to be appropriate to conserve energy for hydrocracking reactions and obtain significant production rates for LC and MC. The reaction bed length analysis demonstrated that with higher bed lengths, more LC and MC were produced and the reaction bed length of 35 cm was

appropriate for hydrocracking reactions in the micro-scale trickle bed reactor. Without any doubt, the modeling of the hydro-cracking reactor can open the scaling up insight for bio-fuel production.

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CHAPTER 5

Catalytic Conversion of Oleic Acid in Bio-oil to Liquid Hydro-carbon Fuels

CHAPTER 5

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Author Contributions

By signing the Statement of Authorship, each author certifies that their stated contribution to the publication is accurate and that permission is granted for the publication to be included in the candidate's thesis.

Name of Principal Author (Candidate)	Amir Ahmad Forghani	
Contribution to the Paper	Developed ideas, Performed simulations and calculations, interpreted data, wrote the manuscript and acted as corresponding author.	
Signature		Date: 20/10/2014

Name of Co-Author	Phillip Pendleton	
Contribution to the Paper	Supervised development of the work, helped in developing ideas, data interpretation and manuscript evaluation.	
Signature		Date: 20/10/2014

Name of Co-Author	Akshat Tanksale	
Contribution to the Paper	Supervised development of the work, helped in experimental works, data interpretation and manuscript evaluation.	
Signature		Date: 17.10.14

Name of Co-Author	David Lewis	
Contribution to the Paper	Supervised development of the work, helped in developing ideas, data interpretation and manuscript evaluation.	
Signature		Date: 20/10/14

Catalytic Conversion of Oleic Acid in Bio-oil to Liquid Hydrocarbon Fuels

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Abstract

In this research, catalytic conversion of oleic acid as main component of the plant-based oils was performed over nickel based catalysts. Two cheap and famous supports named ZSM-5 and Zeolite β were selected and impregnated with Ni (NO₃)₂.6H₂O and calcined in 500 °C. These two types of inexpensive catalysts were characterised with nitrogen adsorption, SEM and SEM-EDX to analyse the nickel impregnation and measure the surface area and pore size distribution. Conversion rates and product yields of each catalyst sample were determined in hydro-cracking reactions with temperature range of 300-450 °C and 30 Bar pressure. Both samples have a significant increase in oleic acid conversion between temperatures of 300 °C to 350 °C. Ni-Zeolite β has better oleic acid conversion in comparison with Ni-ZSM-5. Moreover, production yields of Nonane, Decane and Dodecane were analysed over the both catalyst samples.

Keywords: Ni-Zeolite based catalyst, Upgrading, Hydro-cracking, biofuel production.

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1. Introduction

In the recent century the consumption of fossil fuels has been increased dramatically and this lead to fossil fuel depletion and greenhouse gases enhancement in the atmosphere. Plant based oil such as micro-algae and vegetable oil and their biomass have been identified as a substitute feedstock instead of fossil fuel feedstock [1, 2]. Recently, bio-oil upgrading to applicable fuels becomes more highlighted due to low heating value, high viscosity and poor stability of crude bio-oil [3-5]. Esterification (solvent addition), Hydro-treating and hydro-cracking are three major existing processes for bio-oil conversion to fuels [6]. Esterification is the catalytic reaction between bio-oil and short chain alcohol as solvent such as methanol and ethanol and it is very popular in bio-diesel production but it needs a large amount of solvent [6, 7]. Hydro-treating is simple hydrogenation which has been applied in refineries to convert aromatics to naphthenes at temperatures above 500°C and atmospheric pressure but recently it is applied for bio-crude conversion over sulfided Co & Mo/Al₂O₃, Ni & Mo/Al₂O in order to remove oxygen from triglyceride [8, 9]. Hydro-treating yield is low and due to sulfided catalyst application, it produces a lot of char and coke in the process which can result reactor clogging and catalyst deactivation [6].

One of the recent upgrading methods is catalytic hydro-cracking of bio-oil to liquid hydrocarbon fuels [10-15]. Hydro-cracking is combination of different cracking reactions with hydrogenation in high temperatures (above 350°C) and high pressures (above 7 bar) [16, 17] over dual-function catalysts. Dual-function catalysts have a zeolite or silica alumina base which is provide the cracking function and metal oxides such as nickel, molybdenum which are catalysing the

reactions towards light hydrocarbons [6-8, 17-20]. Zeolitic catalysts are emerging as effective materials for efficient bio-oil hydro-cracking due to their high heating stability and strong acidity [7, 20, 21]. The main advantage of using hydro-cracking process is performing this process in one single step process which can consume less energy than other upgrading processes [7, 20, 22]. The overall goal of this study is investigating the hydro-cracking of bio-oil component over zeolitic catalysts to produce bio-fuels.

Most types of bio-oils have major oxygenated components such as oleic acid, stearic acid, linoleic acid and palmitic acid. These oxygenated components in bio-oil cause high viscosity, poor thermal and chemical stability, and corrosive nature of hydrocarbon bio-fuels [9, 23]. Therefore, the oxygen in the oxygenated compounds should be removed by deoxygenation process. Two deoxygenation methods are existed named hydro-deoxygenation and decarboxylation [24, 25]. In the first method, the oxygen molecule is removed in the form of water but in the second method, oxygen is converted to CO₂. Hydro-deoxygenation which is a main cracking reaction in hydro-cracking, has a significant efficiency to remove oxygen from oxygenated components [26]. Some research attempts had been done to perform the deoxygenation over sulfided catalysts with zeolite and alumina support [9, 20, 27-29] but applying sulfided catalysts such as Ni & Mo and Co & Mo supported on meso-porous zeolite or γ -Al₂O₃ support needed pre-sulfidation process with H₂S or dimethyl-disulfide due to catalyst activation before hydro-processing [20, 25]. The sulfur in the catalyst structure is caused bio-oil contamination and catalyst deactivation [6, 29]. The main advantage of deoxygenation in hydro-cracking is improving yields of straight chain of alkanes

after the isomerisation reaction [30]. Moreover, several researches have been performed based on hydro-cracking over non-sulfided catalysts with base of zeolite or Al_2O_3 and metal oxide function such as Ni, Pd and Pt [26, 31-33]. Among different metal oxides, application of nickel on zeolitic structures is cost effective and efficient in hydro-processing of oxygenated compounds in bio-oil. Therefore, in this presentation two types of inexpensive non-sulfided Ni-based bi-functional catalysts are introduced characterised and then analysed in hydro-cracking reactor. Temperature, residence time, and catalyst structure are investigated as effective parameters on reaction conversion and production yield.

2. Materials & Methods

2.1. Catalyst preparation

Ni/ZSM5 and Ni/ β -Zeolite were prepared with conventional impregnation method. ZSM-5 and β -Zeolite were purchased from ACS Materials Company and Zeolyst International respectively (with $\text{SiO}_2/\text{Al}_2\text{O}_3$ Molar Ratio of 38 for both of them) and then the impregnation of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma Aldrich) solution on ZSM-5 and β -Zeolite supports was performed. The supports were mixed with the nickel impregnation solution and after stirring for 2 hours, it was dried in the oven and then calcined in the furnace with starting temperature increase of $10^\circ\text{C}/\text{min}$ to 500°C and keep this temperature for 5 hours.

2.2. Characterisation of catalyst

2.2.1. Nitrogen adsorption isotherm measurements

Nitrogen gas adsorption experiments were carried out at 77 K using a Belsorp-Max automated manometric gas adsorption apparatus. Samples were degassed prior to the experiments at 300 °C and a background vacuum of 0.1 MPa for 4 hours. Ultra high purity (99.999%) helium and nitrogen from BOC Gases Australia were used for dead-space measurements and adsorption experiments respectively.

2.2.2. Scanning electron microscopy (SEM) assisted with energy dispersive X-ray analysis (EDAX)

SEM-EDAX analysis was carried out to investigate the morphology of the catalyst surface and also to analyse the atomic composition on the examined surface. SEM analysis was made by using a Philips XL- 20-FEG microscope with an accelerating voltage of 5 kV, equipped with an energy dispersive X-ray spectrometer (EDXS) analyser (Adelaide Microscopy, model 6587). Specimens were prepared by gold sputtering of catalyst samples deposited as powders on aluminium pin flat stubs.

2.3. Hydro-cracking Reaction

To analyse the prepared catalyst structures in hydro-cracking reactions, a commercial micro-scale trickle bed reactor (Autoclave Engineers' BTRS-Jr) was applied. For each run of the reactor, one gram (1 gr) of catalyst was weighted and then loaded in the stainless steel tubular reactor with the inside diameter of 1.2 cm and the catalytic bed of 20 cm. The reactor was situated in a furnace to run in high temperatures. Hydrogen pressure was controlled by a back pressure regulator. An

HPLC pump was used to pump the liquid in to the reactor and maintained the liquid flow through the catalyst bed. Oleic acid was selected as a feed because it is one of the main components of plant based oil special micro-algae oil. The oleic acid percentage in algae oil is varying from 39-60% [20, 34]. Oleic acid was injected with large volume of hydrogen in the reactor and after passing through catalyst bed, the products, unreacted reactant and excess hydrogen passed through separator and liquid samples were obtained from the bottom of the separator. The schematic of hydro-cracking lab-scale process is shown in figure 1. Furthermore, the hydrocracking reactions were performed in different reaction bed temperatures and the mentioned operating conditions in table 1.

Table 1. Catalyst loading and operating conditions

Catalyst mass	1 g
Catalyst shape	Powder
Bed length	10 cm
Reactor diameter	1.01 cm
Reaction temperature range	300-450 °C
Reaction pressure	30 Bar
Oleic acid flow	0.1 ml/min
Hydrogen/Feed	1000 NI/1

