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

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Abstract Over the last hundred years, fossil fuels consumption has increased dramatically leading to a significant increase in greenhouse gas emissions, the depletion of natural reserves of fossil fuels and increase fuel production costs. Consequently, renewable and sustainable fuel sources such as bio-oil are receiving increased attention. In bio-oils, such as microalgae 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 catalytic hydro-cracking. This chapter presents research on the catalytic conversion of oleic acid (main component in all types of bio-oil) in bio-oil to liquid hydrocarbon fuels employing two catalysts. These catalysts include Ni-ZSM-5 and Ni-Zeolite β, which were prepared by impregnating cheap catalyst supports (ZSM-5 and Zeolite β) with $Ni(NO_3)_2 \cdot 6H_2O$ calcined at a temperature of 500 °C. The catalysts were characterized using the Brunauer–Emmet–Teller Nitrogen Adsorption technique, scanning electron microscopy (SEM) and SEM–EDX (energy-dispersive X-ray spectroscopy) to analyse nickel impregnation and measure surface areas and pore size distribution. Conversion rates of oleic acid and product yields of liquid hydrocarbon fuels using each catalyst sample were determined via hydro-cracking reactions run at a temperature range of 300–450 °C and under a 30 bar pressure.

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1 Introduction

Nowadays, dramatic increases in the atmospheric concentration of greenhouse gases and carbon dioxide, lead to worldwide concern about global warming (Metz 2005; Figueroa et al. 2008). The most abundant greenhouse gases in the Earth's atmosphere are: vapour of water (H_2O), carbon dioxide (CO_2), methane, oxides of nitrogen and ozone (O_3) and chlorofluorocarbons (CFCs) (Luque et al. 2008). However, CO_2 has the major contribution to global warming, due to its high concentration in the atmosphere (Yamasaki 2003; Caspeta et al. 2013). During the last decades, significant global attempts have been allocated to developing new technologies that enables preventing CO_2 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 biosources. Currently, biofuels contribute about 2.7 % of the global energy consumption especially in the transport sector (Chum et al. 2011) and this mirrored in the evidence of high attention to bio-fuel technologies. Various resources exist for biofuel production which are categorised to edible and non-edible feedstocks (Luque et al. 2008; Brennan and Owende 2010). Non-edible feedstock such as Jatropha oil, Palm oil and algal oil is one of the major feed sources for economical biofuel production (Milne et al. 1990; Mortensen et al. 2011). Different types of bio-oil are produced in different places in the world. For instance, Malaysia and Indonesia are the key producers of more than 90 % of palm oil in the world (Sumathi et al. 2008). India is the most active country in Jatropha oil production (more than 400,000 ha plantation) and currently, several projects are active on bio-diesel production from Jatropha oil (Study 2008). Moreover, based on the Algae 2020 report, the governments of USA, Australia and New-Zealand allocated significant budgets for algal oil production (Demirbas and Fatih Demirbas 2011). But most of the bio-oil production plants for biofuel production are at research and development stage and have not been commercialised yet. For instance, Muradel, a company in South Australia, is one of the biggest algal oil production companies in Australia. This company can produce 30,000 L of green crude-oil per year (Vorrath 2014). The bio-oil from different feedstocks such as palm oil and algal oil, can be used directly in diesel engines, but the direct engine combustion causes carbon deposits and coking on the injectors and high viscosity of bio-oil interferes with engine operation (Bezergianni and Kalogianni 2009; Kumar et al. 2010). The afore-mentioned problems prove that bio-oil requires upgrading. Recently, bio-oil upgrading to applicable fuels has been highlighted due to low heating values, high viscosity and poor stability of crude bio-oil (Sharif Hossain and Salleh 2008; Sharma et al. 2012; Pragya et al. 2013). The overall aim of this chapter is focused on bio-oil upgrading towards biofuels with cost-effective catalysts. In the following sections, the different upgrading methods are investigated in details.

1.1 Bio-oil Upgrading Processes and Applied Catalysts

Bio-oil upgrading to applicable fuels is mandated due to low heating values, high viscosity and poor stability of crude bio-oil (Czernik and Bridgwater 2004; Elliott 2007; Wang et al. 2012). Bio-oil upgrading began with vegetable oil conversion over acidic and basic catalysts in the 1920s (Idem et al. 1997). Al_2O_3 and $AlCl_3$ were the early cracking acidic catalysts which were operated in batch reactors between temperatures of 450–500 °C (Leung et al. 1995; Idem et al. 1997). Esterification, hydro-treating and hydro-cracking are the three major existing processes for bio-oil conversion to fuels (Xiu and Shahbazi 2012). Esterification is the catalytic reaction between bio-oil and short chain alcohols as solvent such as methanol and ethanol and it is very popular in bio-diesel production but requires large amounts of solvent (Shi et al. 2012; Xiu and Shahbazi 2012). Hydro-treating is a simple hydrogenation process which has been applied in refineries to convert aromatics to naphthenes at temperatures above 500 °C and atmospheric pressure (760 torr), and has recently been applied for bio-crude conversion over sulfided Co and Mo/Al_2O_3, Ni and Mo/Al_2O in order to remove oxygen from triglyceride (Nava et al. 2009; Yang et al. 2009). Yields from hydro-treating processes are low due to sulfided catalyst applications as this produces significant amounts of char and coke in the process which can result in reactor clogging and catalyst deactivation (Xiu and Shahbazi 2012). Hydro-cracking is a combination of different cracking reactions with hydrogenation at high temperatures (above 350 °C) and high pressures (above 7 bar) (James and Jorge 2007; Mortensen et al. 2011) over dual-function catalysts. Dual-function catalysts have a zeolite or silica alumina base which provides the cracking function and metal oxides such as nickel, molybdenum which are catalysing the reactions towards light hydrocarbons (Milne et al. 1990; Nava et al. 2009; Mortensen et al. 2011; Tiwari et al. 2011; Verma et al. 2011; Shi et al. 2012; Xiu and Shahbazi 2012).

