

# **CATALYTIC SONOLYSIS OF USED MOTOR OIL**

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# **CATALYTIC SONOLYSIS OF USED MOTOR OIL**

**by**

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# SONOPEMECAHAN MINYAK MOTOR TERPAKAI DENGAN KEHADIRAN PEMANGKIN

## ABSTRAK

Minyak motor digunakan sebagai pelincir untuk pelbagai jenis alat mekanikal dalam industri dan dalam kehidupan harian kita yang tujuannya adalah untuk melindungi peralatan serta memastikan ia beroperasi dengan cara yang betul dan memanjangkan hayatnya. Kitar semula minyak motor yang digunakan dapat mengurangkan isu pelupusan. Minyak motor mengandungi bahagian minyak berat yang boleh diproses menjadi minyak ringan dan boleh digunakan sebagai bahan bakar untuk tujuan pemanasan. Rawatan ultrasonik digunakan dalam kajian ini untuk memecahkan hidrokarbon yang lebih berat dalam minyak motor yang digunakan dan untuk mengurangkan kelikatan. Kobalt dan nikel telah digunakan dalam kajian ini. Parameter yang berbeza seperti amplitud ultrasonik, tempoh tindakbalas, jumlah pemangkin dan jenis pemangkin dikaji untuk menentukan kesan sonopemecahan kepada minyak motor yang digunakan. Melalui eksperimen ini, hasilnya menunjukkan bahawa parameter dan pemangkin yang digunakan meningkatkan kelikatan minyak motor yang digunakan dan sebahagian besar produk mempunyai minyak berat yang lebih banyak dalam julat kajian parameter. Melalui eksperimen ini, hasilnya menunjukkan bahawa pelbagai parameter yang digunakan (amplitud 20% -60%, masa tinggal 5-30 minit) dan jenis pemangkin (Co / HZSM-5 dan NiCo / HZSM-5) meningkatkan kelikatan motor yang digunakan minyak dari awal 116.7cP kepada 179.23cP tanpa keadaan pemangkin, amplitud 60% dan 25 minit masa kediaman. Dalam keadaan ini, peratusan residu dikurangkan daripada 64% kepada 51%. Bagi eksperimen lain, kandungan residu meningkat. Untuk mendapatkan keputusan yang diingini, julat parameter lain perlu digunakan.

# CATALYTIC SONOCRACKING OF USED MOTOR OIL

## ABSTRACT

Motor oil is used as lubricant for various types of mechanical contraption in industry and in our daily life which its purpose is to protect the equipment, ensure that it operates in a correct manner and lengthen its lifetime. Since it was used widely, its disposal method become an issue as the used motor oil is hydrocarbon that need to be disposed properly in order to protect the environment. Therefore recycling of used motor oil can reduce the disposal. The motor oil contains heavy portion that can be cracked into lighter oil and can be used as fuel for heating purposes. The used motor oil usually has high viscosity that make the transportation process difficult. Ultrasonic treatment is used in the present study to crack the heavier hydrocarbon in the used motor oil and to reduce the viscosity. Cobalt and nickel are commonly used catalysts in the petroleum industry and their effect on the cracking of used motor oil using ultrasonic treatment are investigated. In this research different parameters such as amplitude of the ultrasonic, residence time, catalyst amount and catalyst type were studied to determine the sonocracking effect to the used motor oil. Through this experiment, the result showed that the used parameter range (20%-60% amplitude, 5-30 minutes residence time) and catalyst type (Co/HZSM-5 and NiCo/HZSM-5) increased the viscosity of the used motor oil from the initial of 116.7cP to 179.23cP in no catalyst condition, 60% amplitude and 25 minutes residence time. In this condition, the residue percentage reduced from 64% to 51%. As for the other experiments, the residue content increased. To obtain the desired result, different parameters study range and catalyst type could be investigated.

# CHAPTER 1

## INTRODUCTION

### 1.1 Background

Motor oil is commonly used as the lubricant for the moving mechanical parts in various contraptions such as engines. Without the presence of the motor oil, the friction will be high, and the system cannot run as it was supposed to be. The parts will also break in a short time and will need replacement very often. The motor oil has its own lifespan, and it needs to be replaced from time to time to maintain the efficiency of the system. The used motor oil is quite difficult to be disposed because it is not biodegradable, and contains harmful components, such as, resins, oxidation inhibitors, lacs, metals, rust inhibitors, non-consumed additives, non-burned fuel, dust etc. Commonly, the used motor oil was recycled for other purposes (Tsoncheva et al., 2018).