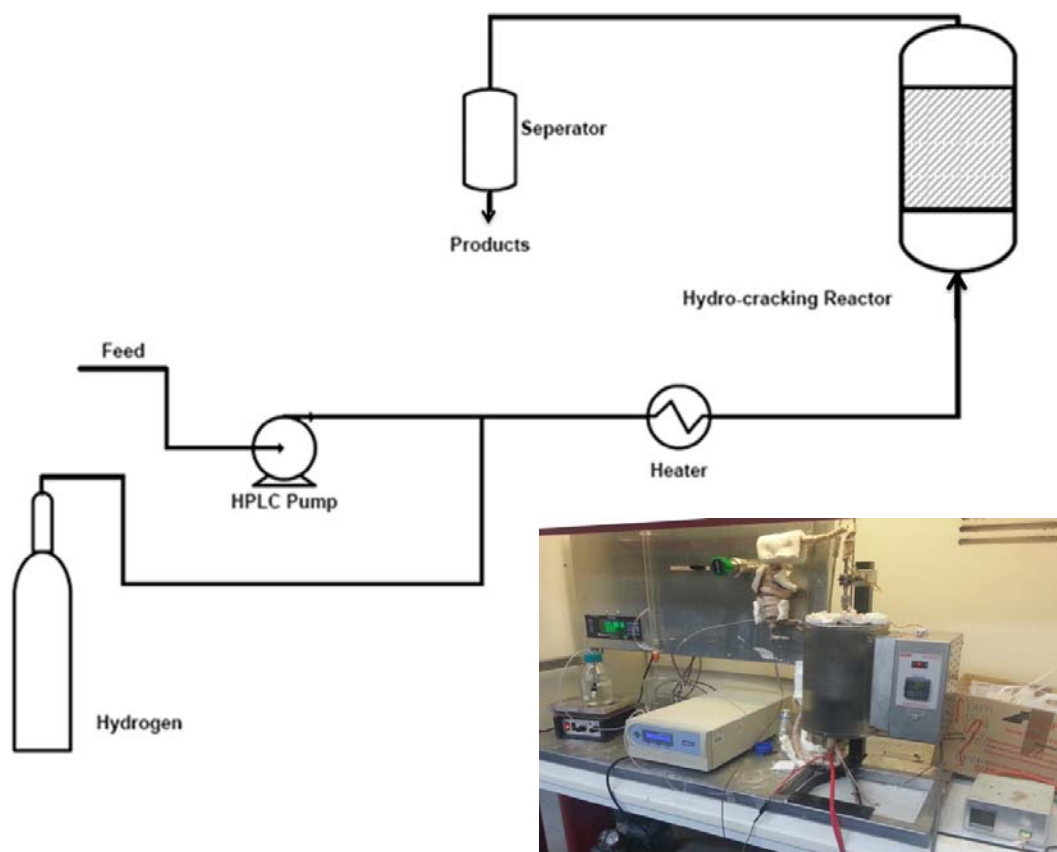


Figure 1. Hydro-cracking lab-scale set up to analyse the prepared catalyst

2.4. Product Analysis

The product samples were collected at the end of separator and they were analysed with gas chromatography (GC) machine (Shimadzu GC2010 with a flame ionization detector (FID)) and a Varian 3800-GC column, 30 m, 0.25 mm, 0.1 μm , was applied for product analysis. Helium was selected as carrier gas with high purity. Nonane (C_9), Decane (C_{10}) and Dodecane (C_{12}) were purchased from Sigma Aldrich as standard samples to analyse and measure the outlet products of hydro-cracking reactions. C_9 , C_{10} and C_{12} are the main components of jet-fuel and by using them as standard samples, a calibration curve in different concentrations

were identified to measure the yields of C₉, C₁₀ and C₁₂ for each catalyst. The GC analysis was performed for all samples under a certain conditions, FID temperature was 200°C and the oven temperature program was increased from 50°C to 150°C at the rate of 10°C/min and then from 150°C to 200°C at the rate of 15°C/min. The performance of each type of catalyst was evaluated based on their efficiency towards the oleic acid conversion and yield of jet fuel range of hydrocarbons. Conversion and yields of C₉, C₁₀ and C₁₂ were calculated with the calibration curve data of the feed (oleic acid) and product which were defined with the following equations:

$$\text{Conversion (\%)} = \frac{\text{Mass of oleic acid in the feed (g)} - \text{Mass of oleic acid in the product (g)}}{\text{Mass of oleic acid in the feed (g)}} \quad (1)$$

$$\text{Yield of hydrocarbon (wt. \%)} = \frac{\text{Mass of hydrocarbon in the product (g)}}{\text{Mass of feed (g)}} \quad (2)$$

3. Results & Discussions

3.1. Catalyst Characterisation

Figure 2 shows scanning electron microscopy images of Ni-Zeolite β (a) and Ni-ZSM-5 (b) catalysts. In Figure 1 particles are shown as grey rectangular structures agglomerated in some areas. Black field corresponds to inter-particle spacing and bright white spots correspond to impregnated Ni on catalyst surface. Images clearly show presence of Ni agents on the surface of both catalyst

samples. To make sure bright white spots are impregnated nickel, energy dispersive X-ray spectroscopy (EDXS) test is ran over the random selected bright white spots. The average spectrum is shown in Figure 3. Nickel has K and L emission energy rates of 7.477 and 0.851 keV, respectively. Figure 3 (a) shows two pronounce peaks for Ni at corresponding Ni energy rate for Ni-Zeolite β . Figure 3 (b) also shows a single peak at K energy rate of Ni. Analyses of EDXS results together with electron microscopy images confirm presence of nickel on the catalyst surface.

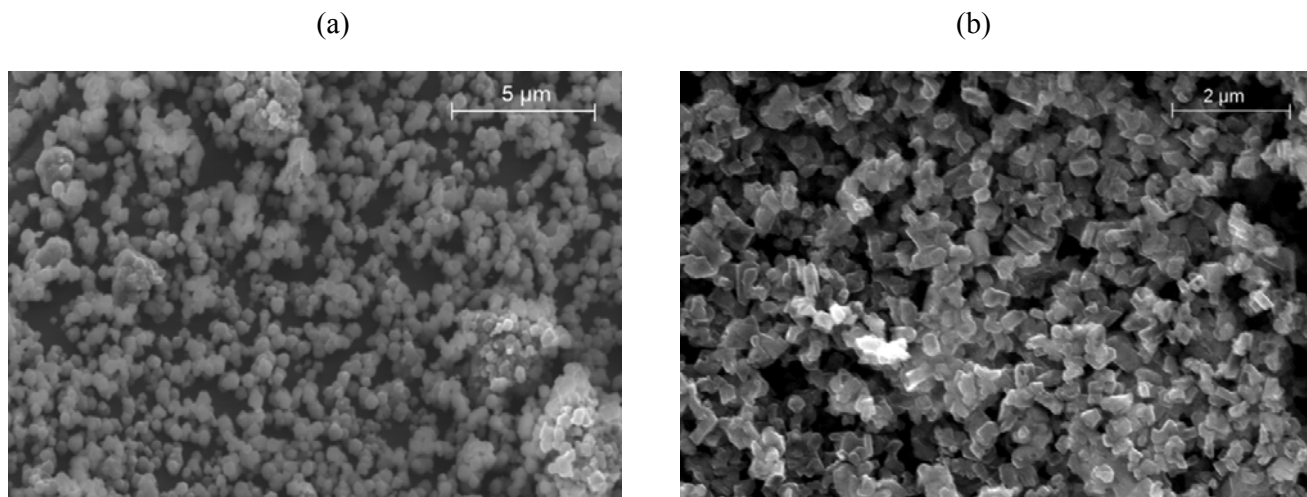


Figure 2. Scanning electron microscopy (SEM) images of Ni-Zeolite β (a) and Ni-ZSM-5 (b)

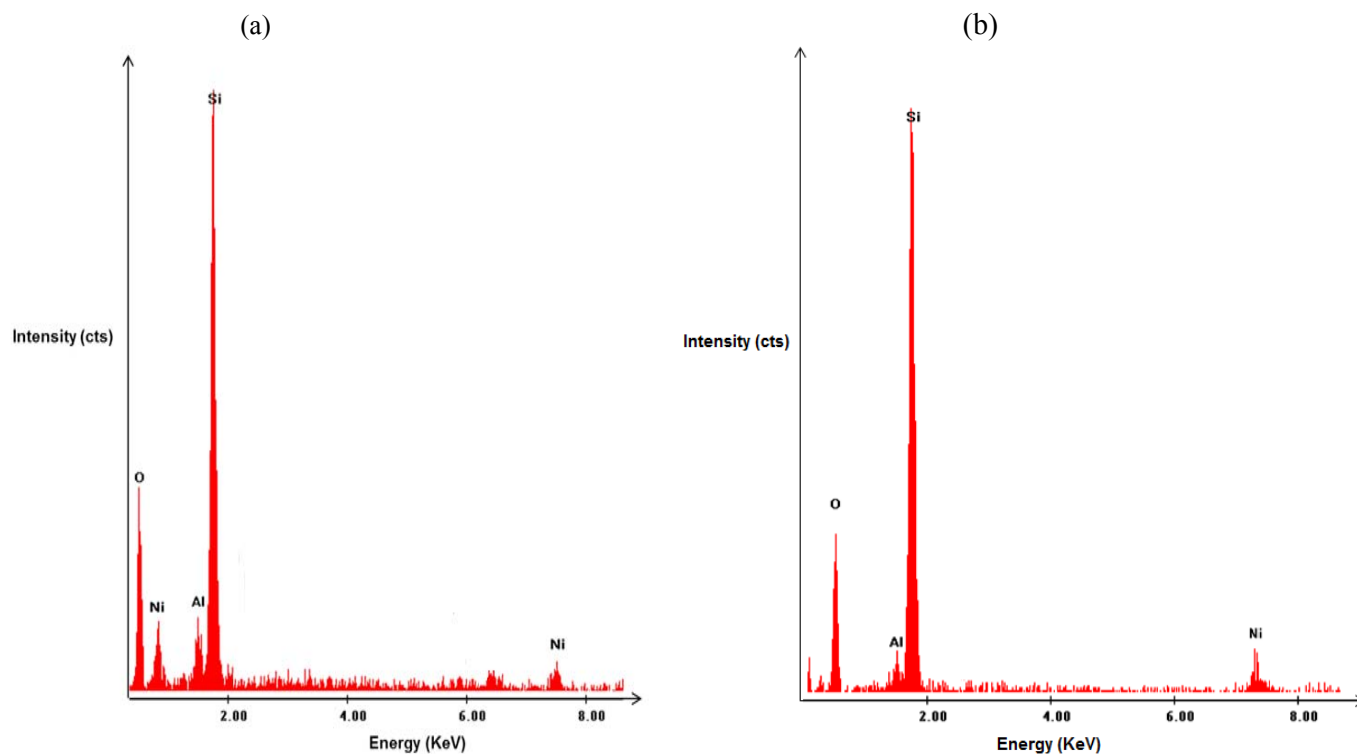


Figure 3. Energy-dispersive X-ray spectroscopy for Ni-Zeolite β (a) and Ni-ZSM-5 (b)

The nitrogen adsorption isotherms, pore size distribution, and textural properties of the Ni-ZSM5 and Ni-Zeolite β are provided in Figure 2 and Table 1. Both catalysts show similar type of adsorption isotherm including a relatively large contribution of micropores, significant contribution of mesopores, and a type H4 hysteresis loop in desorption branch. The hysteresis loop is more pronounced for Ni-ZSM-5 due to large contribution of mesopores and for Ni-Zeolite β , it can hardly be seen in adsorption isotherm.

Calculated PSD for both adsorbents show a narrow sharp peak in micropore range (around 5 Å) and small but wider peaks in large micropore and mesopore ranges (around 14 and 28 Å for Ni-ZSM-5 and a wide peak extended from 13 to 25 Å for Ni-Zeolite β). Both samples have relatively the same pore volume (≈ 0.28

cm³/g). Ni-Zeolite β is more microporous and have a larger contribution of micropores; 86% of total porosity is microporosity (see Table1 for comparison between two catalysts). Due to the large microporosity in Ni-Zeolite β, this sample has a larger surface area and if the surface area is accessible for reactants and nickel is impregnated uniformly all over the external surface and porosity, this catalyst is more desirable for hydro-cracking reactions.