One of the recent upgrading methods is catalytic cracking of bio-oil to liquid hydrocarbon fuels (Benson et al. 2008; Bezergianni et al. 2009b; Kumar et al. 2010; Anand and Sinha 2012; Sharma et al. 2012; Pragya et al. 2013). The main advantage of using catalytic bio-oil cracking is that it is a single step process consuming less energy than other upgrading processes (Sharif Hossain and Salleh 2008; Verma et al. 2011; Shi et al. 2012). Catalytic upgrading of bio-oil consists of several complex reactions such as cracking, de-carbonylation, de-carboxylation, hydro-cracking, hydro-deoxygenation and hydrogenation. These complex reactions have been reported to take place on zeolitic supported catalysts (Adjaye and Bakhshi 1995a, b; Wildschut et al. 2009). Hence, bio-oil catalytic upgrading over zeolite catalysts became an alternative method for bio-oil and triglyceride conversion to usable fuels (Twaiq et al. 1999). Zeolitic catalysts are emerging as effective materials for efficient bio-oil cracking due to their high heating stability and strong acidity (Verma et al. 2011; Shi et al. 2012; Saxena and Viswanadham 2014). 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 (Katikaneni et al.

1995; Twaiq et al. 1999). These three types of zeolite catalysts were operated in the temperature range of 350–450 °C yielding 99, 82 and 53 % conversions with gasoline selectivity of 28, 22 and 7 %, respectively (Katikaneni et al. 1995; Twaiq et al. 1999). Also HZSM-5 led to produce aromatic hydrocarbons especially benzene and toluene, USY favoured the formation of diesel range of hydrocarbons while BEA formed fewer diesel (Katikaneni et al. 1995; Idem et al. 1997; Twaiq et al. 1999). 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 for HZSM-5, an issue correlating with pore diameter. Increased pore diameters intensifies coke formation inside the catalyst (Katikaneni et al. 1995; Zhao et al. 2013), but ZSM-5 and HZSM-5 catalysts have a great potential to produce gasoline- and jet fuel-range of hydrocarbons with less coke formation [14, 26, 27]. Application of ZSM-5, HZSM-5 and MCM-41 as catalyst for fatty acids and bio-oil conversion have been investigated (Twaiq et al. 2004; Ooi et al. 2005), demonstrating gasoline selectivity increases to the range of 38–47 % (Twaiq et al. 2004; Ooi et al. 2005). The most important section in bio-oil upgrading to biofuels is oxygen extraction from bio-oil. Recent investigations has shown that oxygen removal can be performed with a number of parallel reactions such as hydro-deoxygenation which produces water, de-carboxylation which produces CO_2 and de-carbonylation which generates carbon monoxide (CO) (Morgan et al. 2012). Based on this approach, several researchers developed a single step process with different ranges of zeolitic catalysts to convert bio-oil to paraffinic fuels. The single step process of bio-oil upgrading has been termed catalytic hydro-treating. Since, this process is performed in only one step, it is energy efficient and it can be performed over metal based catalysts.

In Table 1, the list of various catalysts which were applied in single step hydro-processing of bio-oil from different feedstocks is provided. In this table, the bio-oil feedstocks were categorised as vegetable oil, Jatropha oil and Algal oil. All of the listed catalysts were analysed in continues flow reactors.

In the next part, the application of various metal-based catalysts and their advantages and disadvantages for bio-oil hydro-treating are discussed in detail.