Since it is used globally, it leads to a large quantity of the used motor oil. In the United States of America alone, the production of used motor oil is around 570 million litres per annum, and out of the value, more than 50% was recycled (Donovan, 1994). There are used motor oils being disposed improperly, such as simply onto the ground, into the drains or trash. The issue concerning soil contamination can be observed in more developing countries, since the used motor oil was dumped into the ground directly. The used motor oil contains a broad range of aliphatic hydrocarbons with chains ranging from C15 to C50. The poor disposal method to the surroundings is harmful due to the presence of carcinogenic elements in it and will cause short and long-term effects. Based on the US Environmental Protection Agency, used motor oil can pollute fresh water supply for 50 people every year. Out of the aforementioned value, over 40% of the

used motor oil comes from motor. Currently, The contaminated sites are treated by excavating the soil to other safe areas (Rudyk and Spirov, 2017).

The amount of used motor oil is increasing due to the development process and this component cannot be dumped easily. Used motor oil, is still considered as valuable product, since it can be refined and be used for heat generation. Wider re-utilization of used motor oil will lead to reduction on dependency for petroleum resource and conserve them at the same time, more energy and money will be saved. The issue of recovery, reuse, and treatment is to find an effective way to lower the hazardous effect of the used motor oil. Recent survey found out that used motor oil recovery dominates all other wastes recycling since 1960 to be used again as new lubricating oil or industrial burner fuel (Krivtsov et al., 2004, Hassanpour, 2015).

There are different methods to recycle the used motor oil, such as acid-clay method and solvent de-asphalting. The traditional acid-clay method to clean the used motor oil has been replaced by new method solvent de-asphalting because the acid-clay method will produce hazardous waste of acidic clay (Unnisa and Hassanpour, 2017). The new method is able to degrade the used motor oil into new product but also have their own limitation, such as the cost of it is quite expensive, and only suitable for large quantity of used motor oil only. In one of the recovery process, it uses propane and hydrofinishing step to remove a percentage of pollutant that is difficult to be removed in vacuum distillation. Using ethane as a substitute for propane are also possible, but since both chemicals are highly flammable, it is considered as a hazardous process (Unnisa and Hassanpour, 2017).

Incineration/Combustion of the used motor oil is very common method in most countries, but these methods are not feasible and not environmentally friendly because

of the additives inside the used motor oil. Simply combusting the used motor oil may release toxic substances to the surrounding and affect human. Another disposal method is pyrolysis, where the used motor oil can be degraded to oil and solid residue in inert atmosphere. Oil sludge (Cheng et al., 2016), waste automotive engine oil, and waste lubricant oil also can be used in the pyrolysis process to produce gas and liquid product (Lam et al., 2012). The pyrolysis process however will consume high energy to degrade the used motor oil. Another method to degrade the used motor oil is Co-pyrolysis. It has attained much attention from research community in recent years, and they used various kinds of waste feedstock to study its product. Using oily waste, the co-pyrolysis shows some advantages where more liquid fuel and upgraded fuel due to synergistic effect. When oily waste is used in the co-pyrolysis, it acts as a good solvating medium that improves the fuel characteristics (Uçar et al., 2016). The product is very good, nevertheless, the process has its own disadvantage. Because the process itself require high temperature, it will consume a lot of energy to degrade the chemical. Therefore, there are no guarantee that the process will return more energy than it consumed.

In oil industry, the viscosity of the oil is preferred to be low, as it eases off the transportation process. Therefore few methods had been applied to increase its fluidity, such as heating, mixing low-viscosity oil with high-viscosity oil and adding reagents. These methods however are costly and require considerable amount of energy. Ultrasonic treatment is one of the possible method to achieve the reduce the viscosity (Abramov et al., 2017). It is possible to reduce the viscosity of the crude oil product using ultrasound. Ultrasonic treatment shall during sonication process and could have broken down the heavy oil into lighter oil. As a result, the viscosity could be reduced permanently. Ultrasonic treatment on super heavy oil has reduced its viscosity

significantly. Even using paraffin oil instead of crude oil, the viscosity also reduced slightly (Wang and Xu, 2015). Since the concept is the same, it was expected that same results for used motor oil.