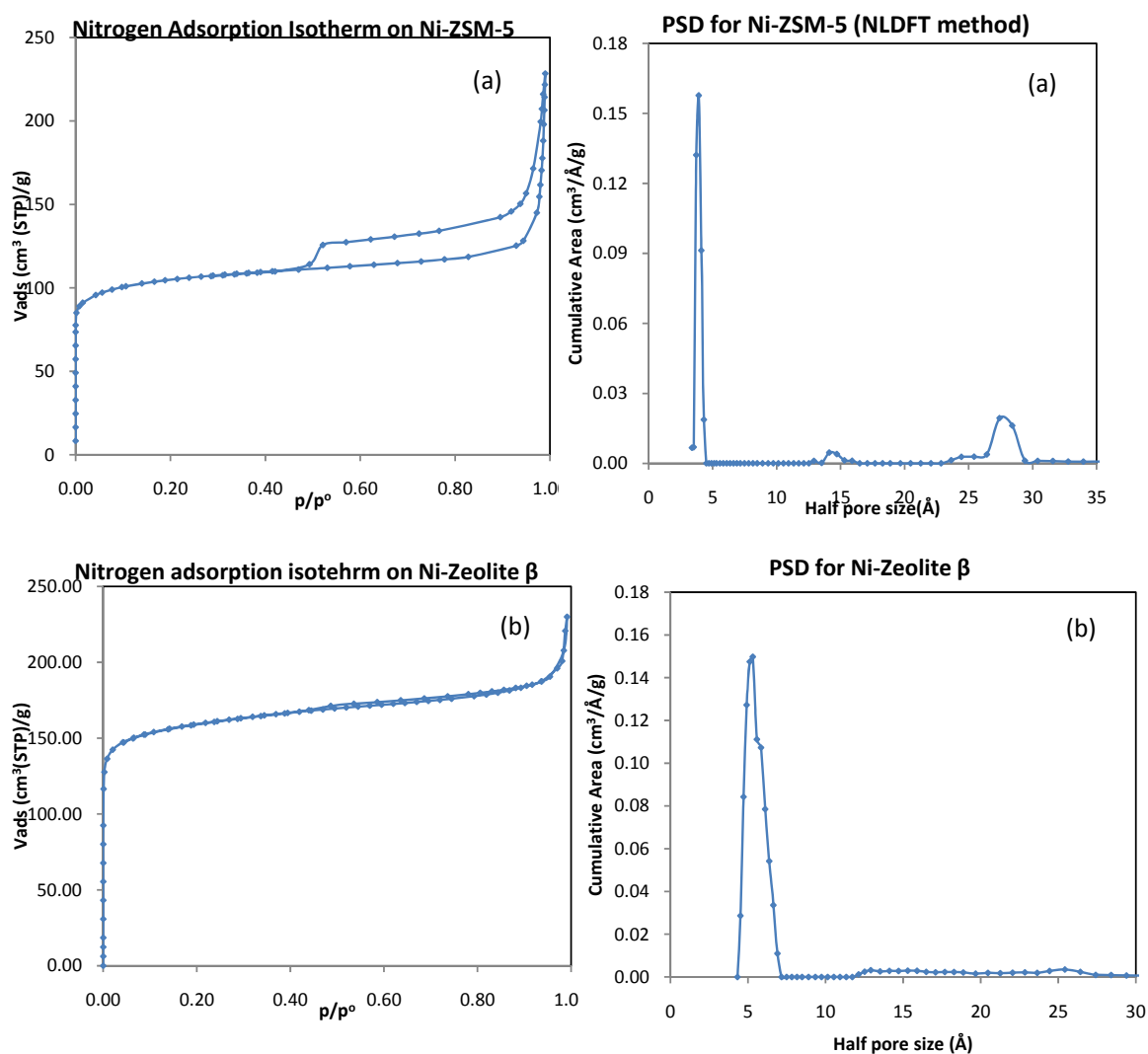


Figure 4. Nitrogen adsorption isotherm and PSD results of Ni-ZSM-5 (a) and Ni-Zeolite β (b) catalysts

Table 1. Textural properties of Ni-ZSM-5 and Ni-Zeolite β

Catalyst	BET equivalent area (m ² /g)*	Micro-pore volume (cm ³ /g)**	Total pore volume (cm ³ /g)***
Ni-ZSM-5	396.743	0.157	0.278
Ni-Zeolite β	591.053	0.247	0.287

* Surface area is calculated based on BET method [35].

**Micropore volume is calculated based on α_s method [36].

*** Total pore volume is calculated based on nitrogen amount adsorbed at near saturation pressure converted to liquid volume.

Based on the porosity of catalysts, two different reaction mechanisms are expected; if the reactant (oleic acid) and the products (C9-C12) can diffuse in whole the porosity of samples including micropores and mesopores, since whole the surface area would be available for the reaction, reaction yield would be larger for the catalyst with the higher surface area (Ni-Zeolite β). If the size of the reactant and products are larger than micropores ($\approx 5\text{\AA}$), micropore surface area wouldn't be accessible for reaction and reaction yield for the sample with higher mesoporosity would be larger (Ni-ZSM-5). Since the reactant (Oleic acid) and products (C₉-C₁₂) are all linear shaped hydrocarbons, their kinetic diameter is in the order of the kinetic diameter for linear hydrocarbons (normally less than 5 \AA). For instance, kinetic diameter for n-Nonane (C₉) is reported 4.3 \AA in the literature [37]. We expect for the reactant and products to be able to diffuse in whole the porosity and the total surface area for both samples to be accessible for reaction. Results in next section shows higher reaction yield for Ni-Zeolite β which is consistent with our expectation.

3.2. Hydro-cracking of oleic acid

The hydro-cracking of oleic acid over Ni-ZSM-5 and Ni-Zeolite β were investigated in figures 5, 6 and 7. Figure 5 represents the oleic acid conversion versus time over Ni-ZSM-5 and Ni-Zeolite β . The results of figure 5 were obtained in the temperature of 425 °C and other operating conditions were remained as table 1. Conversion of each type of catalyst was obtained based on the GC calibration curve which was achieved from the standard samples of oleic acid. Oleic acid conversion as a key parameter in the hydro-cracking reactions remains stable after 30 minutes and the variation of conversion is not significant over time. The conversion rate of oleic acid is ~ 94% and ~ 87% for Ni-Zeolite β and Ni-ZSM-5 respectively at the temperature of 425 °C. Figure 5 proves that after 30 minutes the reactor and hydro-cracking reactions reach to the steady state condition and the variation in oleic acid conversion is insignificant.

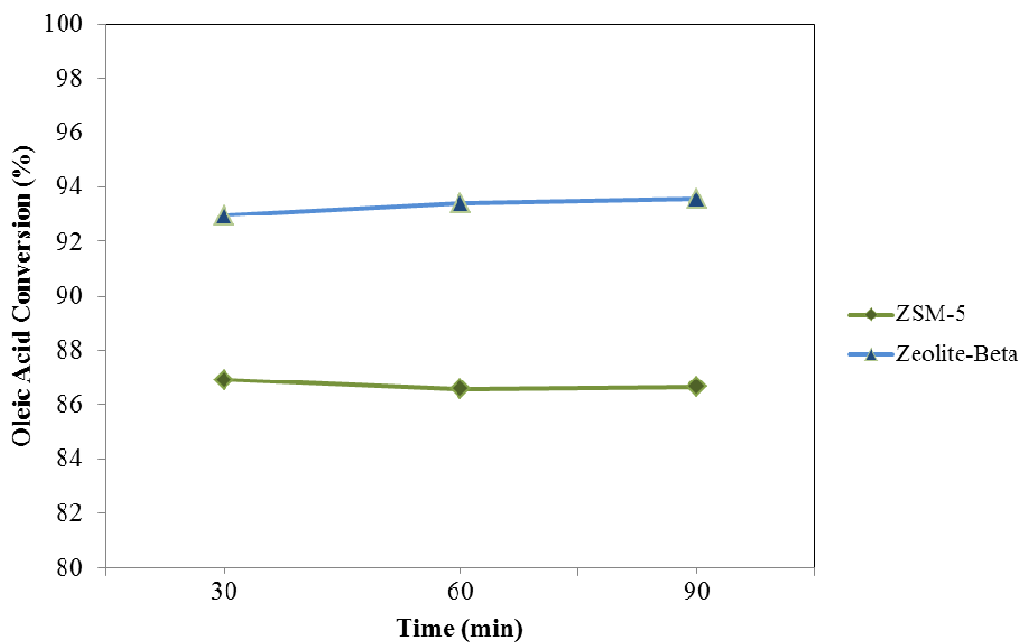


Figure 5. Oleic acid conversion as a function of time over Ni-ZSM-5 and Ni-Zeolite β

Figure 6 shows the oleic acid conversion over Ni-ZSM-5 and Ni-Zeolite β in different reaction bed temperatures. Temperature as a key parameter of hydro-cracking reactions has a great influence on catalyst effectiveness and activity. The effectiveness of hydro-cracking reactions is measured with oleic acid conversion which is defined in equation 1. The hydro-cracking reactions of oleic acid are dependent to reaction temperature, it is clearly observed that with temperature increment, oleic acid conversion increased over both catalyst samples but Ni-Zeolite β has greater conversion rate in comparison with Ni-ZSM-5 and the reason is the larger total surface area of Ni-Zeolite β compared with Ni-ZSM-5 catalyst sample. Also the maximum oleic acid conversion increment occurred from temperature rising of 300°C to 350°C which is 35.4% and 50.5% for Ni-ZSM-5 and Ni-Zeolite β respectively. In addition, previous studies show that hydro-cracking reactions special deoxygenation of oxygenated compounds such as oleic acid are more active in higher temperatures [38-40].

Moreover, this point should be mentioned that to measure the oleic acid conversion rate over each catalyst sample, the Hydro-cracking process reached to steady state conditions and figure 5 proves this matter.

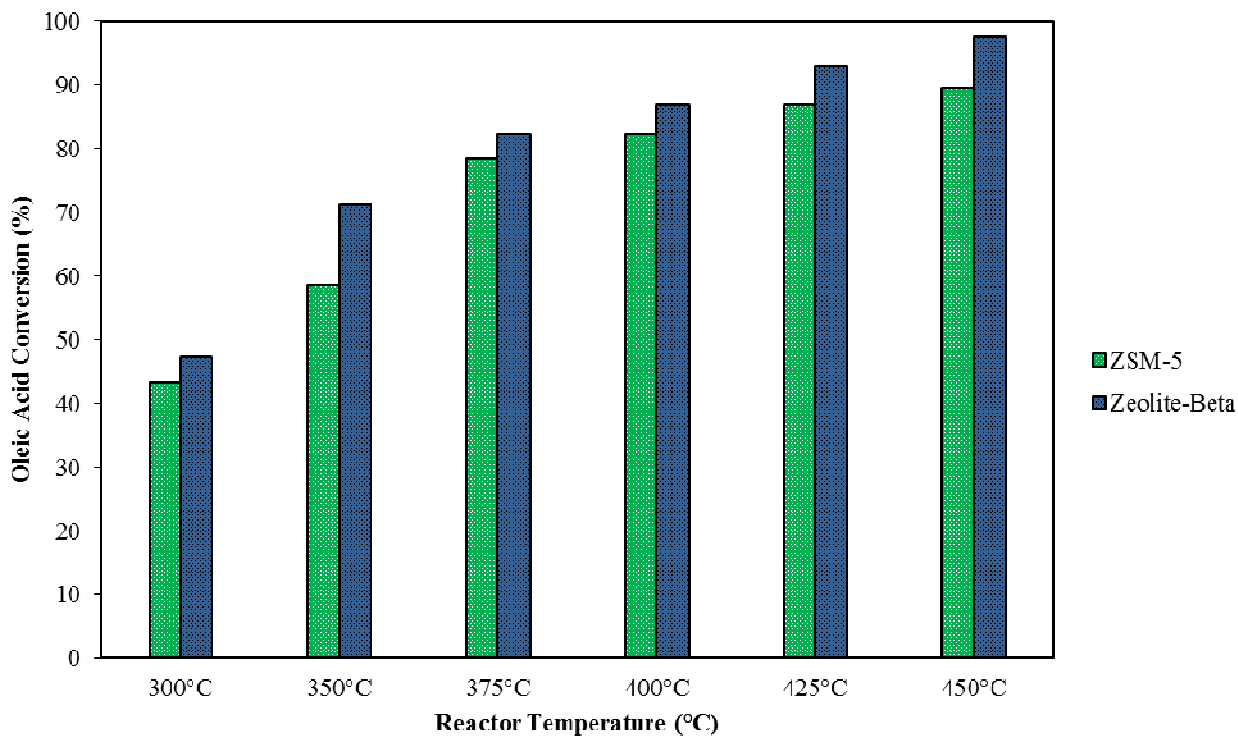


Figure 6. Dependence of oleic acid conversion on reaction bed temperature for Ni-ZSM-5 and Ni-Zeolite β