1.2 Application of Supported Metal Sulfide Catalysts

Metal-based catalysts for bio-oil and triglyceride conversion can be categorised as two main types: metal-sulfide catalysts and sulfur-free metal catalysts. The common sulfided catalysts for bio-oil conversion are conventional Ni–Mo and Co–Mo sulphide catalysts over zeolites. They are used in petroleum refineries to produce straight-chain alkanes ranging from C_{12} to C_{18} at temperatures of 350–450 °C in the presence of hydrogen with pressures of 40–150 bar (Donnis et al. 2009; Choudhary and Phillips 2011). The sulfided catalysts have been analysed widely in hydro-treating of bio-oil to produce diesel and middle range of hydrocarbons. For example, Bezergianni et al. analysed catalytic hydrocracking of waste cooking oil

Table 1 Hydro-processing of different bio-oil feedstocks over a range of catalysts (Verma et al. 2011; Zhao et al. 2013)

Feedstock	Catalyst	T (°C)	t (h)	Conversion (%)
Vegetable oil	1 % Pt/SiO$_2$	300	12	2.4
	1 % Pt/SiO$_2$–Al$_2$O$_3$	300	12	5.6
	1 % Pt/HZSM-5	300	12	68
	1 % Pt/HZSM-5	300	12	43
	1 % Pt/USY	300	12	90
	1 % Pt/USY	300	12	75
	1 % Pt/BEA	300	12	25
	1 % Pt/HY	300	12	30
	1 % Pt/H-MOR	300	12	2.3
	1 % Pt/FER	300	12	52
	1 % Pt/L	300	12	1
	5 % Pd/C	350	10	23
	1 % Pt/C	350	10	30
	20 % Ni/C	350	10	92
	RANEY® Ni	340	9	85
	27 % Ni/Al$_2$O$_3$	340	9	90
	5 % Pt/Al$_2$O$_3$	325	5	46
Jatropha oil	1 % Pt/HZSM-5	270	12	100
	1 % Pt/USY	270	12	31
	1 % Pt/HZSM-5	270	12	22
	4 % NiO, 18 % MoO$_3$/Al$_2$O$_3$	370	–	99
Algal oil	10 % Ni/HBEA	260	8	100
	10 % Ni/ZrO$_2$	270	8	100
	4 % NiO, 18 % MoO$_3$/Al$_2$O$_3$	370	–	99
	5 % NiO, 18 % MoO$_3$/H-ZSM-5	410	–	98

with sulfided Ni–Mo/γ-Al$_2$O$_3$ to produce white diesel. Hydrocracking increases the H/C ratio, and removes hetero-atoms S, N, O, and metals from the bio-oil feedstock (Bezergianni et al. 2010a, b). In their studies, temperature increase from 330 to 398 °C led to an increase in the fraction of iso-paraffins from 5 to 38 %, and the lighter alkanes (C$_8$–C$_{14}$) increased also to 22 % at 398 °C. A main disadvantage of this liquid fuel is the poor flow properties at lower temperatures (Bezergianni et al. 2010a, b). Gusmao et al. investigated hydrocracking of soy bean and babassu oils in a batch reactor at a temperature range of 350–400 °C and at H$_2$ partial pressures of 10–200 bar. They applied sulfided Ni–Mo/γ-Al$_2$O$_3$ and reduced Ni/SiO$_2$ catalysts, and found that only double bonds were hydrogenated in soy bean oil at a reaction temperatures <200 °C. The decomposition of triglycerides accompanied by hydrogenation of the decomposition products was detected above a temperature of 290 °C. Compared to reduced Ni catalyst, sulfided 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 (Gusmão et al. 1989).

Kubička et al. researched hydro-processing of rapeseed oil for the production of components in the diesel fuel range (Smejkal et al. 2009; Kubička and Kaluža 2010; Šimácek et al. 2010). Rapeseed oil was hydro-processed at 260–340 °C under a hydrogen pressure of 70 bar in a continuous trickle bed reactor. Three $Ni-Mo/Al_2O_3$ sulfide hydro-treating catalysts were evaluated. Reaction products included water, H_2-rich gas, and an organic liquid product. The main components of the organic liquid product were C_{17} and C_{18} 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 the diesel range of hydrocarbons (Smejkal et al. 2009; Kubička and Kaluža 2010; Šimácek et al. 2010). Furthermore, Ni/Mo-based catalysts were applied in hydro-processing of Jatropha oil, Palm oil, Canola oil and sunflower oil (Topsøe et al. 1996; Huber et al. 2007; Gutiérrez et al. 2011). Corma et al. analysed the hydro-processing of pure sunflower oil over sulfided $Ni–Mo/Al_2O_3$ at 350 °C and achieved complete oil conversion with 71 % yield of $C_{15}–C_{18}$ alkanes (Huber et al. 2007). Also Jatropha, Palm and Canola oil were tested over Ni/Mo-based catalysts in a high pressure fixed bed flow reactor at a temperature of 350 °C and hydrogen pressure of 40 bar (Topsøe et al. 1996; Gutiérrez et al. 2011). Among the Ni/Mo-based catalysts, Ni–Mo/H-Y and Ni–Mo/H-ZSM-5 formed a high yield of gasoline-range 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].

