CONVERSION OF WASTE COOKING OIL INTO BIOFUELS USING TRIMETALLIC CATALYST

by

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Nur Alya binti Rashid

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LIST OF ABBREVIATIONS

Al	Aluminium
Al_2O_3	Aluminium Oxide
Co	Cobalt
Cu	Copper
FCC	Fluidized Catalytic Cracking
Fe	Iron
GC-MS	Gas Chromatography Mass Spectroscopy
H^+	Positive Charged Proton
H_2	Hydrogen Gas
LCO	Light Cycle Oil
N	Nitrogen
Ni	Nickel
O	Oxygen
OLP	Organic Liquid Product
S	Sulphur
Si	Silica
Sn	Tin
UVO	Used Vegetable Oil
WCO	Waste Cooking Oil

PENUKARAN SISA MINYAK MASAK KEPADA BIO-BAHAN API MENGGUNAKAN PEMANGKIN TRI-LOGAM

ABSTRAK

Minyak masak adalah penting untuk kegunaan harian terutamanya di restoran, pengeluar makanan, dan isi rumah. Minyak masak kebanyakannya diperbuat daripada minyak sawit, sayuran, kelapa atau minyak asli. Walau bagaimanapun, minyak masak terpakai kerap dibuang melalui saliran dari singki dapur. Hampir 50,000 tan sisa minyak masak yang berasal daripada minyak sayuran atau lemak haiwan telah dilepaskan ke alam sekitar tanpa rawatan yang sewajarnya. Ini boleh menyebabkan pelepasan bau yang tidak menyenangkan dan juga penyebaran bakteria yang menyebabkan herpes mulut dan alat kelamin. Oleh itu, mengitar semula sisa minyak masak kepada bio bahan api bukan sahaja akan memberi manfaat kepada bahagian pengangkutan tetapi juga membantu dalam pengurusan sisa. Keretakan bermangkin digunakan dalam kajian ini adalah untuk menghasilkan bio bahan api menggunakan sisa minyak masak. Dalam kajian ini, jenis mangkin berbeza (Zeolit Y, Cu/Zeolit Y, Ni/Zeolit Y, Cu-Ni/Zeolit Y, Cu-Ni-Fe/Zeolit Y dan Cu-Ni-Zn/Zeolit Y) , suhu operasi (300°C, 350°C dan 400°C) dan masa kajian (60, 90 dan 120 minit) telah dikaji untuk menentukan kesan terhadap keretakan bermangkin sisa minyak masak. Hasil cecair, kok dan gas telah disiasat untuk semua tindak balas. Hasil cecair juga telah dianalisis menggunakan penyulingan ASTM. Melalui kajian ini, parameter operasi terbaik ialah; menggunakan mangkin tri-logam Cu-Ni-Zn/Zeolit Y, 350 ˚C dan 60 minit kerana ia menghasilkan hasil cecair tertinggi (78.43%), hasil gas (21.44%) dan kok terendah (0.13%) dan peratusan sisa terendah (28%) dengan jumlah hidrokarbon yang tinggi. Hasil hidrokarbon mengandungi gasoline (1%), kerosene (16%) dan diesel (55%).

CONVERSION OF WASTE COOKING OIL INTO BIOFUELS USING TRIMETALLIC CATALYST

ABSTRACT

Cooking oil is essential for daily used especially in restaurants, food manufacturers, and households. The cooking oil is mostly made up from palm, vegetable, coconut, or natural oils. However, the used cooking oil is often disposed through the drainage from the kitchen sinks. Nearly 50,000 tonnes of waste cooking oil derived from vegetable oils or animal fats were released into the environment without appropriate treatment. This could lead to emission of unpleasant odour and disturb the nearby residents. Therefore, recycling waste cooking oil into biofuels not only will benefit the transportation section but also help in waste management. Catalytic cracking is used in this study is to produce biofuel from waste cooking oil. In this study, different type of catalysts (Zeolite Y, Cu/Zeolite Y, Ni/Zeolite Y, Cu-Ni/Zeolite Y, Cu-Ni-Fe/Zeolite Y and Cu-Ni-Zn/Zeolite Y), operating temperature (300°C, 350°C and 400°C) and residence time (60, 90 and 120 minutes) were studied to determine their effects on catalytic cracking of the waste cooking oil. The as liquid yield, coke and gas yield were investigated for all the reactions. The liquid product was also anaylyzed with ASTM distillation. Through this study, the best operating parameters are; using tri-metallic catalyst Cu-Ni-Zn/Zeolite, the temperature of 350 ˚C and 60 minutes as it produced the highest liquid yield (78.43%), the lowest gas yield (21.44 %) and coke yield (0.13 %), and the lowest residues percentage (28 %) with high amount of hydrocarbon. The hydrocarbon yield consists of gasoline (1%), kerosene (16%) and diesel (55%).

CHAPTER 1

INTRODUCTION

1.1 Catalytic Cracking of Waste Cooking Oil

Changes in lifestyle and population growth have accelerated energy consumption significantly over the last few decades. The increase in energy demand has been met primarily by the use of fossil gas resources, which are limited and pose serious environmental problems. As a result, renewable fuel, such as biofuel, are in high demand (Meka et al., 2007). Because of its abundant resources and environmental benefits, biofuel has gained attention as an alternative fuel. This biofuel can be made from a variety of oils, both edible and non-edible. Non-edible oils include jatropha, microalgae, neem, rubber seed, and many others (Demirbas et al., 2009). Meanwhile, edible oils are extracted from plants, animals, or microorganisms, like vegetable oil or primarily palm oil for Malaysia.