Yield of production over both catalyst types are investigated in figure 7. To measure the production yields, hydro-cracking reactions were performed at 400 °C and 30 Bar pressure with Hydrogen/Feed of 1000 NI/l. According to the literature, the hydro-cracking temperature was chosen and maintained at 400 °C because this temperature is an optimum temperature for hydro-cracking [19, 20]. Yields of three targeted components (C_9 , C_{10} and C_{12}) were calculated based on equation 2. It is clearly seen that the Nonane (C_9) and Decane (C_{10}) production yields over Ni-Zeolite β are greater than Ni-ZSM-5 but for Dodecane, Ni-ZSM-5 β has better performance. The reason for higher production yield for Nonane and Decane in Ni-Zeolite β is higher surface area and micropore concentration in Ni-Zeolite β but higher yield production of C_{12} over Ni-ZSM-5 is related to high

mesopore concentration of Ni-ZSM-5 which can be appropriate for larger molecules production such as Dodecane and improve the selectivity of deoxygenation reaction towards C_{12} in comparison with Ni-Zeolite β . The difference of Dodecane production yield of for both types of catalysts is 10.5%.

Hence, better performance of Ni-Zeolite β evidenced by the higher oleic acid conversion and higher production yields of C_9 and C_{10} but Ni-ZSM-5 has better performance for C_{12} yield of production. Thus, Ni-Zeolite β has a great potential to apply in large scale of hydro-cracking reactions to convert bio-oil towards C_9 , C_{10} and C_{12} hydrocarbons which are the main components of jet fuel.

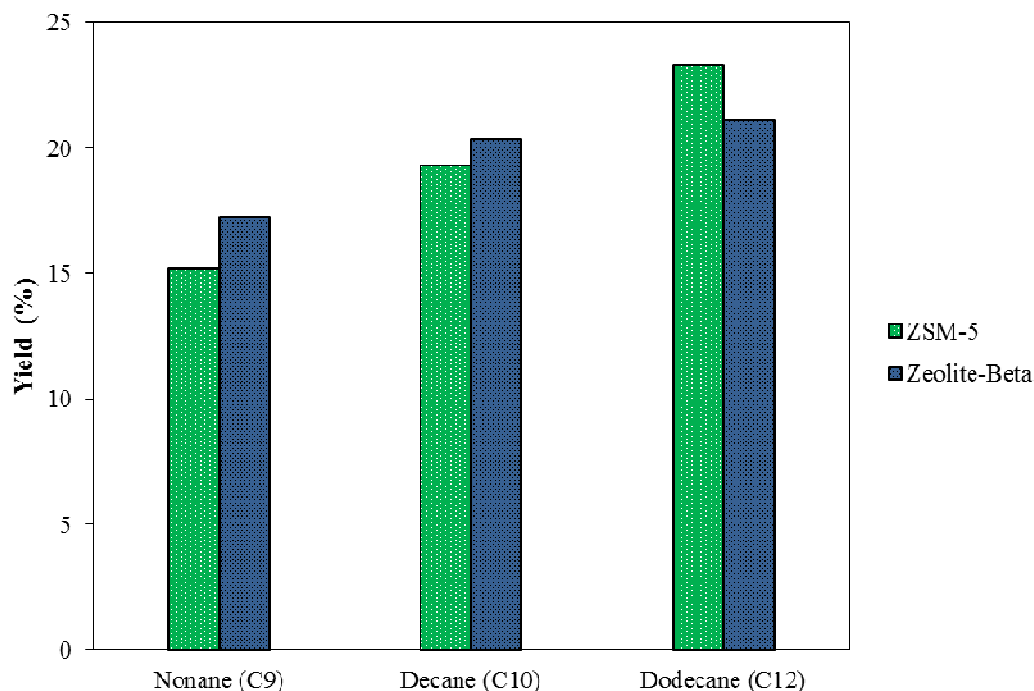


Figure 7. Production yield of Nonane (C_9), Decane (C_{10}) and Dodecane (C_{12}) over Ni-ZSM-5 and Ni-Zeolite β at temperature 400 °C

4. Conclusion

Hydro-cracking of oleic acid with two nickel impregnated catalysts based with ZSM-5 and Zeolite β was performed to produce bio-fuel. In this study, nickel was impregnated over ZSM-5 and Zeolite β and then these two catalyst samples were characterised with nitrogen adsorption, SEM and SEM-EDX. Results of SEM and SEM-EDX proved that nickel was impregnated properly over the zeolitic support. The nitrogen adsorption results and pore size distribution analysis confirmed that Ni-Zeolite β has larger surface area in comparison with the Ni-ZSM-5 but Ni-ZSM-5 sample has higher mesopore concentration in its structure. The large surface area of Ni-Zeolite β played as a significant parameter in conversion of oleic acid. Ni-Zeolite β has larger production yields of Nonane and Decane but Ni-ZSM-5 is more selective to Dodecane due to larger production yield of Dodecane in comparison with the Ni-Zeolite β . Therefore, Ni-Zeolite β and Ni-ZSM-5 are cheap to utilise as the catalyst of hydro-cracking reactions with appropriate efficiency in bio-oil conversion towards C_9 , C_{10} and C_{12} hydrocarbons which are the main components of jet fuel.

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Chapter 6

Hydro-conversion of Oleic Acid in Bio-oil to Liquid Hydro-carbons: an Experimental and Modelling Investigation

CHAPTER 6

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By signing the Statement of Authorship, each author certifies that their stated contribution to the publication is accurate and that permission is granted for the publication to be included in the candidate's thesis.

Name of Principal Author (Candidate)	Amir Ahmad Forghani		
Contribution to the Paper	Developed ideas. Performed simulations and calculations, interpreted data, wrote the manuscript and acted as corresponding author.		
Signature		Date	18/12/14

Name of Co-Author	David Lewis		
Contribution to the Paper	Supervised development of the work, helped in developing ideas, data interpretation and manuscript evaluation.		
Signature		Date	19/12/14

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Contribution to the Paper			
Signature		Date	

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Hydro-conversion of Oleic Acid in Bio-oil to Liquid Hydro-carbons: an Experimental and Modelling Investigation

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Abstract

BACKGROUND: This study focused on the understanding of the reaction kinetics for hydrocracking process. Oleic acid, as the main component of most bio-oils, was selected as a feedstock of the hydrocracking process. The hydrocracking of oleic acid was performed in a laboratory scale trickle-bed reactor in presence of a Ni-Zeolite β catalyst and hydrogen for hydrogenation. The concentrations of oleic acid and three main produced components of jet fuel range of hydrocarbons, which are nonane, decane and dodecane (C_9 , C_{10} and C_{12}), were measured with GC analysis.

RESULTS: According to the aforementioned component's concentrations, the rate of reaction and the related Arrhenius equation parameters were estimated. The reaction kinetic calculations were subjected to the hydrocracking reactor modeling to gain a better understanding of the hydrocracking. The concentrations of C_9 , C_{10} and C_{12} were assumed as a separate lump of the produced hydrocarbons, namely middle hydrocarbon (MC). The reactant and MC lump concentrations along the reactor were measured and compared with experimental data. The modeling and experimental results are in reasonable agreement in terms of MC lump production and oleic acid conversion. Furthermore, the oleic acid and MC concentration profiles and reactor wall temperature profiles along the reactor were examined in this research.

CONCLUSION: The outcome of this study can be applied in simulation and commercialisation of the hydro-cracking as a potential process in biofuel production.

Keywords: Oleic acid hydro-conversion, Reactor Modeling, Nickel-Zeolite catalyst, Kinetic investigation.

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CHAPTER 6

Nomenclature

a	specific surface area of catalyst (m^2/m^3)
C_i^L	Liquid concentration of each component (mol/m^3)
C_p^L	Liquid specific heat capacity ($\text{J}/\text{kg}\cdot\text{K}$)
h_G	Gas heat transfer coefficient ($\text{W}/\text{m}^2\cdot\text{K}$)
h_l	Liquid heat transfer coefficient ($\text{W}/\text{m}^2\cdot\text{K}$)
k_i	Rate constant of major reactions ($1/\text{s}$)
K_i^g	mass transfer coefficients in gas phase (m/s)
L_0	Reactor length (m)
$LHSV$	Liquid hourly space velocity ($1/\text{h}$)
m_g	Gas mass flow-rate (kg/s)
P_i^g	Partial pressure (Pa)
P_i^*	saturation pressure in the liquid-gas phase interface (Pa)
r	Rate of reaction ($\text{mol}/\text{m}^3\cdot\text{s}$)
R	Universal gas constant ($\text{J}/\text{mol}\cdot\text{K}$)
Re	Reynolds number
Sc	Schmidt number
Sh	Sherwood number
T_L	Liquid phase temperature (K)
T_g	Gas phase temperature (K)
T_w	Reactor wall temperature (Tube) (K)
X	Each point along the reactor length (m)
Y	Yield
ΔH_i	Enthalpy of reaction for each lump (kJ/mol)
ε	Bed porosity

Superscripts and subscripts

<i>amb</i>	Ambient
<i>i</i>	Each component
<i>in</i>	Inside
<i>L, l</i>	Liquid
<i>MC</i>	Middle hydrocarbons
<i>OA</i>	Oleic Acid
<i>out</i>	Outside
<i>w</i>	wall

1. Introduction

Petroleum refineries use hydrocracking extensively to crack large molecules and/or to remove sulfur, nitrogen and metals from petroleum derived feedstocks such as gas and oil (1). The main element for hydrocracking is the use of acidic catalysts, such as zeolitic catalysts that can drive the hydrocracking reactions towards favorable hydrocarbons (2, 3). Recently, the hydrocracking process has been utilised in bio-oil upgrading due to the promising alternative of fossil fuels. Several types of plant-based oils (bio-oils) such as vegetable oil and micro-algae oil or distilled fraction of bio-oil have been subjected to hydrocracking processes with acidic catalysts (4-6). Among the acidic type of catalysts, zeolite materials are very selective to convert bio-oil to the gasoline range of hydrocarbons (7). Furthermore metals impregnation, such as nickel, as supporters for acidic type catalysts have a significant role in improving the efficiency of hydrocracking processes towards biofuel production (8). For example, supported noble metal catalysts such as Pd/C and Pt with zeolite have been utilised for hydrocracking of fatty acids derived from bio-oil (9-11). Nobel metals are very selective towards alkane production, but they are not cheap to operate at commercial scale hydrocracking processes. The application of nickel and molybdenum as cost effective supports for acidic catalysts used in hydrocracking have been investigated (12-18). The hydrocracking process consists of several reactions, which are categorized as hydro-deoxygenation, decarboxylation and decarbonylation; to convert oxygenated compounds in bio-oil such as oleic acid to hydrocarbon fuels (15, 19). Hydro-deoxygenation produces a water molecule and a related chain of hydrocarbon. In decarboxylation, a molecule of carbon dioxide

and chain of hydrocarbon is yielded and finally a molecule of carbon monoxide, a water molecule and a chain of related hydrocarbon are produced in decarbonylation (8, 17, 20, 21).