1.3 Application of Supported Sulfured-Free Metal Catalysts

Supported noble metal catalysts such as Pd/C are frequently analysed for de-carboxylation and de-carbonylation of fatty acids in different bio-oil feedstocks (Maier et al. 1982; Kubicková et al. 2005; Snåre et al. 2006; Immer et al. 2010; Immer and Lamb 2010; Ping et al. 2010, 2011; Arend et al. 2011; Fu et al. 2011; Ford et al. 2012). For instance, 5 wt% Pd/C can yield 100 % C_{17} and C_{18} from stearic acid at a temperature of 300 °C (Snåre et al. 2006). Noble metal catalysts showed high activities and selectivity for fatty acid conversion in a comprehensive analysis by Murzin et al. (Mäki-Arvela et al. 2006; Snåre et al. 2007, 2008; Lestari et al. 2008; Lestari et al. 2009a, b; Simakova et al. 2009). However, activities and selectivities for the targeted alkanes for triglycerides conversion were considerably lower (Simakova et al. 2008; Morgan et al. 2010). The high price of noble metals limits their industrial applications as catalysts.

Furthermore, Peng et al. (2012) used base metal catalysts such as Ni supported on zeolites for hydro-deoxygenation of fatty acids. Ni/HZSM-5 (10 wt%) catalysed

complete conversion of stearic acid to dodecane at a temperature of 260 °C for 6 h in the presence of 40 bar hydrogen pressure. Zhang et al. (2013) prepared Ni-based catalysts over γ-Al_2O_3 and HZSM-5 (Si/Al = 38) for hydro-treatment of bio-oil. Their catalysts were analysed in a temperature range of 160–240 °C achieving a conversion of 91.8 %. Yakovlev et al. (2009) investigated nickel-based catalysts due to their cost-effective property and found that applying nickel in the catalytic upgrading system of bio-oil could conduct the upgrading reactions at lower temperatures and cost and produce biofuel with low sulphur content.

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, sulfided metal-based zeolitic catalysts led to product contamination with sulfur and deactivation of the catalyst by S removal. Consequently, application of non-sulfur metal-based catalyst over zeolite is the most cost-effective option for bio-oil upgrading which is investigated in this research. In this chapter two types of inexpensive non-sulfided Ni-based bi-functional catalysts are introduced characterised and then analysed in a bio-oil upgrading process.

Sulfur present in catalyst structures caused bio-oil contamination and catalyst deactivation (Bui et al. 2011; Xiu and Shahbazi 2012). As mentioned before, several researchers have published hydro-cracking of bio-oil based on non-sulfided catalysts with zeolite or Al_2O_3 as a base and metal-oxide function such Pd and Pt (Díaz et al. 2007; Fisk et al. 2009; Zhao et al. 2009; Zhang et al. 2013; Forghani et al. 2014; Forghani and Lewis 2015). Among different metal oxides, application of nickel on zeolitic structures is cost-effective and efficient in hydro-processing of oxygenated compounds such as oleic acid in bio-oil. Therefore, in this presentation two types of inexpensive sulfur-free, Ni-based bi-functional catalysts are introduced, characterised and then analysed in a lab scale hydro-cracking unit. Temperature, residence time, and catalyst structure are investigated as effective parameters on reaction conversion and production yield.

2   Materials and Methods

2.1   Catalyst Preparation

Ni/ZSM5 and Ni/β-Zeolite were prepared using a conventional impregnation method. ZSM-5 and β-Zeolite were purchased from ACS Materials Company and Zeolyst International, respectively (with SiO_2/Al_2O_3 molar ratio of 38 for both of them). The impregnation of $Ni(NO_3)_2 \cdot 6H_2O$ (Sigma Aldrich) solution on ZSM-5 and β-Zeolite supports was performed, by mixing the supports with the nickel impregnation solution under stirring for 2 h, followed by drying in an oven. Materials were then calcined in a furnace with starting temperature increases of 10 °C/min to 500 °C and kept at this temperature for 5 h.