Vegetable oils play a significant role in all Malaysian cuisine, particularly fried foods. Cooking oils are mostly made up of palm, vegetable, coconut, or natural oils. Restaurants, food manufacturers, and households are the primary consumers of cooking oil. Cooking oils not only transfer heat when cooking, but they also contribute to the flavour of the food. As Malaysia's population grows, so does the demand for cooking oil to satisfy the demands for food. According to the report, nearly 50,000 tonnes of waste cooking oil derived from vegetable oils or animal fats were released into the environment without appropriate treatment (Loh et al., 2006). This action has an impact on drainage and soils, which could lead to pollution of the environment. Waste cooking oils are not only found at food stalls, hawker centers, and food courts; they are also found in regular households, where waste cooking oils are drained away from kitchen sink drains (Haruhiro et al., 2015). If these habits are passed down to the next generation, they will have a negative impact on the environment.

One solution is to recycle used cooking oil into something more beneficial to our environment and economy. We can reduce wastewater clean-up expenditures by recycling waste cooking oil, which is plentifully disposed of. As previously stated, waste cooking oil is mostly discarded into the kitchen sink and then flows into the sewage disposal. As the temperature drops, the oil solidifies and blocking up the drain pipe and sewage system. It will cause issues with the sink sewage system since it will be unable to properly drain the waste water. As a result, the property owner will need to hire a plumber to fix the system. If the oil gets into the sink, it will emit an unpleasant odour and the contents may overflow onto the street. It can also spread bacteria that cause disease, such as measles, and others. So, in order to avoid such a situation, recycling the oil can be favourable to both the human health and the environment (Fuels, 2017).

Used cooking oil can be converted into renewable energy, which many sectors can use to manage their products. Waste cooking oil has become the talk of the town because it can be transformed into biofuels that may replace fossil fuels. Vehicles that use diesel as their fuel can fully benefit from this production, and businesses involving automobiles or machines can shift their focus to developing diesel-functioning systems, potentially lowering the cost for their users (Zafar et al., 2021).

Biodiesel is made up of long-chain fatty acids mono-alkyl esters derived from vegetable oils or animal fats. Transesterification, a reaction involving triglycerides and alcohols in the presence of catalysts to form fatty acid alkyl esters, is the most common method of producing biodiesels. This reaction produces glycerol known as glycerine as a byproduct. However, there are two major issues with transesterification: the process is time consuming, and oil separation is needed. As a result, another option for improving biodiesel production from waste cooking oil is catalytic cracking (Baskar et al., 2019).

Catalytic cracking is the process of breaking down large compounds into smaller hydrocarbons using acidic catalysts. Conventional catalytic cracking can be accomplished in two ways; liquid phase cracking and vapour phase cracking. The reaction mixture in liquid phase catalytic cracking is kept at a temperature of around 500˚C and a pressure of 20 atm. Silica or zeolite compounds are frequently used as catalyst because they have a larger surface area. This system produces octane numbers ranging from 65 to 70. Temperatures of around 600 ˚C and pressures of 10 atm are used in vapour phase catalytic cracking. Zeolite is used as the catalyst. This cracking is completed in the presence of hydrogen gas. It is also known as hydrocracking. Here, carbon-carbon bonds are broken down. (Madhusha, 2017).

1.2 Problem Statement

Waste cooking oil is used in the production of biofuels because it is economical, abundantly available, and reduces environmental issues related to waste cooking oil disposal. Catalytic cracking is in favour compared to the typical transesterification. Due to the extra post-treatment processes of separation, water washing, and heating, transesterification is an expensive technique for producing biofuel (Suthar et al., 2019). Catalytic cracking is a super approach since it does not require any post-treatment, which lowers operating costs. Converting used cooking oil to biofuel reduces reliance on both domestic and imported fossil fuels. Fossil fuels emit greenhouse gases, which contribute to global warming. Biofuels emit little to no carbon and have a low sulphur content, making them safer for the environment and human health. Catalytic cracking of different vegetable oils was carried out utilising mono and bimetallic catalysts and resulted in increase coke production and decrease organic liquid product (OLP). There has been limited study for the catalytic cracking reaction using tri-metallic catalysts. Therefore, the purpose of this research is to develop a tri-metallic catalyst for the catalytic cracking of waste cooking oil. The effect of different operating parameters such as reaction temperature and residence time for the reaction have also been carried out.

1.3 Research Objectives

The objectives of this research are:

i. To compare the performance of different tri-metallic catalysts on the catalytic cracking of waste cooking oil into biofuel.

ii. To investigate the effects of operating temperature and residence time in the reaction.

CHAPTER 2

LITERATURE REVIEW

This chapter is divided into six sections. The first section discusses waste cooking oil as a feedstock for catalytic cracking. This follows with the catalytic cracking as a method of producing bio fuel. The third section is about the catalyst used during the reaction and the fourth to sixth sections is about the effect of various operating parameters.

2.1 Waste cooking oil as a feedstock for catalytic cracking

Waste cooking oil (WCO) is produced when edible vegetable oils such as sunflower, palm and maize oil has been fried various of times. During the frying process, it changes the physical and chemical characteristics of the fresh cooking oils. Due to the enormous growth in human population, the amount of WCO produced by households and restaurants are increasing rapidly. WCO cost double to triple lesser than freshly produced vegetable oil leading to a substantial decrease in overall production cost. When compared to traditional diesel, the cost of biofuels production becomes a significant impediment to its commercialisation. To get the budget-friendly biofuels, the cost of the feedstocks must be lessened. Since using the waste that will be disposed anyway, the cost of the raw material is negligible compared to the fresh vegetable oil for the production of biofuel. As a result, used cooking oil is an attractive feedstock for producing biofuel. Furthermore, WCO usage will not deplete the food resources, as is the case with the virgin edible oils usage, which eliminates any potential dispute in this regard (Yaakob et al., 2013).

The main components in waste frying oil are oleic acid and linoleic acid. Table 2.1 shows the chemical and physical properties of WCO, reported by Wen et al (2010).