To commercialise the hydrocracking process, a better understanding of the reaction pathways and kinetic analysis is required. Kinetic studies can improve our understanding of hydrocracking reaction mechanisms and they can be applied in a mathematical framework (22). The overall aim of this work was to investigate the kinetics of hydrocracking processes and compare the results with modeling studies. Several limited studies were undertaken to investigate the hydrocracking reaction pathways, for example in 2012, Anand & Sinha elucidated the reaction kinetics of *Jatropha* oil hydrocracking reactions over sulfide Co-Mo/Al₂O₃ at different temperatures. The catalytic cracking of unsaturated triglycerides was investigated by Benson et al (2009) who elucidated the triglyceride-cracking pathway (20). According to the open scientific literature, hydrocracking kinetic investigations of a single component of bio-oil and the subsequent modeling of the hydrocracking process has not been reported. This study is based on applying one of the main components of all types of bio-oils (oleic acid) in hydrocracking processes to quantify the reaction kinetics and utilise in hydrocracking modeling.

In this research, based on our previously reported work, a nickel based catalyst over Zeolite β was applied in a hydrocracking process due to its efficient conversion towards the jet-fuel range of hydrocarbons (23). The Ni-Zeolite β was prepared by the impregnation method to construct a cost-effective hydrocracking catalyst. The catalyst was analysed with oleic acid injection in a lab-scale hydrocracking reactor. Oleic acid was selected as a feed because it is one of the

major components of plant based oil and micro-algae oil. The oleic acid percentage in micro-algae oil varies from 39 to 60% (16, 24). Three main components of jet-fuel hydrocarbons are defined as nonane, decane and dodecane (C_9 , C_{10} and C_{12}) and they are the goal components in hydrocracking. The main goal of the hydrocracking experiment is identifying the reaction rate of production and obtaining the Arrhenius equation parameters and applies them in a non-isothermal, heterogeneous mathematical model for hydrocracking reactor. The hydrocracking model output was compared with experimental data in terms of oleic acid conversion and product concentrations. Based on the literature, this reaction rate identification combined with reactor model development has not been performed before and it can improve the commercialisation aspect of hydrocracking process.

2. Materials and methods

2.1. Catalyst preparation

Ni/Zeolite β was prepared with a conventional impregnation method. β -Zeolite was purchased from Zeolyst International Company (with SiO_2/Al_2O_3 Molar Ratio of 38) and then the impregnation of $Ni(NO_3)_2 \cdot 6H_2O$ (Sigma Aldrich) solution on β -Zeolite support was performed. The support was mixed with the nickel impregnation solution and after stirring for 2 hours, it was dried in the oven and then calcined in the furnace with starting temperature increase of $10^\circ C/min$ to $500^\circ C$ and keep this temperature for 5 hours. After preparation, the catalyst was characterised with nitrogen gas adsorption. Nitrogen gas adsorption experiments were carried out at 77 K using a Belsorp-Max

automated manometric gas adsorption apparatus. Samples were degassed prior to the experiments at 300 °C and a background vacuum of 0.1 MPa for 4 hours. Ultra high purity (99.999%) helium and nitrogen from BOC Gases Australia were used for dead-space measurements and adsorption experiments respectively.

2.2. Hydrocracking Reaction

To analyse the prepared catalyst structure in hydrocracking reactions, a commercial micro-scale trickle bed reactor (Autoclave Engineers' BTRS-Jr) was utilised. For each run of the reactor, one gram of catalyst was weighed and loaded into the stainless steel tubular reactor, which had an inside diameter of 1.2 cm and a catalytic bed of 20 cm in length. The reactor was situated in a furnace so as to run in high temperatures. Hydrogen pressure was controlled by a backpressure regulator. An HPLC pump was used to transfer the oleic acid into the reactor and maintain the liquid flow through the catalyst bed. As mentioned before, Oleic acid was selected as a feed since it is one of the major components of plant based oil and micro-algae oil. The Oleic acid specifications are reported in table 1. Oleic acid was injected with a large volume of hydrogen through the reactor. The products, unreacted reactant and excess hydrogen passed through a separator where liquid samples were obtained from the bottom of the separator. The schematic of the hydrocracking lab-scale process is shown in Figure 1. Furthermore, the hydrocracking reactions were performed at different reaction bed temperatures; the operating conditions in shown in Table 2.

CHAPTER 6

Table 1. Oleic Acid specification

Formula	$C_{18}H_{34}O_2$
Molar Mass	$282.46 \text{ g/mol}^{-1}$
Density	0.895 g/ml
Melting Point	$13-14 \text{ }^\circ\text{C}$

Table 2. Catalyst loading and operating conditions

Catalyst mass	1 g
Catalyst shape	Powder
Bed length	10 cm
Reactor diameter	1.01 cm
Reaction temperature range	$350-450 \text{ }^\circ\text{C}$
Reaction pressure	30 Bar
Oleic acid flow	0.1 ml/min
Hydrogen/Feed	1000 NI/1

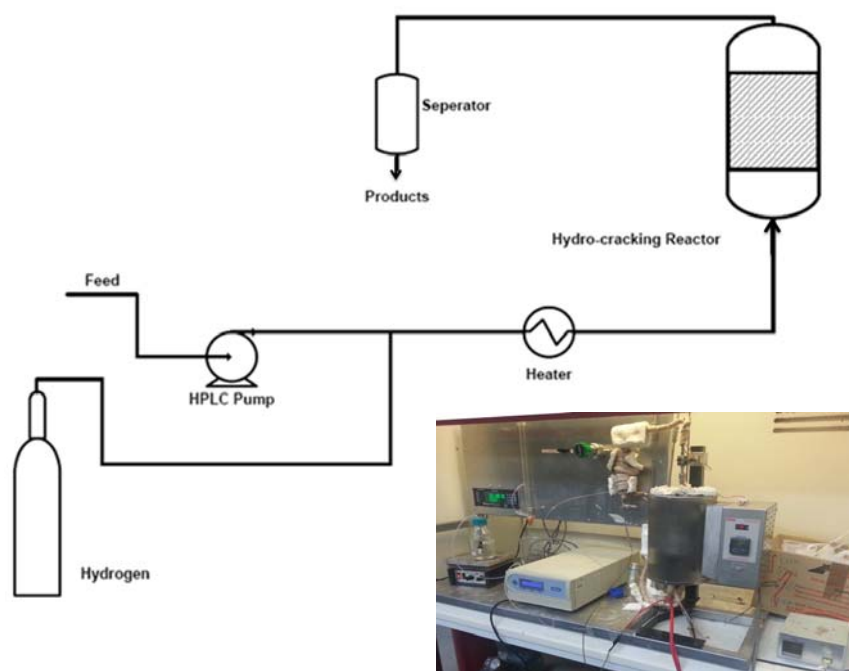


Figure 1. Hydrocracking lab-scale apparatus

2.3. Product Analysis

The product samples were collected at the end of separator and analysed with a gas chromatograph (Shimadzu GC2010 with a flame ionization detector, FID) where a Varian 3800-GC column, 30 m, 0.25 mm, 0.1 μm , was employed for product analysis. Helium was selected as carrier gas with high purity. Nonane (C_9), Decane (C_{10}) and Dodecane (C_{12}) were purchased from Sigma Aldrich as standard samples to analyse and measure the outlet products of the hydrocracking reactions. C_9 , C_{10} and C_{12} are the main components of jet-fuel and by using them as standard samples, a calibration curve with different concentrations were identified to measure the yields of C_9 , C_{10} and C_{12} for each catalyst. The GC analysis was performed for all samples under specific conditions; the FID temperature was 200°C and the oven temperature program was increased from 50°C to 150°C at the rate of $10^\circ\text{C}/\text{min}$ and then from 150°C to 200°C at the rate of $15^\circ\text{C}/\text{min}$. The performance of the catalyst was evaluated based on their effectiveness for oleic acid conversion and subsequent yield of jet fuel ranges of hydrocarbons. Conversion and yields of C_9 , C_{10} and C_{12} were calculated with the calibration curve data of the feed (oleic acid) and product, which were defined with the following equations:

$$\text{Conversion (\%)} = \frac{\text{Mass of oleic acid in the feed (g)} - \text{Mass of oleic acid in the product (g)}}{\text{Mass of oleic acid in the feed (g)}} \quad (1)$$

$$\text{Yield of hydrocarbon (wt. \%)} = \frac{\text{Mass of hydrocarbon in the product (g)}}{\text{Mass of feed (g)}} \quad (2)$$

2.4. Modeling of the Hydrocracking Reactor

A schematic representation of the hydrocracking reactor is shown in Figure 2 (a). The process consists of a catalyst bed reactor. The oleic acid (OA) as a rich feed, and hydrogen at high-pressure entered the reactor from the bottom of the apparatus. Through the reactor, shown in Figure 2 (b), hydrogen from the gas phase was transferred to the liquid-solid inter-phase for the hydrocracking reactions. The measured products were Nonane, Decane and Dodecane, which are, situated in the middle range of hydrocarbons (MC). The MC dispersed through the gas and liquid phases depending on the operating temperature and pressure within the reactor. An element of the reactor, shown in Figure 2 (c), with length of Δz was considered for deriving the mass and energy balance equations for the model.