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 h. 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 analyses were carried out on 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   Hydrocracking 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 g) of catalyst was weighted (based on the reactor design) and then loaded into the stainless steel tubular reactor with an inside diameter of 1.2 cm and a catalytic bed of 20 cm. The reactor was situated in a furnace to run at high temperatures. Hydrogen pressure was controlled by a back pressure regulator. An HPLC pump was used to pump the liquid into 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 especially micro-algae oil. The oleic acid percentage in algae oil varies from 39–60 % (Demirbas and Fatih Demirbas 2011; Verma et al. 2011). Oleic acid was injected together with a large volume of hydrogen into the reactor and, after passing through the catalyst bed, the products, unreacted reactant and excess hydrogen passed through a separator and the liquid samples were obtained from the bottom of the separator. The schematic of the hydro-cracking lab-scale process is shown in Fig. 1. Furthermore, the hydrocracking reactions were performed at different reaction bed temperatures and the operating conditions are mentioned in Table 2.
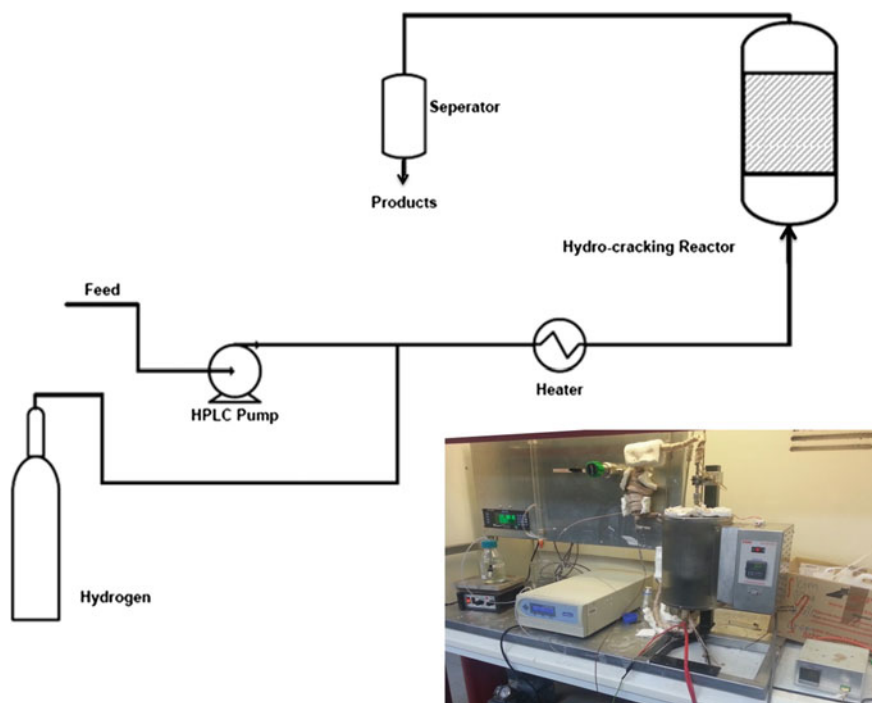
Fig. 1 Hydro-cracking lab-scale set up to analyse performance of the prepared catalyst

Table 2 Catalyst loading and operating conditions

Catalyst mass	1 g
Catalyst shape	Powder
Bed length	10 cm
Reactor diameter	1.1 cm
Reaction temperature range	300–450 °C
Reaction pressure	30 bar
Oleic acid flow	0.1 mL/min
Hydrogen/feed	1000 Nl/l

2.4 Product Analysis

The product samples were collected at the end of the separator and they were analysed by gas chromatography (GC) [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 standards to analyse and measure the outlet products of the hydro-cracking reactions. C_9, C_{10} and C_{12} are the main components of jet-fuel and

by using them as standards, a calibration curve was used to measure the yields of C_9, C_{10} and C_{12} for each catalyst. The GC analysis was performed for all samples at an FID temperature of 200 °C and the oven temperature program was increased from 50 to 150 °C at the rate of 10 °C/min and then from 150 to 200 °C at the rate of 15 °C/min. The performance of each type of catalyst was evaluated based on their efficiency for conversion of oleic acid and yields of the jet fuel range of hydrocarbons. Conversion and yields of C_9, C_{10} and C_{12} were calculated based on calibration curves of the feed (oleic acid) and products which were defined with the following equations:

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

$$(1)$$

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

3 Results and Discussions

3.1 Catalyst Characterisation

Figure 2 shows scanning electron microscopy images of Ni-Zeolite β (a) and Ni-ZSM-5 (b) catalysts. Particles are agglomerated in some areas, shown as grey rectangular structures. Black areas correspond 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) tests were randomly selected bright white spots. The average spectrum is shown in Fig. 2c. Nickel has K and L emission energy rates of 7.477 and 0.851 keV, respectively. Figure 2c shows two pronounced peaks for Ni at corresponding Ni energy rates for Ni-Zeolite β. Figure 2d also shows a single peak at K energy rate of Ni. Analyses of EDXS results together with electron microscopy images confirmed the presence of nickel on the catalyst surface.

The nitrogen adsorption isotherms, pore size distribution, and textural properties of the Ni-ZSM5 and Ni-Zeolite β are provided in Fig. 3 and Table 3. Both catalysts show similar types of adsorption isotherms including a relatively large contribution of micropores, significant contribution of mesopores and a type H4 hysteresis loop in the desorption branch. The hysteresis loop is more pronounced for Ni-ZSM-5 due to large contribution of mesopores than for Ni-Zeolite β, where it can hardly be seen in the adsorption isotherm.