Table 2.1: Chemical and physical properties of WCO by Wen et al. (2010)

Property	**Units**	**Value**
Palmitic acid	wt%	8.5
Stearic acid	wt%	3.1
Oleic acid	wt%	21.2
Linoleic acid	wt%	55.2
Linolenic acid	wt%	5.9
Others	wt%	4.2
Water content	wt%	1.9
Density	cm^3/g	0.91
Kinematic viscocity (40˚C)	mm^2/s	4.2
Saponification value	mgKOH/g	207
Acid value	mgKOH/g	3.6
Iodine number	$\mathrm{gl_2 100g^{-1}}$	83
Sodium content	mg/kg	6.9
Peroxide value	mg/kg	23.1

2.2 Catalytic cracking

Back in 1920, thermal cracking is used to convert the gas oils into naphtha. However, the production created unstable naphthas and has high coke-formation as the by-product. While they were successful in increasing gasoline yields slightly, the introduction of the fluid catalytic cracking method in 1942 had set the stage for modern petroleum refining. The catalytic cracking process is not only provided a very efficient method of turning high-boiling gas oils into naphtha to fulfil the expanding market for higher gasoline, but it also marked a breakthrough in catalyst technology. The use of a catalyst in the cracking reaction boosts the yield of high-quality products while working under far less harsh circumstances than thermal cracking. A catalyst helps to remove a negatively charged hydride ion from a paraffin molecule or to add a positively charged proton (H+) to an olefin compound (Encyclopedia Britannica. 2015). As a result, a carbonium ion is formed, which is a positively charged molecule with a very short life as an intermediary chemical that transmits the positive charge via the hydrocarbon. As hydrocarbon molecules come into contact with active areas on the catalyst's surface that stimulate the ongoing addition of protons or the removal of hydride ions, carbonium transfer continues. As a result, many of the hydrocarbon molecules' carbon-carbon bonds weaken, causing them to split into smaller compounds.

Modern catalytic cracking reactors typically operate at temperatures ranging from 480 to 550°C (900 to 1,020 °F) and at comparatively modest pressures ranging from 0.7 to 1.4 bars (70 to 140 KPa), or 10 to 20 psi. Initially, natural silica-alumina clays were used as catalysts, but by the mid-1970s, zeolitic and molecular sieve-based catalysts had taken their place. Zeolitic catalysts increase product selectivity while decreasing gas and coke formation. The catalytic cracking procedure was used to create biofuel from vegetable oil. Catalytic cracking outperforms to thermal cracking because it can occur at considerably lower temperatures, provides high octane gasoline, and reduces the production of heavy fuel oils and light gases. The table 2.2 shows the comparison of thermal and catalytic cracking.

Table 2.2: Comparison of thermal and catalytic cracking.

Parameters	**Thermal Cracking**	**Catalytic Cracking**
Description	Heat is used to break down bigger hydrocarbons into smaller ones.	Heat is used to break down bigger hydrocarbons into smaller ones in the presence of catalysts.
Temperature	400-1000 °C	Reactor temperature: 470-540°C Regenerator Temp: 591-610°C
Regenerator	Not Required	Required for the recovery of catalyst
Waste Generation	Large amount of coke formed	Low amount of coke formed
Pressure	10 – 15 kg/cm^2	<5 kg/cm^2
Mechanism	Free Radical Mechanism	Carbonium Ion Mechanism
Pre-treatment of feed	General treatments, such as the elimination of nonvolatile gases and the removal of S and N, are adequate.	Highly selective and extensive to protect the life of the catalyst while also removing S.

2.3 Catalyst

2.3.1 Zeolite (ZSM-5)

It has been observed that employing ZSM-5 yields a greater gaseous product due to its textural qualities. The shape-selective action of the zeolite ZSM-5 tiny pore system dictates its stronger inclination to crack mostly n-alkanes to generate light hydrocarbon gases. Because the catalytic cracking process is carbenium ion-based, the catalyst acidic sites is critical in activating the cracking intermediates (olefins, gasoline-range and LCO-range). The increased production of carbenium ions drives additional cracking to generate light alkanes and alkenes. The increased propylene formation is associated to the increased acidity of FCC-ZSM-5 compared to FCC-ECAT. In terms of liquid product yield, the larger potential for light gas creation in FCC-ZSM-5 manifests itself in a lower liquid yield than in FCC-ECAT. Catalytic cracking using FCC-ZSM-5 leads to a decreased total yield of the main liquid product – gasoline. The latter is connected to the effect of FCC-ZSM5 addition in the industrial FCC process. The increase in the production of light alkenes results in a decrease in the yield of gasoline. The coke yield from WCO cracking employing FCC-ZSM-5 is low relatively. The observed tendency can be attributed to the limited structural capacity of zeolite ZSM-5 to generate the poly-aromatic compounds that comprise cracking coke (Lovás et al., 2015).

To create propylene, zeolite β and ZSM-5 catalysts were used in the catalytic cracking of n-heptane. Alnaimi and Garforth (2015) discovered that ZSM-5 had higher activity which is more than 90mol% propylene output than zeolite β which only exhibit around 5 to 60 mol% of propylene yield. Although zeolite β had a wider spectrum of conversion, it was more vulnerable to deactivation. It was also observed that adding zeolite β to ZSM-5 increased propylene output and enhanced catalytic cracking performance by 5mol%. However, cracking with ZSM-5 resulted in an increase in gaseous product due to over-cracking of the primary product, resulting in a lower propylene yield (liquid product) and an increase in gaseous product. Zeolite β, on the other hand, increased propylene yield while maintaining low gaseous emissions.

2.3.2 Supported Metal Catalysts

O, Al, and Si are present in ZSM-5 catalyst, with a Si/Al ratio of 14.71 (Alfernando et al., 2019). The active metal Ni was added to the catalyst surface to enhance the active side on the catalyst surface. As a result, high Ni content in ZSM-5 Increased the gasoline output as the active site increased.

Rafiani et al., (2020) states that when compared to bimetal catalysts, Ni/SiAl catalyst produced the more heptadecane product. The incorporation of Fe, Cu, and Co metals to Ni /

SiAl catalyst promoted octadecane production. The hydrodeoxygenation (HDO) reaction of stearic acids produced heptadecane and octadecane products with varying values when Ni/SiAl catalysts and Ni-M / SiAl bimetal catalysts (M: Fe, Cu, Co) are utilised. Cu is an active metal as a second metal in Ni/SiAl catalysts. In comparison to the addition of Co and Sn metals to Ni-based catalysts, Li et. al., (2016) found that Cu metal gave high selectivity. The NiCu/SiAl catalyst with the largest product area of alkane compounds has a high product concentration value because the product area of alkane compounds measured by GC-MS analysis was directly proportional to the product concentration.