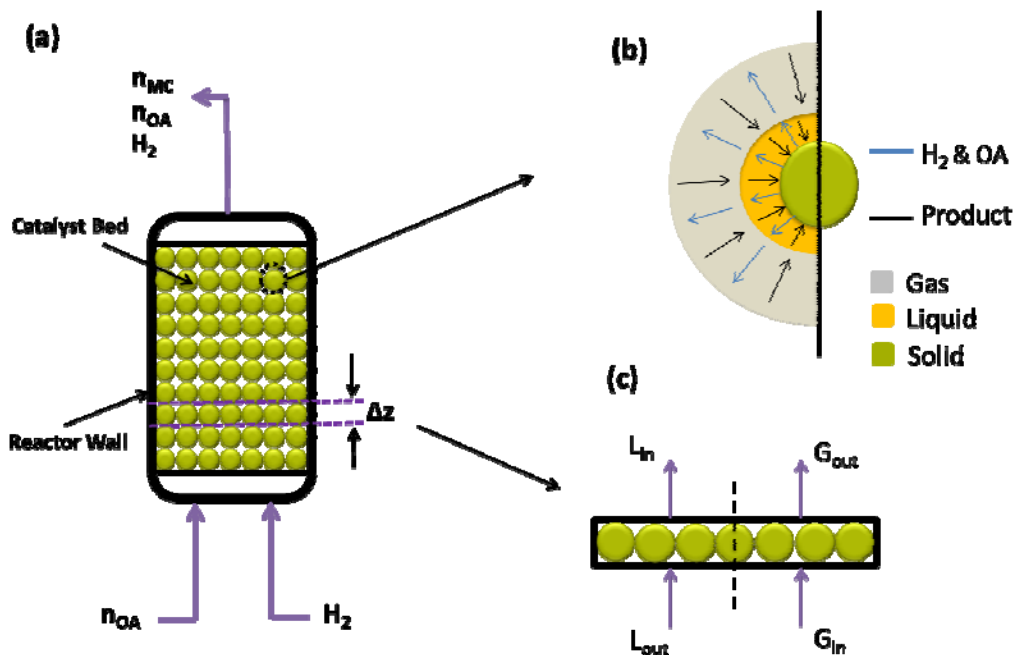


Figure 2. (a) Schematic representation of the trickle-bed reactor, (b) Film theory over the catalyst and (c) The selected element of the trickle-bed reactor for development of the governing equations

2.4.1. Mathematical model of the hydrocracking reactor

To set up a hydro-processing plant, a comprehensive evaluation should be done to check the plant performance, which is time consuming, risky and expensive if the actual plant is used for optimization. The use of mathematical modeling is one of the most efficient ways to evaluate plant performance. Recently, mathematical models were employed to optimise the impact of changes in design variables (30-33). The first step required to develop an efficient model is the formation of the appropriate mass and energy balance equations. To this set of equations, suitable kinetic equations that represent the MC rate of production and oleic acid rate of consumption are added, which are calculated from hydrocracking experimental data (25).

In this study, a three-phase heterogeneous reactor model was developed for hydrocracking of OA. The model considers two-film theory, which incorporates mass transfer at the gas-liquid and liquid-solid interfaces and employs correlations, which were presented in the literature (25-29). In the present model used for this investigation, the catalyst was represented as the solid phase; hydrogen as the reactant in the gas phase, and OA and MC products in the liquid phase. The following assumptions were made for the three-phase heterogeneous reactor model (22, 30-33):

- 8) Plug flow was considered along the reactor and there was no radial concentration gradient.
- 9) The hydrocracking reactor was operated at steady state conditions.

- 10) The developed reaction kinetics from experimental data was applied in the model.
- 11) For model validation, the reactor was operated isothermally.
- 12) Axial dispersion of heat was neglected.
- 13) The phase change of light components is negligible.
- 14) All reactions assumed to be performed in the liquid phase (22).

All the assumptions are deemed reasonable for application within the mathematical model. For example, because the length per diameter ratio of the hydrocracking reactor was $\gg 1$, the first and fifth assumption were justified. The experimental data was collected at steady state conditions with the lab-scale hydrocracking reactor. Also the lab-scale of hydrocracking reactor was operated isothermally to obtain experimental data for validation, justifying the fourth assumption. For justification of the 7th assumption, at the temperature and pressure conditions during the hydrocracking reactions, all components such as oleic acid and all products remained in the liquid phase (22).

Using the stated assumptions the mass balances and energy balances equations were obtained to set up the base of mathematical model. The energy balances and mass distribution along the reactor in both, gas and liquid phases for different components were developed based our previously reported study (22), shown in Appendix A. The developed energy and mass balances equations with a combination of the reaction rate of oleic acid hydrocracking were solved numerically. To solve the sets of energy and mass balance differential equations,

they were discretised and solved simultaneously using the Gauss–Seidel iteration technique (30, 31).

3. Result & Discussion

The reported results of oleic acid hydrocracking over Ni-Zeolite β were obtained from the lab-scale hydrocracking reactor when operated at the operating conditions shown in Table 2. The data was used to determine the Arrhenius equation and rate of oleic acid conversion to the three major components of the middle range of hydrocarbons. The Arrhenius equation and the rate of reaction were applied in the mathematical model for the hydrocracking reactor. The results are divided into three sections, which are experimental results, model validation and reactor model results.

3.1. Nitrogen Adsorption Results

The nitrogen adsorption isotherm, pore size distribution, and textural properties of the Ni-Zeolite β are provided in Figure 3 and Table 3. A relatively large contribution of micropores, significant contribution of mesopores, and a type H4 hysteresis loop in desorption branch were observed in the catalyst sample. Calculated PSD shows a wide peak extended from 13 to 25 Å for Ni-Zeolite β . The sample has relatively the pore volume of about 0.29 cm³/g. Ni-Zeolite β is microporous and it has a large contribution of micropores and the 86% of total porosity is microporosity (see Table 3).

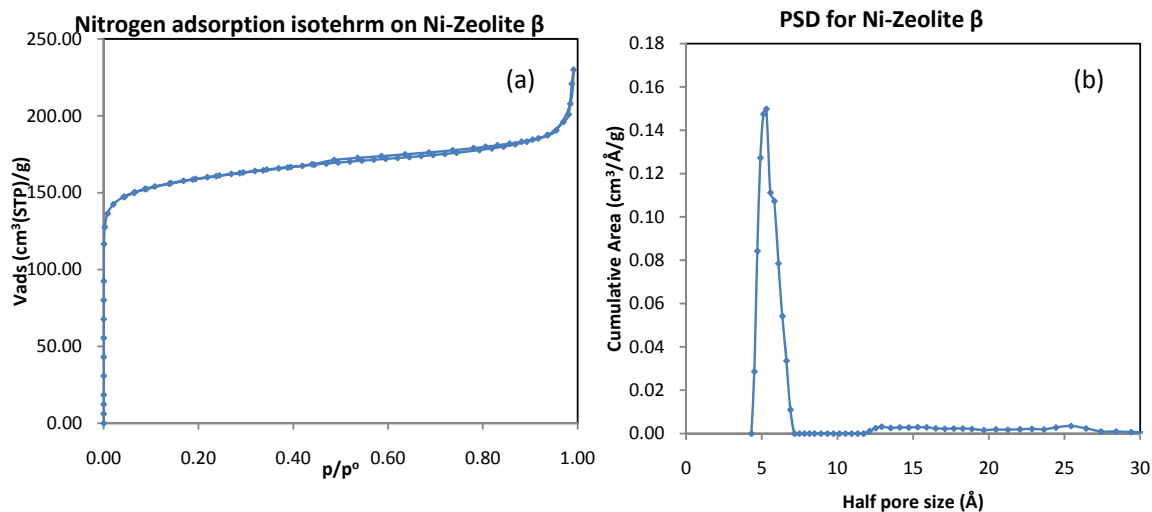


Figure 3. Nitrogen adsorption isotherm (a) and PSD (b) results of Ni-Zeolite β catalyst

Table 3. Textural properties of Ni-ZSM-5 and Ni-Zeolite β

Catalyst	BET equivalent area (m^2/g)*	Micro-pore volume (cm^3/g)**	Total pore volume (cm^3/g ***)
Ni-Zeolite β	591.053	0.247	0.287

* Surface area is calculated based on BET method (37).

**Micropore volume is calculated based on α_s method (38).

*** Total pore volume is calculated based on nitrogen amount adsorbed at near saturation pressure converted to liquid volume.

3.2. Experimental Results

The hydrocracking reaction data of oleic acid over Ni-Zeolite β is shown in Figures 4 and 5. The production yields of nonane (C9), decane (C10) and dodecane (C12) are shown in Figure 4 from the hydrocracking process and were calculated using Equation 2. To obtain the production yields of the aforementioned components, the hydrocracking reactions were performed at 400°C and the other operating conditions as stated in Table 2. The production

yields of decane and dodecane were higher than nonane. Oleic acid conversion in various hydrocracking temperatures was examined and reported in Figure 5.

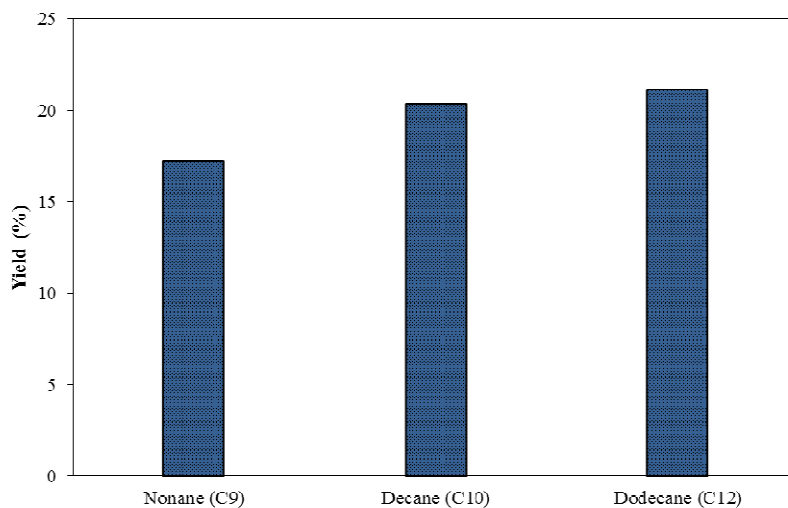


Figure 4. Production yields of Nonane (C₉), Decane (C₁₀) and Dodecane (C₁₂) as middle hydrocarbons lump obtained from hydrocracking experiment at temperature of 400°C

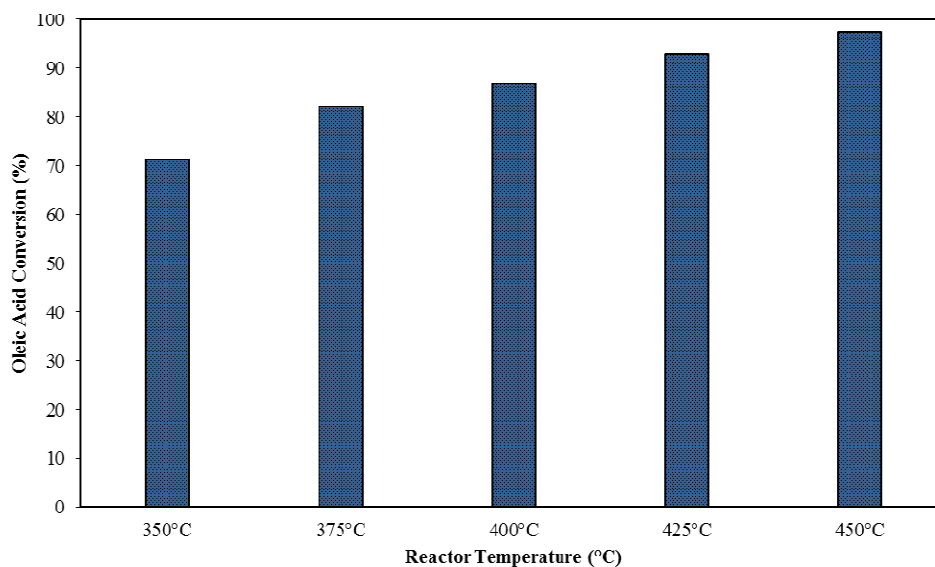


Figure 5. Oleic acid conversion in various hydrocracking temperatures over Ni-Zeolite β catalyst

One of the key components of the hydrocracking reactor modeling is obtaining the rate of reactions. The assumed rate of reaction is considered as a first order equation with a reaction constant which are reported in Appendix A. the reaction constant can be defined by Arrhenius equation and the Arrhenius equation and kinetic rates of the hydrocracking reactions towards the middle range of hydrocarbons were obtained from the hydrocracking experimental data. Firstly, the C₉, C₁₀ and C₁₂ components were considered as a single lump of hydrocarbons, named MC. To determine the Arrhenius equation constants for oleic acid conversion to MC components, the data of oleic acid conversion in various hydrocracking temperatures were applied and the frequency factor and activation energy values for the reactant and MC lump were quantified and are reported in Table 4.