Calculated pore size distribution (PSD) for both adsorbents show a narrow sharp peak in the micropore range (around 5 Å) and small but wider peaks in the larger
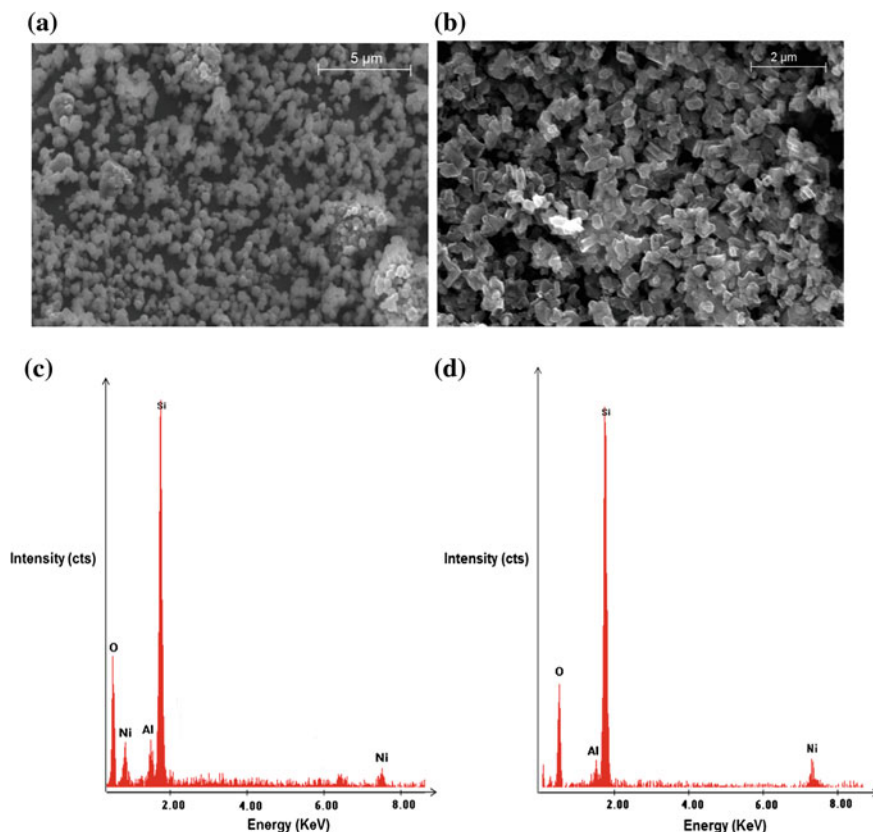
Fig. 2 Scanning electron microscopy (SEM) images of Ni-Zeolite β (**a**) and Ni-ZSM-5 (**b**) and Energy-dispersive X-ray spectroscopy for Ni-Zeolite β (**c**) and Ni-ZSM-5 (**d**)

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 had relatively the same pore volume (≈ 0.28 cm^3/g). Ni-Zeolite β was more microporous and had a larger contribution of micropores; 86 % of total porosity was due to microporosity (see Table 3 for comparison between two catalysts). Due to the large microporosity in Ni-Zeolite β, this sample had 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.

Based on the porosity of the catalysts, two different reaction mechanisms are expected; if the reactant (oleic acid) and the products (C$_9$–C$_{12}$) can diffuse within and across the entire porosity of samples including micropores and mesopores, the entire surface area would be available for the reaction, reaction yields 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 (≈ 5Å), micropore surface area

(a)

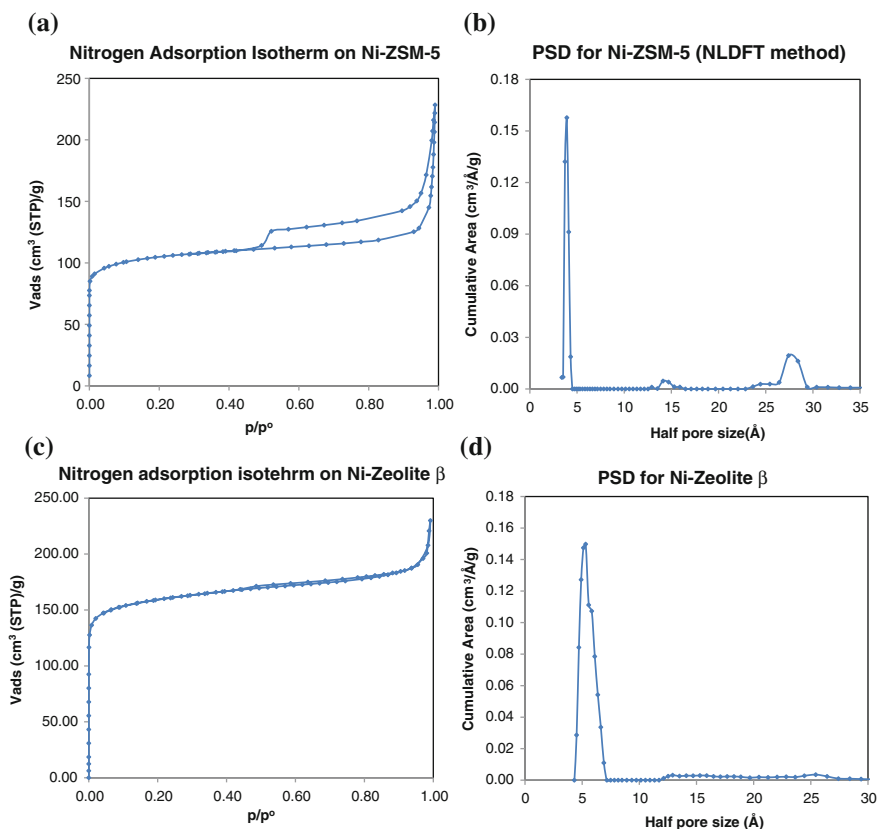

(b)

(c)

(d)