With conversions ranging from 66.1 to 95.3 mol%, mono- and bimetallic catalysts are both active in anisole deoxygenation. The activity of quartz and the alumina support was restricted. The bimetallic catalysts converted anisole in a limited range of 70–80 mol%, and there was no apparent trend as a function of the Ni-Cu ratio. In the sequence, the $16Ni_2Cu$ is the most active. The monometallic Ni on Al_2O_3 catalyst converts at a lesser rate (66.1 mol%) than bimetallic catalysts, indicating that Cu addition has a favourable impact. The greater activity of Ni-Cu catalysts compared to monometallic Ni might be related to Cu's reduction of Ni spinel formation. When compared to monometallic Ni, the bimetallic Ni-Cu catalyst has lower Al2O3 lattice characteristics, suggesting that less Ni is integrated in the Al_2O_3 structure and transformed to inactive spinels (Ardiyanti et al., 2012).

For oleic acid conversion, Ni- and Cu-modified bimetallic catalysts were utilised to improve catalytic conversion efficiency (Zheng et al., 2020). The conversion ratio of oleic acid has improved to varying degrees after modification. The maximum conversion ratio was found in mesoporous catalysts, whereas the lowest was found in metal oxide supports. Furthermore, the synergistic modification of Ni and Cu increased the pyrolysis of oleic acid, resulting in an increase in C8-C14 concentration and the deoxygenation/decarbonylation ratio, promoting the production of hydrocarbons and increasing oxygen removal efficiency. The inclusion of bimetals modified the pyrolysis reaction pathway of oleic acid, enhanced the deoxidation reaction pathway, and reduced oxygenated products, according to the findings.

Using Ni-Fe bimetallic catalysts, H_2 yield was dramatically enhanced, reaching a high of 61.17 % in the presence of NiFe13 catalyst. Among all the catalytic studies, NiFe21 produced the lowest H_2 output of 48.92 %. In terms of total gas yield, catalysts with a greater Ni to Fe ratio had higher activity than NiFe13 and NiFe12, however the trend was in the other direction for carbon deposition yield. NiFe13 had a carbon deposition rate of 50.9 wt%, which was greater than NiFe11, NiFe21, or NiFe31 (about 45 wt%). NiFe13 and NiFe12, which contain more Fe species, appear to be more suitable for carbon deposits than catalysts with a Ni to Fe ratio greater than 1. It might be because the connection between the metal and the NiFe13 support is fairly weak (based on TPR measurements), resulting in a higher carbon yield than 1 (Yao et al., 2017).

The presence of an active Ni-Fe/Zeolite catalyst can speed up cracking processes, as indicated by the fact that there are more cracking products created for 2 hours when compared to non-catalyst thermal cracking products. This demonstrates that the metal-coated zeolite may operate as a catalyst. At 450˚C, the sample from the Ni-Fe55/ZAk catalyst generates the greatest cracking product, 94 mL. And the yield was calculated to be 31.3wt %. This can be noticed since the sample employs a Ni-Fe55/ZAk catalyst, which is carried by the same Ni and Fe metal (5wt%:5wt%), and the presence of Ni and Fe metals scattered uniformly in the zeolite cavity can boost acidity, allowing it to function as an optimal catalyst. A big surface area and a tiny pore radius facilitate this (Santoso et al., 2019).

20C5N2Z/Z appears to be a viable catalyst for the direct conversion of levulinic acid to 1,4-pentanediol. The following are some of the benefits of the 20C5N2Z/Z catalyst. Firstly, through preferential adsorption of levulinic acid (LA) and subsequent ring formation, the combination of B sites of H-ZSM-5 and L sites of the Zn-promoted CuNi alloy can trigger the conversion of levulinic acid to γ-valerolactone (GVL). Next, the nanosized Zn promoted CuNi alloy sites can facilitate dissociative H_2 adsorption and increase the number of weakly bonded H atoms at the Cu sites via H_2 spillover, allowing the hydrogenation of reaction intermediates (e.g., -AL, GVL, 4-hydroxypentanal, and 5-hydroxy-2-pentanone) to occur even at a low processing temperature of 130 °C. Furthermore, the trimetallic catalyst's high number of L sites and nanosized CuZn alloy sites can help with GVL adsorption. Lastly, through ring opening and subsequent hydrogenation, the Zn-promoted CuNi alloy sites can accelerate the hydrogenation of GVL to 2- HMeTHF and then to 1,4-pentanediol. (Karanwal et al., 2021).

2.4 Effect of Operating Conditions

2.4.1 Catalyst Loadings

Because of its importance in product yield and component selectivity for biofuels, catalyst selection is critical in catalytic cracking processes. The surface area, pore size, pore volume, and active site of the catalyst all influence its catalytic cracking performance. The influence of catalyst concentration on OLP yield was studied using cracking processes with catalyst loadings of 1, 2, 4, 6, and 8 wt%. The yield of OLP (64–83 wt%) and 64.33–81.83 wt%) rose when catalyst loading increased from 1 to 4 wt%, respectively**.** This is clear since the rate of catalytic cracking is proportional to the active sites on the catalyst, therefore a higher catalyst loading will offer more active sites for the reaction. This is true up to a certain catalyst loading, after which catalyst loading ceases to be a limiting factor Wako et al. (2018) reported that there was no substantial increase in OLP yield above 4 wt% catalyst loading. The production of OLP was practically consistent at 6 wt %. It was discovered that when the catalyst loading was increased to 8%, the yield of OLP declined. This is because increasing the catalyst loading caused the active sites of the catalyst to aggregate, lowering the catalytic activity (Wako et al., 2018).