## 1.2 Problem statement

Motor oil is used as a lubricant for engines for cars, motorcycles, machines in plant and other vehicles. This motor oil has their own life time, and at some point, it need to be replaced with new motor oil to ensure that the contraption run smoothly. The motor oil will protect the equipment by reducing the frictional force at moving parts of them. For car, standard motor oil is usually only can be used for 5000km-10000km. After it has reached the limit, the motor oil need to be removed, and replace with a new one. The problem arises on the disposal the used motor oil, as it is harmful to the environment if not handled correctly. The conventional thermal catalytic cracking and pyrolysis need to be run at a very high temperature, usually more than 450°C, which imply a high cost recycling process. On the other hand, sonolysis using ultrasonic system, does not require high temperature facility. It could be another pathway to recycle the used motor oil.

## 1.3 Objectives

- I. To study the effect of amplitude of the ultrasonic wave on the upgrading of used motor oil.
- II. To study the effect of residence time on the sonolysis of used motor oil.
- III. To study the effect of catalyst type and weight on the sonocracking reaction in used motor oil.

## CHAPTER 2: LITERATURE REVIEW

Catalytic cracking is a process to break up the carbon-carbon (C-C) bond in hydrocarbon. While it cracks the C-C bond, it also cracks C-H bond. This process has been used by the engineers for ages in order to provide fuel for the society, such as gasoline, diesel, and kerosene (Sadrameli, 2016). The crude oil extracted from the oil rig consists of multiple types of hydrocarbons and cracking is an inevitable process. This process is one of the most popular to recycle the used motor oil by cracking them into lighter oil to be used again. However, the process requires high temperature and consume a lot of energy. The sonocracking utilize the same concept but different energy source. The conventional thermal cracking provides the energy via thermal energy, while the sonocracking provides the energy through the ultrasonic wave. Because the cracking concept is same, the catalyst used in thermal cracking was studied and similar result was expected.

### 2.1 Metals on zeolite

Cracking processes widely used in the petroleum industries are fluid catalytic cracking (FCC) and thermal catalytic cracking which is to crack the raw hydrocarbon with high molecular weight such as heavy oil into lower molecular weight, such as gasoline and kerosene. The lighter components can be used as a fuel, either directly or blended or further processed into different chemical feedstocks. A research about the ability of novel cobalt on the cracking of n-butane was reported (Kaliya and Kogan, 2005). The Co-N on alumina catalyst showed high performance in the oxidative cracking process of n-butane to ethylene and propylene. The conversion of n-butane was high, 82% at 600°C. The total wt.% of olefins were 47.7%, with 31% ethylene

and 13% propylene. By characterizing the catalyst, it was concluded that cobalt oxynitrite formed has led to low oxygen binding energy, which enriched the mobile, low energy oxygen and improved the formation of lower olefins (Kaliya and Kogan, 2005).

A study on Lanthanum and Copper functionalized ZSM-5 in cracking reaction was also reported. The ZSM-5 was modified using NaOH, before being impregnated with 10wt% of La and Cu. The pre-treatment of ZSM-5 extract silica and alumina and caused loss of strong acid sites which could enhanced accessibility (Xue et al., 2010). The catalyst prepared using this method have quite high olefin selectivity, at 68%, with optimum propylene to ethylene ratio ( $P/E = 1.2$ ), and good stability. The ZSM-5 have micropore for the active site, but it also ideal for the deposition of coke, therefore acidity of the support was adjusted. The alkali treatment was selected due to its simplicity and economical reason. Due to the presence of La and Cu, the acidity was improved, and prevent the coke formation on the catalyst and its deactivation were prevented. This research manipulated the activity of the catalyst and modifying the structure of the pores to obtain the optimum condition to maximize the P/E ratio (Xue et al., 2010).

Catalyst using Li on MgO have a great promise of oxidative cracking of hexane, but it suffers from low catalytic activity and deactivation problem. The catalyst had acceptable conversion of hexane, at 28 mol% and its selectivity towards light olefins was reasonable, at 60 mol%. Oxygen is found to vital in the regeneration of the active site and improve the radical chemistry while inhibit coke formation at the same time. In high concentration of oxygen, the olefin selectivity was reported influenced slightly (Boyadjian et al., 2010a). Since the research focused on the production of lower olefins, C<sub>2</sub>-C<sub>4</sub>, modification using sol-gel method for Li-MgO with MoO<sub>3</sub> was done to



investigate its performance with its loading. As a result, they found out that the best loading for MoO<sub>3</sub> was 0.5% minimum, shows the best yield of C<sub>2</sub>-C<sub>4</sub> olefins. At 7% MoO<sub>3</sub> loading, heavy product C<sub>6</sub> was obtained. The promotion using MoO<sub>3</sub> maintains the large surface area during calcination process at temperature over 500°C, remarkably improving the stability of the catalyst by reducing the surface carbonate formation. This catalyst also has lower amount Li<sub>2</sub>CO<sub>3</sub> that initially present on the Li-MgO, with higher surface area (Boyadjian et.al., 2010).