Fig. 3 Nitrogen adsorption isotherm and pore size distribution (PSD) results of Ni-ZSM-5 (**a**) and Ni-Zeolite β (**b**) catalysts

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

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

[a]Surface area is calculated based on BET method (Brunauer et al. 1938)
[b]Micropore volume is calculated based on α_S method (Sing 1968)
[c]Total pore volume is calculated based on nitrogen amount adsorbed at near saturation pressure converted to liquid volume

would not be accessible for reaction and reaction yields for the sample with higher mesoporosity would be larger (Ni-ZSM-5). Since the reactant (Oleic acid) and products (C_9–C_{12}) are all linear shaped hydrocarbons, their kinetic diameter is in the

order of the kinetic diameter for linear hydrocarbons (normally less than 5 Å). For instance, kinetic diameter for n-Nonane (C_9) is reported 4.3 Å in the literature (Grillet et al. 1993). Hence, we expect the reactant and products to be able to diffuse throughout the porosity and across the total surface area for both samples accessible for reaction. Results in the next section shows higher reaction yields 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 are presented in Figs. 4 and 5. Figure 5 represents the oleic acid conversion versus time over Ni-ZSM-5 and Ni-Zeolite β. The results of Fig. 4 were obtained at a temperature of 425 °C and other operating conditions were maintained as per Table 2. 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, remained stable after 30 min and the variation of conversion was not significant over time. This conversion rates were obtained after all system specifications such as temperature and pressure reached steady state conditions. The conversion rate of oleic acid was ∼94 and ∼87 % for Ni-Zeolite β and Ni-ZSM-5, respectively at a temperature of 425 °C. Figure 4 proves that steady state for the hydro-cracking reactions was reached after 30 min in the reactor and the variation in oleic acid conversion was insignificant. The retention time based on feed flowrate and reactor volume was ∼9.5 min.

Figure 5a shows the oleic acid conversion over Ni-ZSM-5 and Ni-Zeolite β at 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

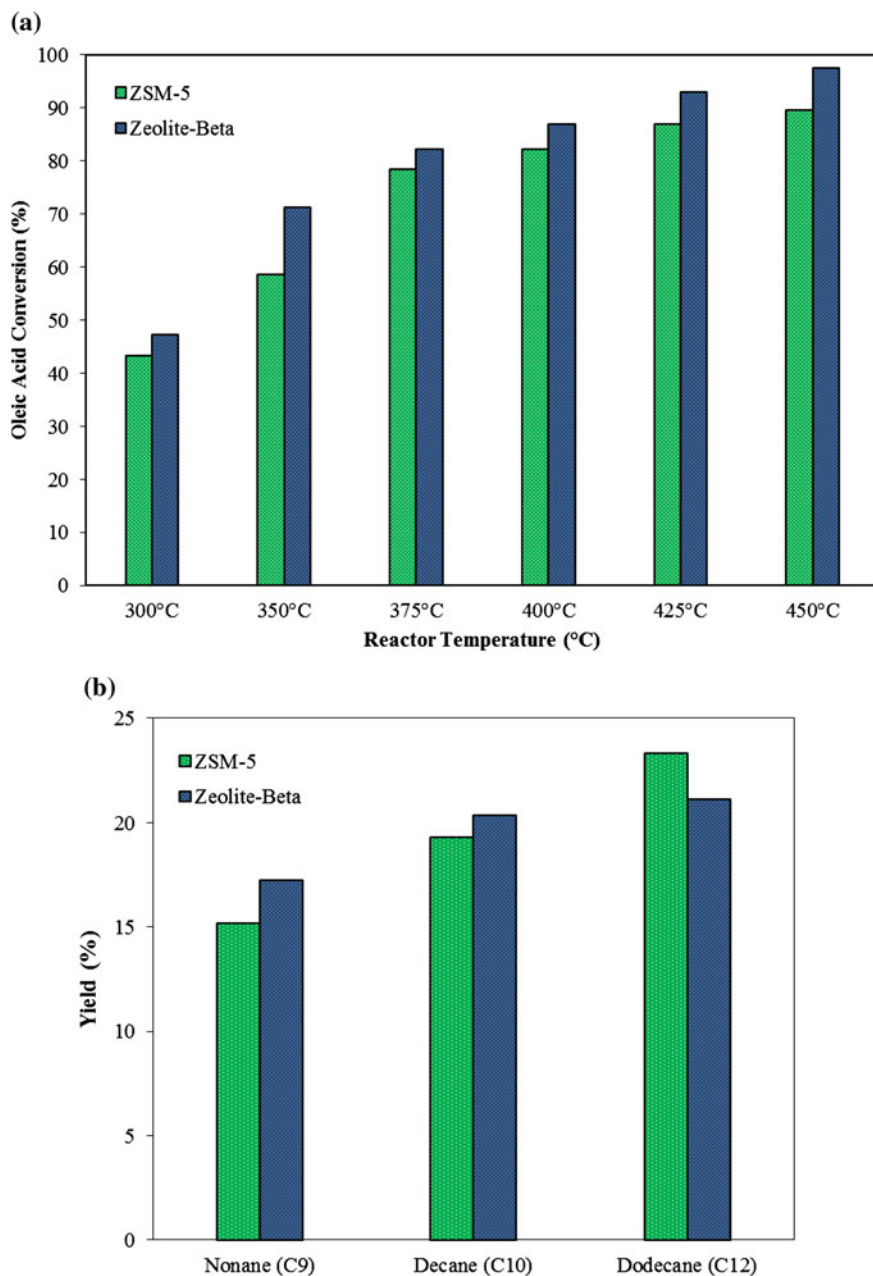**Fig. 4** Oleic acid conversion as a function of time over Ni-ZSM-5 and Ni-Zeolite β