2.4.2 Effect of Temperatures

Taufiqurrahmi et al. (2011) carried out catalytic cracking at five different temperatures viz. 400, 425, 450, 475 and 500 °C. The cracking temperatures were found to have significant influence on the yield of OLP. The yield of OLP steadily increases from 20 wt% (400 °C) to 82.33 wt% (475 °C) and from 18.66 wt% (400 °C) to 81.66 wt% (475 °C) at heating rates of 10 and 20 °C/min, respectively, as the cracking temperature increases from 400 to 500 °C. The greater reaction rate at 450–475°C temperature can be due to the opening of the catalyst sites, which results in more accessible active sites of the catalyst, resulting in higher OLP yield. However, increasing the temperature did not greatly boost the conversion. At 500 °C, there is a drop in OLP yield (76 wt% and 74 wt% for both heating rates). This is due to increased temperature causing secondary cracking, which favours gas yield.

Majed and Tye (2018) who performed catalytic cracking of used vegetable oil (UVO) using Mo/ZSM-5, tested with different operating temperatures ranging from 350 to 450°C. During the operating temperature of 400°C, there was a slightly shift in stearic acid conversion that was higher than the typical conversion (73.50%). This number was greater at steady state in the catalytic cracking of UVO at temperatures of 350°C, which yielded 69.44% and 450°C, which yielded 68.12%. The conversion of UVO should increase with temperature due to the increasing kinetic energy of the molecules in the solution. The optimal temperature for the conversion of palmitic acid and stearic acid included in UVO was found to be about 350-400°C in this study. If the temperature exceeds 400°C, no substantial changes will occur, and undesired responses may occur.

The temperature of the reaction influences the selectivity of the organic liquid product (OLP) as well as proportion C5-C11 from Nyamplung oil. The report shows that the selectivity of the C5-C11 fraction increased at temperatures ranging from 350 to 500°C for a catalyst-to-oil ratio of 0.15. The maximum selectivity was attained at 500°C, with a value of 96.87%. This tendency can be attributed to the increased incidence of endothermic aromatization reactions at higher temperatures. The presence of acid sites in a solid catalyst, combined with high temperatures, allows for the adsorption and subsequent deoxygenation of compounds derived from primary cracking, thereby promoting cyclization, condensation, and aromatization reactions, the products of which can be found in organic liquids (Dewajani et al., 2015). Figure 2.4 shows the selectivity of OLP fraction as a function of reaction temperature at ratio of catalytst to oil = 0.15.

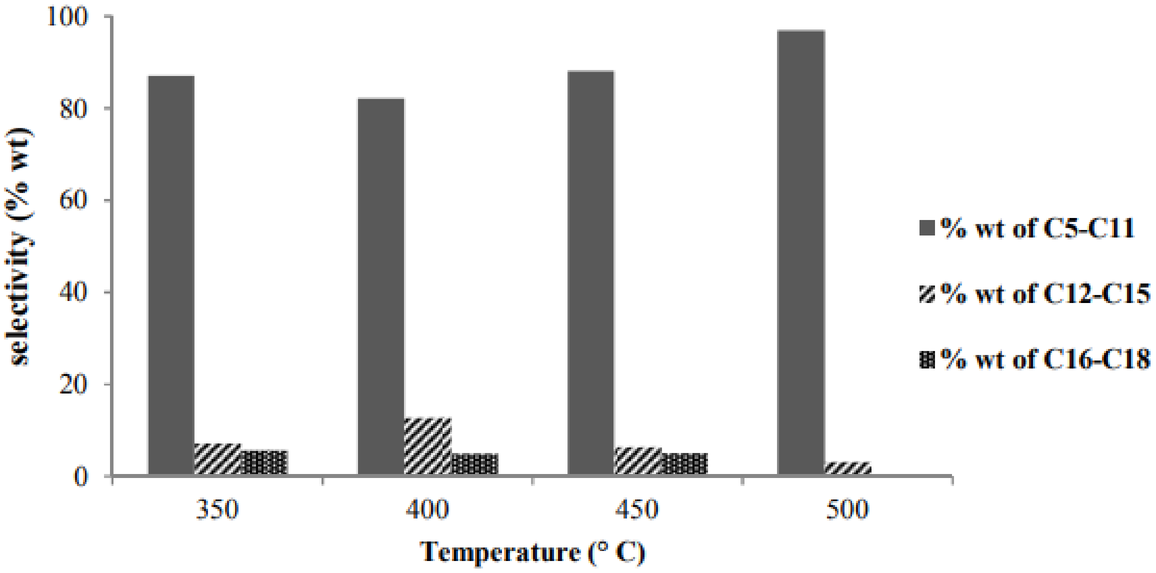

Figure 2.4: Selectivity of OLP fraction as a function of reaction temperature at ratio of catalyst to oil = 0.15 (Dewajani et al., 2015)

Zheng et al. (2018) found that cracking temperature had a considerable impact on product yield. The liquid product yield rose from 67.4 wt% (450°C) to 74.9 wt% (480°C), whereas the solid product yield decreased. However, when the temperature hit 480°C, the liquid product yield fell substantially from 74.9 to 58.7 wt% while the gas product yield climbed noticeably. It can be deduced that high temperatures would increase carbon chain breakage, leading in the generation of a significant number of C1-C5 hydrocarbons. For the catalytic cracking of soybean, they found that 480°C, is the most suitable cracking temperature.

2.4.3 Effect of Residence Time

The study by Wako et al. (2018) shows that WCO cracking time is affected by a variety of elements, including WCO weight, catalyst kind, catalyst loading, and temperature. In this study, the influence of residence time on OLP production was investigated throughout a range of residence times of 60, 120, 180, 240, and 300 minutes. As the residence period rose from 60 to 120 minutes, the yield of OLP increased from 32.33 to 82.33 wt% and from 34 to 81.66 wt%. It can be seen that the OLP yield increases as the residence period increases from 60 to 120 minutes. The reason why the OLP yield is increase up to 120 minutes is because the catalytic cracking optimum residence is 120 minutes. Increased residence time up to 300 minutes had little influence on OLP production, with a minor drop. This might be due to the longer contact time of OLP with the reaction mixture resulted in the formation of side products. As a result, a residence duration of 120 minutes was chosen as the ideal time for obtaining greater amounts of OLP output.