In 2011, the effect of alkali metal loaded on nano-HZSM-5 was studied by (Xu et al., 2011). In the study, fluidized catalytic cracking of C<sub>4</sub> liquefied petroleum gas were used as the feed, different loading of K, Na and Li was reported to obtain the maximum selectivity obtained, 50-60%. Increasing in the reaction time was reported to decrease its catalytic activity, but the selectivity of propylene and ethylene does not increase (Xu et al., 2011).

Iron catalyst was prepared on HZSM-5 in the cracking of 1-butane was studied (Li et al., 2014). The support was modified using phosphorus and it was found to reduce the strong acid sites. The reaction of hydrogen transfer was suppressed, and this decreased the conversion of butane but increase the selectivity toward propylene. This is because it encourages cracking of octane isomer. As a bonus, the phosphorus modification increases the stability of the catalyst, enhancing conversion of butane and selectivity of propylene. The presence of Fe also increased the basicity of catalyst, have some slight effect on the support structure, considerable increase the surface area and micropore volume. Using this preparation method, they obtained the highest selectivity of propylene (Li et al., 2014).

The modification of the support also plays vital role in cracking process. For example, phosphorus was loaded on ZSM-5, and the loading process was done using a template-free technique (Vafi and Karimzadeh, 2015). The activity was investigated using LPG catalytic cracking in a fixed- bed reactor. The production of methane was related to the phosphorus amount, so the optimum amount was being looked for. The minimum methane production (16 %) was at 0.5 wt.% phosphorus. The resulted catalyst had more active site available, but the coke formation and deactivation of catalyst occur at reaction initiation stage. To inhibit the coke formation, steaming process was used, where it dealuminated the mesopore, while not affecting the mesopores itself. Therefore, the coke formation can be reduced. The modification of zeolite using phosphorus increased the light olefin yield by 50% and selectivity by 60%. The coke formation also reduced from 14% to 7% (Vafi and Karimzadeh, 2015).

The iron as catalyst on zeolite performance in catalytic cracking was studied by using isobutene as the feedstock at 600°C and 625°C. It was found that adding more Fe will increase the selectivity of olefins to 32.4%. However, when adding more of it, the selectivity of olefins will decrease and will favour more on aromatics. Chromium was used instead of iron to study its performance and the result is similar where adding more of the metal will increase the aromatics selectivity and decrease the selectivity of methane and olefins (Sadrameli, 2016).

Pouria et al. (2017) study the effect of lanthanum loaded on ZSM-5 zeolite on catalytic cracking process. Few parameters were varied during the calcination process, such as temperature (400-800°C), the calcination time, (120-480 min) and the type of stream used. The maximum selectivity of light olefin (24%) was obtained when nitrogen stream was used at temperature 753°C and 173 minutes. The nitrogen stream prepared catalyst has higher stability compared to air stream. Temperature-

programmed desorption (TPD) technique was used to characterize the catalyst, and it was proven that increment in temperature reduce the strong acid site (especially Bronsted acid site), and this increase the light olefin production and the stability of the catalyst itself. The presence of the Lanthanum increases the hydrothermal stability by phosphorus lability to form  $\text{LaPO}_4$  in the zeolite channel. The stability can be further increased by adding the Lanthanum to the modified HZSM-5 when the amount of Phosphorus is more than Lanthanum. The Lanthanum also notably inhibit the losing of phosphorus from the catalyst surface in high temperature (Pouria et.al., 2017).

One of the catalyst that are needed to assist the process are nickel, and through research, with increasing nickel content, the selectivity of ethylene, conversion of pentane and propylene selectivity will increase. In their research, the HZSM-5 was introduced to phosphorus, to break the Al-O-P bonds. Utilizing this interaction, the tetrahedral framework of the aluminium is increased and will restore some of the Bronsted acid site and enhance the pore volume. The activity was found affected by the Bronsted acid site, especially in butene and pentene cracking, so the catalytic activity will improve as well (Li et al., 2017).