(a)

(b)
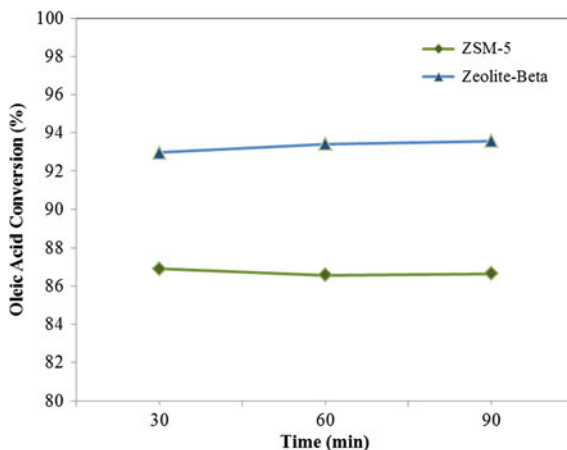
Fig. 5 Dependence of oleic acid conversion on reaction bed temperature for Ni-ZSM-5 and Ni-Zeolite β (**a**) and production yields of Nonane (C_9), Decane (C_{10}) and Dodecane (C_{12}) over Ni-ZSM-5 and Ni-Zeolite β at a temperature 400 °C

conversion which is defined in Eq. 1. The hydro-cracking reactions of oleic acid were 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 rates in comparison with Ni-ZSM-5 due to its larger total surface area. Maximal oleic acid conversion occurred at temperatures of 300 to 350 °C which were 35.4 and 50.5 % for Ni-ZSM-5 and Ni-Zeolite β, respectively. In addition, previous studies showed that hydro-cracking reactions especially deoxygenation of oxygenated compounds such as oleic acid are more active in higher temperatures (Huber et al. 2007; Bezergianni and Kalogianni 2009; Bezergianni et al. 2009a).

Yields of production over both catalyst types are presented in Fig. 5b. To measure production yields, hydro-cracking reactions were performed at 400 °C and a pressure of 30 bar with a Hydrogen/Feed of 1000 Nl/l. The hydro-cracking temperature was chosen and maintained at 400 °C based on the literature—described as an optimum temperature for hydro-cracking (Tiwari et al. 2011; Verma et al. 2011). Yields of three targeted components (C_9, C_{10} and C_{12}) were calculated based on Eq. 2. It is clearly seen that Nonane (C_9) and Decane (C_{10}) production yields over Ni-Zeolite β were greater than Ni-ZSM-5 but for Dodecane, Ni-ZSM-5 showed better performance. The reason for higher production yield for Nonane and Decane in Ni-Zeolite β was 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 production of larger molecules such as Dodecane and improved selectivity of deoxygenation reaction towards C_{12} in comparison with Ni-Zeolite β. The difference of Dodecane production yield was 10.5 %.

Hence, better performance of Ni-Zeolite β was evident by the higher oleic acid conversion rates and higher production yields of C_9 and C_{10} but Ni-ZSM-5 showed better performance for C_{12} yields of production. Nonetheless, Ni-Zeolite β has a great potential to be applicable in large-scale hydro-cracking reactions for the conversion of bio-oil to C_9, C_{10} and C_{12} hydrocarbons, the main components of jet fuel.

4 Summary

Hydro-cracking of oleic acid with two samples of nickel impregnated catalysts on ZSM-5 and Zeolite β was performed to produce bio-fuel. Nickel impregnation of ZSM-5 and Zeolite β was characterised by BET Nitrogen Adsorption techniques, SEM and SEM-EDX and surface areas and pore size distribution was measured. The SEM and SEM-EDX analysis confirmed that nickel was impregnated properly in the two catalyst samples. The BET Nitrogen Adsorption results and pore size distribution analysis confirmed that Ni-Zeolite β had a larger surface area in comparison with the Ni-ZSM-5, but Ni-ZSM-5 had a 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 had higher production yields of Nonane and Decane, but Ni-ZSM-5 achieved higher Dodecane yields due to larger pore sizes compared to the Ni-Zeolite β. Therefore, Ni-Zeolite β and Ni-ZSM-5 are cheap to utilise as catalysts of hydro-cracking reactions with appropriate efficiency in bio-oil conversion towards C_9, C_{10} and C_{12} hydrocarbons, which the main components of jet fuel.

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