Arita et al., (2020) shows the effect of reaction time on biofuel yield in the catalytic cracking of waste cooking oil using a combined H-USY and ZSM-5 catalyst. A reaction time of 60 minutes produces the highest yield of liquid biofuel products (49.35%) at 450 °C reaction temperature, while a 30 minute reaction time produces the smallest amount of yield liquid product at 550 °C reaction temperature.

Based on Li et al., (2016) the yield of OLP initially increasing with the increasing time up until 100 minutes. However when the time further increased from 100 to 120 , the yield shows insignificant changes. During the operating condition, the cracking yield and yield of liquid product were 82.3% and 64.6%, respectively.

CHAPTER 3

MATERIALS AND METHODS

This chapter describes all of the experimental work done for this study. It starts with the materials and substances utilised in the experiment and the research flow. Then, the following sections are about catalyst preparation, catalyst characterization, catalyst activity test and product analysis.

3.1 Materials

The feedstock for this study; waste cooking oil was collected from the cafes inside the Engineering Campus, USM, Nibong Tebal.

Table 3.1: Details of chemicals used

No	Chemical	Supplier	Functions
1	Zeolite Y, CBV300	Zeolyst	As catalyst
2	Copper(II) nitrate trihydrate, $Cu(NO_3)_2 \cdot 3H_2O$	Acros Organics	As precursor for Cu
3	Nickel(II) nitrate hexahydrate, $Ni(NO_3)_2.6H_2O$	Acros Organics	As precursor for Ni
4	Zinc Chloride, $ZnCl_2$	Merck	As precursor for Zn
5	Iron(III) nitrate nonahydrate, $Fe(NO_3)_3 \cdot 9H_2O$	Acros Organics	As precursor for Fe
6	Nitrogen gas	Mox Gases Berhad, Malaysia	As carrier gas

3.2 Research Flow

Figure 3.1 illustrates the flow chart of the experimental work carried out in the present study. It contains three main parts; (i) preparation of catalyst, (ii) thermal and catalyst activity test and (iii) product analysis.

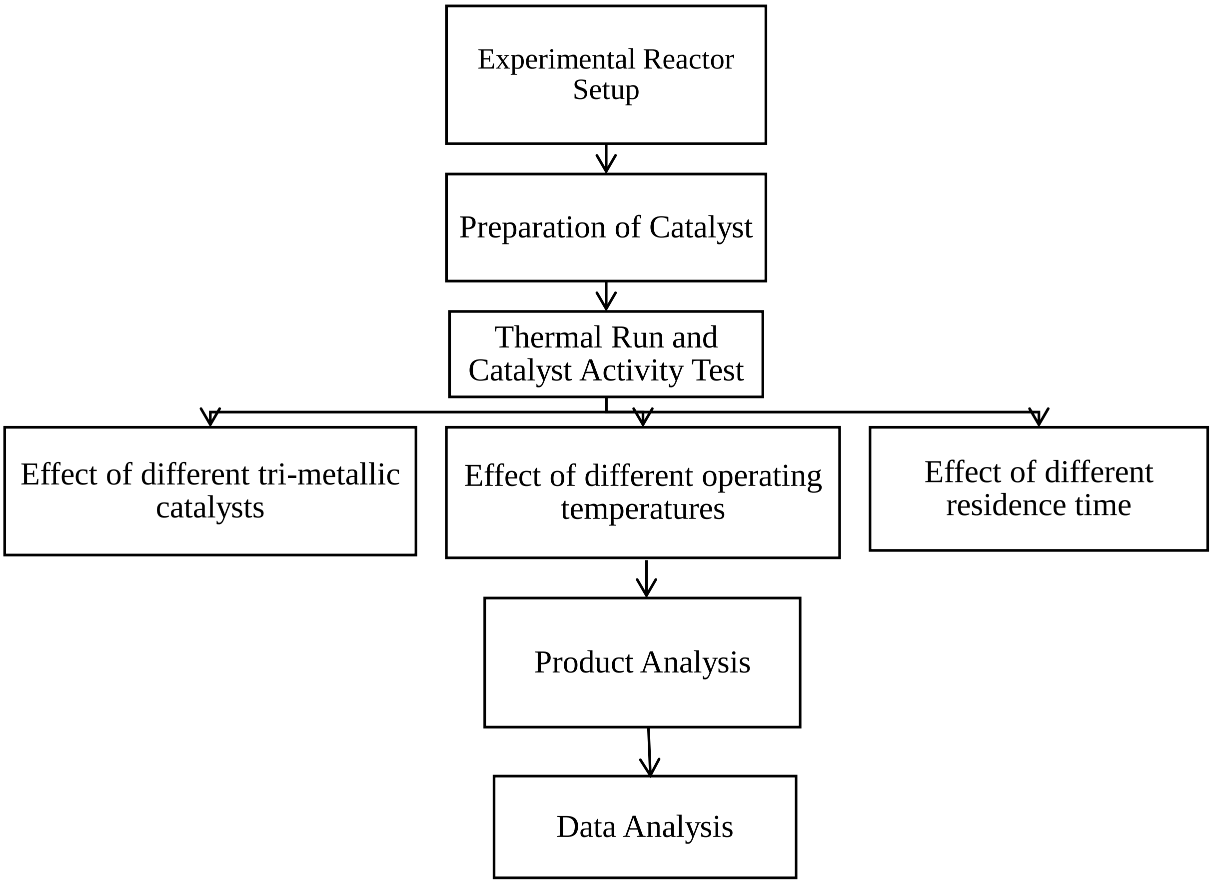

Figure 3.1: Overall research flow chart

3.3 Catalyst Preparation

Cu-Ni-Fe/Zeolite Y

In this experiment, Cu-Ni-Fe/Zeolite Y is prepared by wet impregnation method. Zeolite Y support is obtained commercially. The metal used is with the weight ratio of 1:1:1. Firstly, 4.6525g of copper(II) nitrate trihydrate, $Cu(NO_3)_2 \cdot 3H_2O$ and 4.9547g nickel(II) nitrate hexahydrate, $Ni(NO_3)_2.6H_2O$ were dissolved in deionized water, and mix with zeolite Y. The mixture was dried in air at 120°C for 16 hours in oven and then calcined in a muffle furnace for 8 hours at the temperature of 700°C. Iron then include with the same procedure using iron(III) nitrate nonahydrate, $Fe(NO_3)_3 \cdot 9H_2O$ as a precursor and then, calcined in furnace at 400°C for 2 hours (Taufiqurrahmi et al., 2011).