Typically, the catalyst will be supported on a suitable support material for the catalyst to work efficiently, and this will play a very important role in improving the stability and the activity of the catalyst. Zeolites are famous due to its ability to crack various hydrocarbons and due to their shape-selective feature and acidity (Li et al., 2017). In cracking reactions, ZSM-5 zeolites have a great tendency towards the light and branched hydrocarbon, meanwhile modernite and  $\beta$ -zeolite have tendency towards middle-chain products. The ZSM-5 zeolites also have a high hydrothermal stability, strong acidity and good shape selectivity as well as a kind of microporous alumina-silica zeolites. It can cracks olefins from the gasoline in order to produce propylenes

and butanes (Hussain et.al., 2017). However its application have been limited by diffusion limitation because of small channelling when the reaction involve bulky molecules (Zhang et.al., 2017). The application of HZSM-5 zeolites in catalytic cracking is more than the other due to higher activation and specific structure in their pore sizes (Sadrameli, 2016). Using modified alumina, impregnated with potassium carbonate, the cracking process at 760-820°C is possible, with reduced coke formation. However, the drawback is that the amounts of methane, ethylene, and propylene is reduced as well (Sadrameli, 2016).

By using HZSM-5, coke may be formed over it, and this phenomenon may cover the acid sites blocking the pores, thus reduce the catalytic activity and pose serious threat to the cracking process. By adding appropriate amount of steam, the formation of coke can be avoided, however, this process may damage the structure of the HZSM-5, thus significantly reducing its stability at high temperature. Using nickel as a catalyst are also an option in catalytic cracking of heavy oil, and it was found that this metal decreases the content of aromatic hydrocarbon in the product. The pros of using nickel on HZSM-5 is that it favours the cracking of n-butane and isobutane, and enhance the selectivity of ethylene (Li et al., 2017).

Lu et al. (2018) reported cracking of biomass to obtain monocyclic aromatic hydrocarbons using catalytic cracking. Different ratio of the catalyst on the production of it have been studied. The catalyst used was Mo<sub>2</sub>N/HZSM-5, and they run the experiment at high temperature. The ratio of the catalyst to the biomass had been varied to find the best yield. Under the optimal condition of catalyst-to-biomass ratio of 5, The yield of monocyclic aromatic hydrocarbons was 8.19wt%.

## 2.2 Sonification

Sonolysis, means breakdown using sound is a new technology to break chemical bonds molecularly using sonication process (Mohapatra and Kirpalani, 2016). Ultrasound is an acoustic waves that are beyond human limit of hearing. Any waves that the frequency that over 16kHz can be considered as ultrasonic. The waves can be classified as low frequency, 16kHz to 1MHz and high frequency, which is higher than 1MHz (Charoux et.al., 2017). It is possible to breakdown the hydrocarbons into smaller carbon chain, decrease in asphaltene content that lower the viscosity of hydrocarbon (Mohapatra and Kirpalani, 2016).

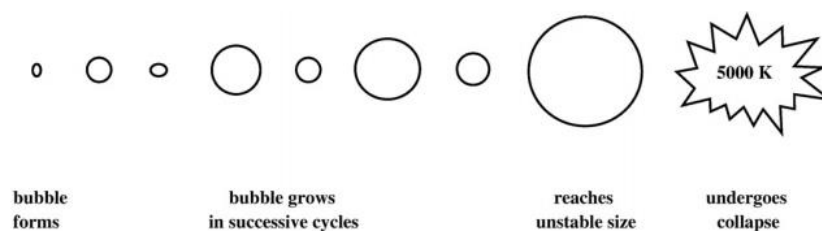
In the recent years, Wang and Xu (2015) reported the advantages of the sonication system in oil production at the oil well, which were simple operation, high adaptability, low cost and zero pollution to the oil reservoir. Comparatively to the oil production using chemical reagents where polymer chemical was injected into the reservoir, is very expensive. The cost of one polymer device needs \$230,000-\$270,000 but the ultrasonic oil production device only needs \$32,000-\$97,000 (Wang et al., 2015). Some of the chemicals are even adsorbed into the rocks in the ground, thus decreasing the efficiency of this method. The oil reservoir will also be polluted by the chemical itself in a long-term. As for the physical method for oil production, such as hydrofracturing, wave treatment, and electromagnetic treatment, have been proven that these methods will need high cost to run (Abramova et.al., 2014).