Table 4. Frequency factor and activation energy to define Arrhenius equation of oleic acid (OA) hydrocracking to middle hydrocarbons (MC) over Ni-Zeolite β

Frequency Factor (h ⁻¹)	Activation Energy (KJ/mole)
9068.745	36.207

3.3. Model Validation

The mathematical modeling of the hydrocracking reactor was based on energy and mass balances equations and the measured hydrocracking rate of reaction. Validation was required to evaluate the accuracy and validity of the mathematical model. The model validated well with the measured experimental data for the hydrocracking reactions over Ni-Zeolite β. Experimental and model data for oleic acid conversion under various hydrocracking temperatures was

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compared and shown in Table 5 and Figure 6. To obtain the validation results, the reactor model was run with a fixed temperature. The minimum and maximum errors between experiment and model data are 0.79% and 7.13% respectively. According to previously reported literature for reactor modeling (30-33), the aforementioned error values show good agreement for the hydrocracking model when compared with full-scale data.

Table 5. Comparison between experimental data and model data of oleic acid conversion in various hydrocracking temperatures

Temperature (°C)	Experimental data	Model Result	Error (%)
Oleic Acid Conversion (%)			
350	71.26	76.34	7.13
375	82.29	82.94	0.79
400	86.90	88.37	1.69
425	92.98	91.79	1.27
450	97.45	95.47	2.03

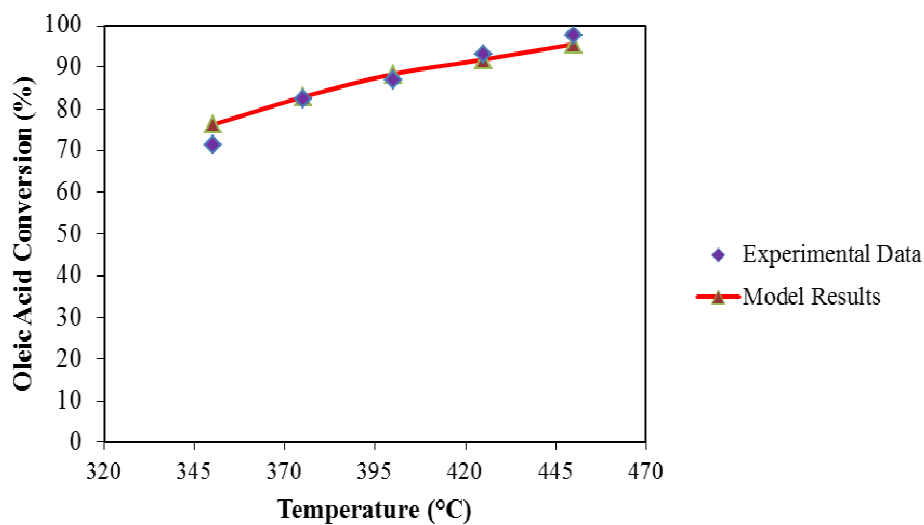


Figure 6. Comparison of Experimental data and model data of oleic acid conversion versus hydrocracking temperature

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The data shown in Table 6 represents the production yields of Nonane, Decane and Dodecane, which were achieved from experimentation and modeling. The average errors for Nonane, Decane and Dodecane production yields were 8.44%, 7.21% and 7.7% respectively. The errors shown in Tables 5 and 6 verified that the modeling results are in appropriate agreement with experimental data.

Table 6. Experimental and model data of Nonane, Decane and Dodecane production yields in order to validate the hydrocracking reactor model

Temperature (°C)	Experimental data	Model result	Error (%)
Production Yield of Nonane			
350	14.72	12.97	11.9
400	17.24	16.38	4.99
Production Yield of Decane			
350	17.39	16.55	4.8
400	20.35	18.39	9.63
Production Yield of Dodecane			
350	18.02	16.93	6.04
400	21.12	19.14	9.37

3.4. Results of Hydrocracking Reactor Model

In this section, the reactor model was investigated in terms of reactant and product concentration and temperature profiles along the reactor. The hydrocracking reactor was placed in a furnace to control the reactor temperature by a constant heat-flow. A constant heat flux of 1000 W/m^2 along the reactor surface was considered in the model. The reactants, which were oleic acid (OA) and hydrogen, data shown in Table 2, were injected concurrently into the reactor.

The applied parameter of X/L_0 was the dimensionless form of the reactor length. In this section, the performance of the hydrocracking reactor in terms of component concentrations and hydrocracking temperature profile were elucidated.

The oleic acid concentration variations along the hydrocracking reactor with various temperatures are shown in Figure 7. At higher hydrocracking temperatures, oleic acid conversion increased, for example, at the reaction temperature of 450°C, the oleic acid mole fraction decreased with higher rates at the beginning of the hydrocracking reactor.

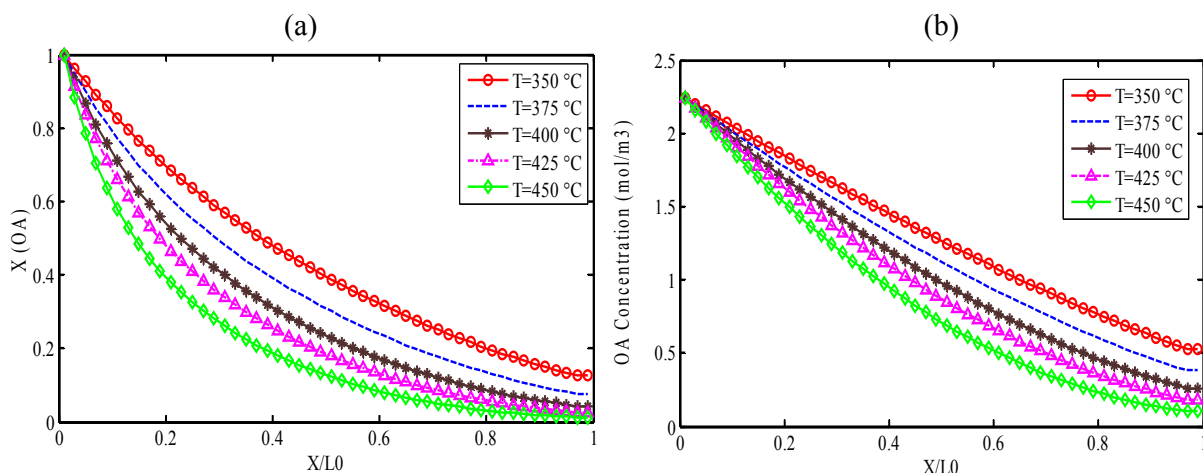


Figure 7. Oleic acid mole fraction (a) and Oleic acid concentration (b) along the hydrocracking reactor in various reaction temperatures

The results shown in Figures 8 and 9 were obtained at a hydrocracking temperature of 400°C. Due to higher conversion of oleic acid in 400°C, low differences in oleic acid conversion between 400°C and 450°C were observed. The reactor model result with a fixed temperature of 400°C was chosen as the fixed hydrocracking temperature in assessing the reactor model.

Based on the measured reaction rate of oleic acid to middle hydrocarbons, the oleic acid and MC lump concentrations along the reactor varied, as shown in Figure 8. The MC lump production rate was higher at the beginning length of the hydrocracking reactor but at the end of the reactor, due to the declining concentration oleic acid, MC production rate decreased.

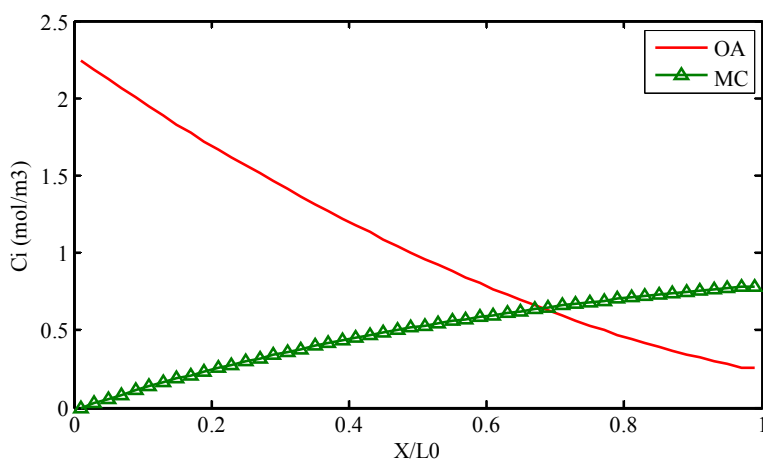


Figure 8. Oleic acid and middle hydrocarbon lump (MC) concentration along the hydrocracking reactor

According to the hydrocracking reactor, a constant heat-flow of 1000 W/m^2 was considered in the model. The inlet temperatures of oleic acid (liquid phase) was at 400°C . Temperature profiles of liquid phase and the reactor wall are shown in Figure 9. Both of temperature profiles increased along the reactor. The liquid temperature profile is less than the wall temperature profile due to the difference in the heat transfer coefficient (16, 34, 35).

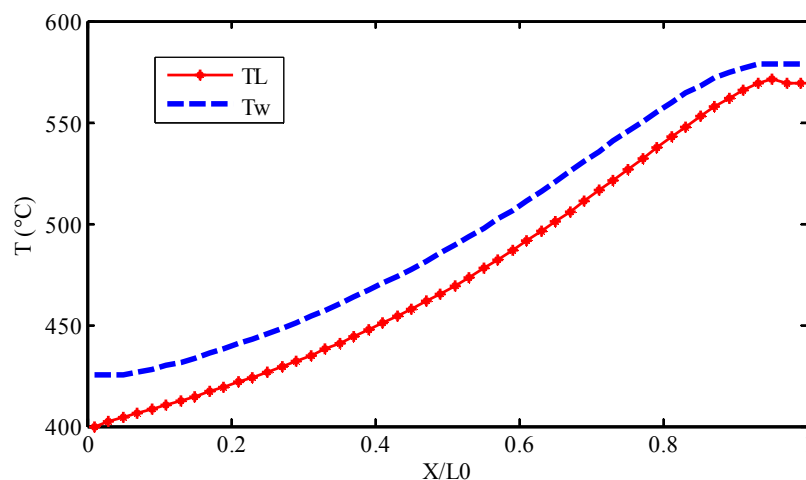


Figure 9. Liquid phase and reactor wall temperature profile along the hydrocracking reactor

4. Conclusion

In this study, the conversion of oleic acid, which is one of the major components of most plant, based oils, to hydrocarbon fuels was investigated. Ni-Zeolite β was prepared and then applied in a lab-scale hydrocracking reactor with set operating conditions. The concentrations of oleic acid and three major components of jet-fuel range of hydrocarbons (C_9 , C_{10} and C_{12}) were measured at the outlet of the hydrocracking reactor. According to the experimental data, C_9 , C_{10} and C_{12} were identified as a separate lump, named middle hydrocarbons (MC) and then the reaction rate of oleic acid conversion to MC was calculated. The reaction rate of oleic acid conversion is a key parameter in modeling of the hydrocracking process. Hence, mathematical model was considered to analyse the hydrocracking reactor. The model and experimental data were compared in terms of oleic acid conversion and C_9 , C_{10} and C_{12} yields of production. When compared with modeled data, good agreement was observed and determined adequate for

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validation of the hydrocracking model. The hydrocracking model was analysed in terms of oleic acid conversion at various hydrocracking reaction bed temperatures, production yields of MC and reactor wall and liquid temperature variation along the reactor. The validated hydrocracking reactor model and experimental data can be applied for further investigation for the production of biofuels.