Cu-Ni-Zn/Zeolite Y

The method is repeated for Cu-Ni-Zn/Zeolite Y catalyst preparation. The metals percursors; copper(II) nitrate trihydrate, $Cu(NO_3)_2 \cdot 3H_2O$, nickel(II) nitrate hexahydrate, $Ni(NO_3)_2.6H_2O$ and zinc chloride, $ZnCl_2$ were mixed simultaneously initially during impregnation (Taufiqurrahmi et al., 2011).

3.4 Catalytic Cracking Test

In this catalytic cracking test, the feed used is waste cooking oil which acquired from staffs' and students' cafes. The waste cooking oil is then put in the oven for 24 hours with temperature of 100°C to ensure the water inside the oil evaporate. The catalytic cracking is performed in a batch reactor with the capacity of 100 ml. The required amount of waste cooking oil and 1wt% of required catalysts are loaded into the reactor. Before the reactor is set for the experiment, it is purged with nitrogen for approximately 3-5 minutes. This is to ensure that there is no oxygen inside the cracking chamber. The reactor is then heated by setting the desired temperature in the controller. The temperature is changed according to the experimental parameter which are temperature of 300, 350 and 400°C. When the reactor reaches the reaction temperature, the stirrer is switched on to ensure efficient mixing and the reaction is considered started. After that the reaction is kept at isothermal condition from 60min to 180min. After the desired time, the reactor is cooled down to room temperature to allow the liquid and solid product to be recovered. The figure 3.4 is the reactor system that was used during the study.

Figure 3.4: Catalytic Cracking Reactor

3.5 Product Analysis

3.5.1 Coke Yield

Coke yield was calculated by measuring coke recovery from the experiment. The product was filtered using filter paper, which was aided by a vacuum pump to speed up the filtration process. The filter paper's original mass was determined. The filter paper containing the recovered coke was washed with acetone and dried in an oven at 100°C overnight. The dried filter paper was weighed once more, and the amount of coke (solid that was not soluble during washing) produced was recorded.

3.5.2 Liquid Analysis

The liquid products are analysed according to the boiling range using ASTM 86 distillation unit in Petroleum Laboratory, School of Chemical Engineering USM. The boiling range of petroleum products such as gasoline (180˚C), kerosene (180°C - 240°C), diesel (240°C - 340°C), and palm oil residual (>340°C) were used to characterise the composition of the cracking liquid product. Catalyst performance is evaluated in terms of product yield in terms of liquid, coke and gas yield. The liquid product yield can be calculated with following equation:

$$\text{Liquid product fraction (wt\%)} = \frac{\text{weight of distillate}}{\text{weight of liquid before distillation}} \text{ x } 100\% \qquad \text{(Eq. 1)}$$

CHAPTER 4

RESULT AND DISCUSSION

In this chapter, the findings of the experiments are presented. This chapter consist of three sections, which include the study of the effect of different catalysts, operating temperatures and residence time. The product yield and hydrocarbon components has been tested, analysed and discussed here. During the study, the best value obtained from the previous parameter study was selected to be used for the next parameter study.

4.1 Effect of trimetallic catalyst in catalytic cracking of waste cooking oil

For the catalyst test, there are different catalysts used which are Zeolite Y, Cu/Zeolite Y, Ni/Zeolite Y, Cu-Ni/Zeolite Y, Cu-Ni-Fe/Zeolite Y and Cu-Ni-Zn/Zeolite Y. The experiments conducted were set at 350˚C and 60 minutes. The catalyst was selected because the metals are commonly used in petroleum industry (Sun et al., 2002). The product yield of different catalysts in the catalytic cracking of waste cooking oil is shown in Table 4.1. Catalytic cracking using only zeolite Y produced the highest coke and gas yield compare to other catalyst. Cu-Ni-Zn/Zeolite Y (78.43%) gave the highest liquid yield compared to all catalysts. Both single metallic catalysts produced relatively high liquid yield, considered for the bimetallic catalyst preparation and testing. By combining copper and nickel into bimetallic, Cu-Ni/Zeolite Y, the coke yield decrease significantly compared to both single catalysts. Among all catalysts studied, the lowest coke formation was observed for catalytic cracking reaction with Cu-Ni-Zn/ZeoliteY.

Table 4.1: Product Yield for the respective experimented catalysts at temperature 350˚C for 60 minutes.

Catalyst	Zeolite Y	Cu/Zeolite Y	Ni/Zeolite Y	Cu-Ni/Zeolite Y	Cu-Ni-Fe/Zeolite Y	Cu-Ni-Zn/Zeolite Y
Liquid Yield (%)	69.09	77.53	78.10	77.74	77.93	78.43
Coke Yield (%)	1.31	1.26	1.20	0.50	0.80	0.13
Gas Yield (%)	29.59	21.21	20.70	21.77	21.27	21.44

Reaction with Cu-Ni-Zn/Zeolite Y catalyst gave the highest liquid product yield (78.43 wt%) and lowest coke yield (0.13 wt%) among the catalysts used. Coke formed when the cracked H combined and formed H_2 gas, later combined with free carbon during the cracking process (Kolhe et al., 2017). Among the catalysts tested, the highest gas yield (29.59 wt%) was obtained in the reaction with purely zeolite Y as the catalyst. Ni/Zeolite Y has the lowest gas yield (20.70 wt%) but has quite amount of coke formation (1.20 wt%). Based on Rahimi (2011), zinc and copper are transition metals that could increase the Lewis acid site of catalyst and promote the cracking which lead to the yield of light olefin.

Referring to Figure 4.1, Cu-Ni-Fe/Zeolite Y yield more residue compared to other catalysts. However, the residue percentage between all the catalysts are ranging between 28% to 31%. The components of oil vary for each catalyst used as shown in Figure 4.1. Most of the catalyst did not produce gasoline except for Zeolite Y and Cu-Ni-Fe/Zeolite Y (1%). The kerosene amount changed a little bit for different catalyst, with Cu-Ni/Zeolite yield the highest amount of kerosene at 22% followed by Cu-Ni-Zn/Zeolite Y at 16%. The increment of the component of oil is noticeable for diesel and residue. For all catalysts, the amount of diesel became the highest fraction of liquid product with Zeolite Y and Cu/Zeolite Y had the highest amount of diesel at 67%. The cracking process is affected by the Bronsted acid site because it increases the formation of carbenium ions (Kissin, 2001). For all type of catalysts, the production is more towards the heavy oil (Rana et al., 2007b). From the experiments with different type of catalysst, the trimetallic Cu-Ni-Zn/Zeolite Y was selected in the following operating parameter studies as it gives the highest liquid yield and lowest coke yield.

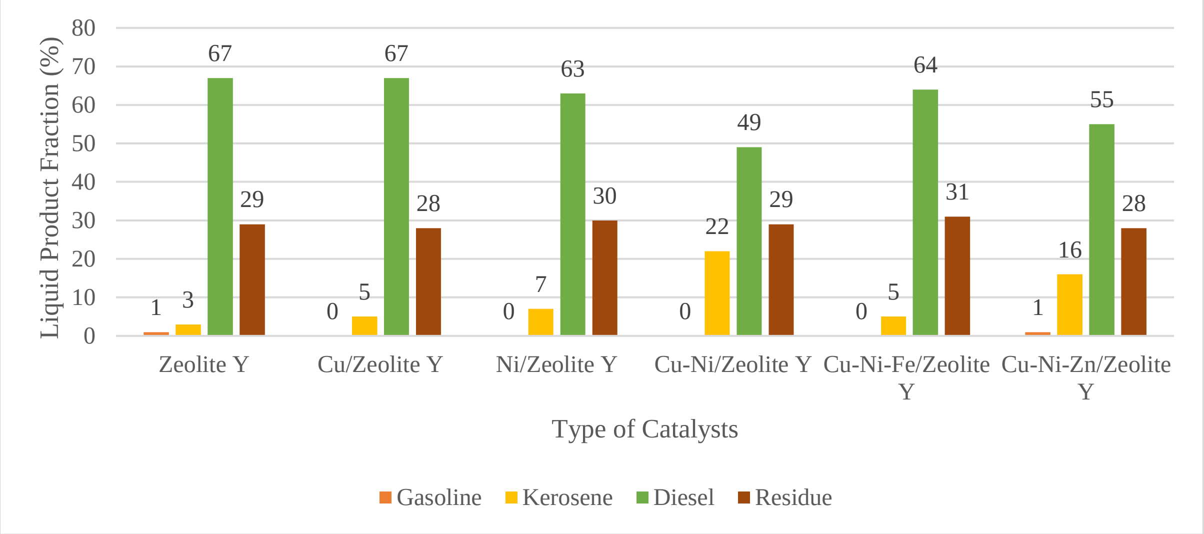

Figure 4.1: Effect of catalyst type to the hydrocarbon yield of the waste cooking oil at temperature 350˚C for 60 minutes

4.2 Effect of different operating temperatures

The catalyst selected for the operating temperature study was Cu-Ni-Zn/Zeolite Y as the catalyst gave the highest liquid yield and lowest coke yield compare to other catalysts. Table 4.2 shows that increasing temperature from 300˚C to 350˚C, the liquid yield increase (77.83 wt% to 78.43 wt%), however when it reaches 400˚C, the liquid yield decrease to 67.00 wt%. Among the temperatures, 300˚C produced the high coke yield at 0.50 wt% followed by 400˚C for 0.14 wt%. Reaction at 400˚C produced the highest gas yield at 32.86 wt%, which is quite high compare to reaction at 300˚C and 350˚C (21.67 wt% and 21.44 wt%, respectively). This is because higher temperatures promote secondary cracking, which increases gas yield (Taufiqurrahmi et al. 2011).

Table 4.2: Yield produced after catalytic cracking using Cu-Ni-Zn/Zeolite Y catalyst at different reaction temperatures for 60 minutes.

Reaction Temperature	**300˚C**	**350˚C**	**400˚C**
Liquid Yield (%)	77.83	78.43	67.00
Coke Yield (%)	0.50	0.13	0.14
Gas Yield (%)	21.67	21.44	32.86

Figure 4.2 illustrates the yield of hydrocarbons in liquid product for catalytic cracking reaction using Cu-Ni-Zn/Zeolite Y catalyst at reaction temperatures 300°C, 350°C and 400°C for 60 minutes. Gasoline yield was only detected in liquid product of catalytic cracking performed at 350°C (1%). There was no gasoline detected at reaction temperatures of 300°C and 400°C in the present study. The highest kerosene yield was obtained when catalytic cracking was performed at 300°C. When comparing the diesel yield, the highest diesel yield was obtained when catalytic cracking was performed at 400°C (58%). There was an increase in diesel yield by 10% when catalytic cracking was performed at 350°C and continue to increase by 3% when catalytic cracking was performed at 400°C. The lowest residues yield was obtained for reaction temperature at 400°C. Although 400°C has the highest hydrocarbon yield compare to the other temperatures, this temperature is not suitable to continue for catalytic cracking due to its low liquid yield. Hence, the optimum temperature, 350°C was used in the following residence time study.