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Appendix A.

The mass distribution along the reactor in both, gas and liquid, phases for different considered components is given by:

$$\text{For oleic acid as the feedstock (OA): } u_g \cdot A \cdot \frac{\partial P_{OA}^g}{\partial z} = -\frac{K_{OA}^l \cdot a \cdot A_c}{R \cdot T_g} (x_{OA} P_{OA}^* - P_{OA}^g), \quad (1)$$

$$\text{For middle hydrocarbon (MC): } u_g \cdot A \cdot \frac{\partial P_i^g}{\partial z} = -\frac{K_i^l \cdot a \cdot A_c}{R \cdot T_g} (x_i P_i^* - P_i^g), \quad (2)$$

$$\text{For hydrogen (H}_2\text{): } \frac{\partial P_{H_2}^g}{\partial z} = -\frac{K_{H_2}^l \cdot a \cdot A_c \cdot R \cdot T_g}{u_g} \left(\frac{P_{H_2}^g}{h_{H_2}} - C_{H_2}^l \right), \quad (3)$$

where, u_g, x_i, P_i^g and K_i^g are the gas velocity, liquid mole fraction in the gas and liquid interface, partial pressure, and mass transfer coefficients in the gas phase, respectively.

The stated equations represent the mass transfer of MC, oleic acid (OA) and the hydrogen from the liquid-gas interface to the bulk of the gas. For MC lump and reactants, the evaporation term was considered.

Mass balance equations in liquid phase

The differential equations of mass balance for the concentrations of hydrogen and middle, hydrocarbons in the liquid phase can be written by equating the concentration gradients for the mass transfer of OA, MC and H₂ across the gas-liquid interface as follows:

For oleic acid as the feedstock (OA):

$$u_L \cdot A \cdot \frac{\partial C_{OA}^L}{\partial z} = -r_{OA} + \frac{K_{OA}^g \cdot a \cdot A_c}{R \cdot T_g} (x_{OA} P_{OA}^* - P_{OA}^g), \quad (4)$$

$$\text{For middle hydrocarbon (MC): } u_L \cdot A \cdot \frac{\partial C_i^l}{\partial z} = r + \frac{K_i^l \cdot a \cdot A_c}{R \cdot T_g} (x_i P_i^* - P_i^g), \quad (5)$$

Where u_L , C_i^L , r_i , P_i^g and P_i^* are the liquid velocity, liquid concentration, rate of reaction for each lump, partial pressure in the gas phase, and saturation pressure in the liquid-gas phase interface, respectively.

Energy balance equation for the reaction bed

$$\text{For liquid phase: } m_g C_p^l \frac{\partial T_L}{\partial z} = \sum r_i \Delta H_i A_c - h_G a A (T_g - T_l) - 2\pi r_m \varepsilon h_l (T_w - T_l), \quad (6)$$

Where m_g , C_p^l , T_L , T_g , T_w , h_G , ε , h_l and ΔH_i are mass flow-rate, specific heat of liquid phase, liquid temperature, gas temperature, reactor wall temperature, gas heat transfer coefficient, bed porosity, liquid heat transfer coefficient and enthalpy of reaction for each component, respectively. Also the calculation of the enthalpy of each lump reaction is shown:

$$\Delta H_i = \sum_{\text{Pr oducts}} \Delta H_p - \sum_{\text{Re ac tan ts}} \Delta H_r, \quad (7)$$

Here ΔH_p and ΔH_r are the enthalpy of all products and reactants respectively, which are oleic acid and hydrogen.

Energy balance equation for the tube of the reactor

$$K \frac{\partial^2 T}{\partial z^2} + K \cdot \frac{1}{r} \frac{\partial}{\partial r} \left(\frac{\partial T}{\partial r} \right) = 0, \quad (8)$$

Boundary conditions:

$$\text{At } r = r_{out} \quad -K \frac{\partial T}{\partial r} = h_{out} (T - T_{amb}), \quad (9)$$

$$\text{At } r = r_{in} \quad -K \frac{\partial T}{\partial r} = h_{in} (T - T_f), \quad (10)$$

$$\text{At } z = 0 \ \& \ z = L \quad \frac{\partial T}{\partial z} = 0, \quad (11)$$

Where T_{amb} and T_f are the ambient and fluid temperature respectively and h_{in} and h_{out} are the heat transfer coefficients inside and outside of the reaction side of the reactor.

Gas-liquid mass transfer coefficient

The correlation for the estimation of the gas-liquid mass transfer coefficients are

(29):

$$ej_D = \frac{0.765}{\text{Re}^{0.82}} + \frac{0.365}{\text{Re}^{0.386}} \quad (12)$$

$$j_D = \frac{Sh}{\text{Re} \cdot \text{Sc}^{1/3}} \quad (13)$$

$$Sh = \frac{K.d_p}{D_{AB}} \quad (14)$$

Here ε , D_{AB} , Sh , Re and Sc are porosity, molecular diffusion, Sherwood, Reynolds and Schmidt numbers respectively.

Molecular Diffusivity

In order to determine the gas-liquid mass transfer coefficient, it is essential to calculate the molecular diffusivity of each component in the liquid and gas. The diffusivity was determined by the Fuller correlation (34).

$$D_{AB} = \frac{1 \times 10^{-8} \cdot T^{1.75} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{0.5}}{P \left[\left(\sum_A v_i \right)^{1/3} + \left(\sum_B v_i \right)^{1/3} \right]^2}, \quad (15)$$

Where P , M_i and v_i are the total pressure, molecular weight and the specific volume of each component respectively.

Chemical Reaction Model

The applied rates of reactions in the hydrocracking reactor model are expressed as follows:

$$-r_{OA} = KC_{OA}, \quad (16)$$

$$r_{MC} = KC_{OA}, \quad (17)$$

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Where K and C_{oA} are reaction rate constant and oleic acid concentration, respectively. The reaction constant for MC lump can be estimated from the Arrhenius equation as follows:

$$K = A \exp\left(\frac{-Ea}{RT}\right), \quad (18)$$

Where K is the MC lump reaction constant in different temperatures and Ea is the activation energy for MC lump and the value which was reported in table 2 which were obtained by hydrocracking experimental data.

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CHAPTER 7

CONCLUSIONS & FUTURE WORK

7.1. Conclusions

This thesis develops the knowledge of catalytic bio-oil cracking towards biofuels. This work is based on modelling and experimental aspects of catalytic hydro-cracking of bio-oil. In the modelling aspect, a comprehensive mathematical model of the hydro-cracking reactor was developed and then the performance of the reactor was analysed with a precise sensitivity analysis. The modelling enables the process to be scaled up and commercialised. In experimental aspect, two types of non-expensive and sulphur free metal based over zeolites were prepared and analysed in a lab scale hydro-cracking unit and finally in chapter 6 both experimental works and modelling are connected together. All these work has been presented as journal publication or manuscripts under review as detailed previously. The following sections outline the specific conclusions drawn from the various parts of this research.

7.1.1. Investigation of the hydro-cracking reactor performance and sensitivity analysis

The modelling for hydro-cracking reactor was developed and the performance of the reactor was analysed with a sensitivity analysis on the inlet feed temperature, the reactor heat flow and the reaction bed length (explained in chapter 3 and 4). The result showed that 97% triglyceride conversion with increasing inlet feed temperatures from 380°C to 450°C was achieved. Moreover, the LC and MC production yields increased 38.3% and 55.04% respectively and HC lump yield decreased 15.19% between the input feed temperatures of 420°C and 450 °C. The input feed temperature of 450 °C was appropriate to maximise

the production concentration of main lump products (LC & MC). The reactor heat flow analysis showed that high liquid, gas and reactor wall temperature variations along the reactor provided negligible increases in LC and MC production rates. Therefore, the heat flow of 500 W/m^2 was found to be appropriate to conserve energy for hydrocracking reactions and obtain significant production rates for LC and MC. The reaction bed length analysis demonstrated that with higher bed lengths, more LC and MC were produced and the reaction bed length of 35 cm was appropriate for hydrocracking reactions in the micro-scale trickle bed reactor.

7.1.2. Hydro-cracking with non-expensive sulfured free zeolite catalysts

To identify an efficient catalyst for bio-oil catalytic hydro-conversion, two nickel impregnated catalysts based with ZSM-5 and Zeolite β were prepared, characterised with nitrogen adsorption, SEM and SEM-EDX. Results of SEM and SEM-EDX and analysed in a lab scale hydro-cracking unit (investigated in chapter 5). The characterisation results showed that nickel was impregnated properly over the zeolitic support. Ni-Zeolite β has larger surface area in comparison with the Ni-ZSM-5 but Ni-ZSM-5 sample has higher mesopore concentration in its structure. The large surface area of Ni-Zeolite β played as a significant parameter in conversion of oleic acid. Ni-Zeolite β has larger production yields of Nonane and Decane but Ni-ZSM-5 is more selective to Dodecane due to larger production yield of Dodecane in comparison with the Ni-Zeolite β . Therefore, Ni-Zeolite β and Ni-ZSM-5 are cheap to utilise as the catalyst of hydro-cracking reactions with appropriate efficiency in bio-oil conversion towards C_9 , C_{10} and C_{12} hydrocarbons which are the main components

of jet fuel. For the next step, the hydro-cracking modelling was applied and analysed for the Ni-Zeolite β catalyst due to higher conversion and production yield. The hydrocracking model was analysed in terms of oleic acid conversion at various hydrocracking reaction bed temperatures, production yields of MC and reactor wall and liquid temperature variation along the reactor. The validated hydrocracking reactor model and experimental data can be applied for further investigation for the production of biofuels in large scale.

7.2. Recommendations for future work

The results of this thesis advance the knowledge of bio-oil upgrading towards commercialisation. However further studies are required to analyse the non-expensive catalysts as hydro-cracking catalyst with various ranges of bio-oil to develop their kinetics and reaction mechanisms which are helpful in modelling applications and process optimisation. The future works are based on commercialisation of bio-oil upgrading and the major actions for future investigations are listed below:

- 1) Analysis of hydro-cracking with other types of bio-oil such as algae oil and vegetable oil over the developed non-expensive catalysts is required to check the performance of the applied catalysts in the hydro-cracking.
- 2) Further studies are required to analyse the catalyst deactivation in bio-oil hydro-cracking which is a significant parameter on biofuel production yields.
- 3) Developing a comprehensive kinetic model for hydro-cracking which is applicable for all bio-oil feedstocks.

- 4) Preliminary study on hydro-cracking pilot plant construction is needed.
This study should contain the process simulation and cost analysis for pilot plant construction.

APPENDIX A

APPENDIX A

CONFERENCE PRESENTATIONS