In 1950s, America is the first country that use ultrasonic oil production into practice. Since then, several high-power downhole tools have been developed. Field application of this tool have been carried out in oil well to determine its performance. The results obtained from the test show that this method increase the oil recovery by

30-50%. They also did test on high viscosity oil fields in America, and they found that the average growth rate of oil production increased to 4.45 tonne per day (Wang and Xu, 2015).

### 2.2.1 Hot Spot Theory

The cracking of hydrocarbon using the energy supplied by ultrasonic is not new in the field, even though it is still under research stage. The treatment using ultrasonic is one of the most promising oil production technique, because of its simple operation, low cost, high adaptability and no pollution to the environment (Wang and Gu, 2018). The cracking of the heavy oil using ultrasonic has been proven possible by multiple researchers. The concept behind the ultrasonic sonication is the cavitation process. The High Intensity Ultrasonic Processor converts the electrical current to high frequency electrical energy, and the it is transmitted to the piezoelectric transducer in the converter, and to the mechanical energy. The vibrations are amplified by probe, creating pressure waves in the fluid as a result. Basically, as the ultrasonic probe vibrates violently in the fluid, creating millions of microbubbles, also known as cavities, which lasts for a very short period, and will implode violently. The microbubbles expand during negative pressure excursion and implode during positive excursion (refer Figure 2.1)(Entezari and Kruus, 1996, Yeong Wu et al., 2013, Chowdhury and Viraraghavan, 2009). This occurrence was referred as cavitation process, and creates millions of shockwaves in the fluid, elevating the pressure and temperature, at the implosion sites. The implosion occurs or few microsecond, and individually, the effect is negligible. However, in this case, the amount of energy release to the fluid is extremely high, due to cumulative effects (Pang et al., 2011).



*Figure 2.1: Hot spot theory (Chowdhury and Viraraghavan, 2009)*

This theory also known as ‘hot spot theory’. The reaction sonolysis of aliphatic hydrocarbon when run in room temperature, the oil undergone cracking and pyrolysis, and decompose to simpler hydrocarbon. Different substance, such n-decane, alkene and paraffin will have different composition in the product. Formation of tar was also possible in after the sonolysis process. Thermodynamically, these processes are expected to be possible at 500°C (Cataldo, 1999).

### 2.2.2 Power

Research on 2015 found out that the ultrasonic treatment of heavy oil resulted in a decrease of the asphaltene content in bitumen. The range of frequencies of the sonication process is 20kHz-1.1MHz and 574kHz was selected with 50% power input resulted in low asphaltene content and lower viscosity, thus improving their transportability. The sonication treatment that was run under this condition also resulted in decrease of H/C ratio. The characterization of asphaltene showed lower metal content (V, Ni, and Fe) (Mohapatra and Kirpalani, 2016).

### 2.2.3 Retention time

Taheri-Shakib et.al., (2017) have done research on the effect of microwave and ultrasonic on the distribution of the asphaltene size and found out that the Ultrasonic treatment resulted smaller size of asphaltene compared to microwave. The crude oil

used in the treatment, showed increase in the viscosity of the oil. The viscosity steadily increases as the radiation time increase. The reason behind this phenomenon is that the longer the time the oil exposed to the radiation, the creation of new component becomes more likely. Meanwhile for the microwave, the viscosity did decrease for a few runs, but then it will increase as the experiment conducted at a longer time. Initially, the heavy molecules are being cracked into lighter oil, however, as the time goes on, the formation of heavy oil will be more than lighter oil. The temperature of the oil also increased during the reaction, causing some of the lighter oil to be vaporized and released to the surrounding, and as the result, more percentage of heavy oil will be left in the oil sample (Duhon and Campbell, 1965, Taheri-Shakib et al., 2017).

Abramov et al. (2017) found out that the reduction of viscosity of the heavy oil is possible by using the ultrasonic treatment with presence of chemicals such as polymers, surfactants and diluents. The experiment was run at different time, and the difference of viscosity was observed. The viscosity reduction is as high as 72.46%. The viscosity reduction without the presence of the chemical are also possible but not as much. The current used methods to decrease the viscosity, such as heating, and mixing are expensive compared to the ultrasonic treatment method, due to the massive amount of energy required and the cost of the additional chemical. If the treatment was run under well condition, the ultrasound will lead to de-emulsification and viscosity reduction (Abramova et al., 2014). The fractional composition of the oil also changed using this ultrasonic method, due to sonocracking process (Abramov et al., 2017).

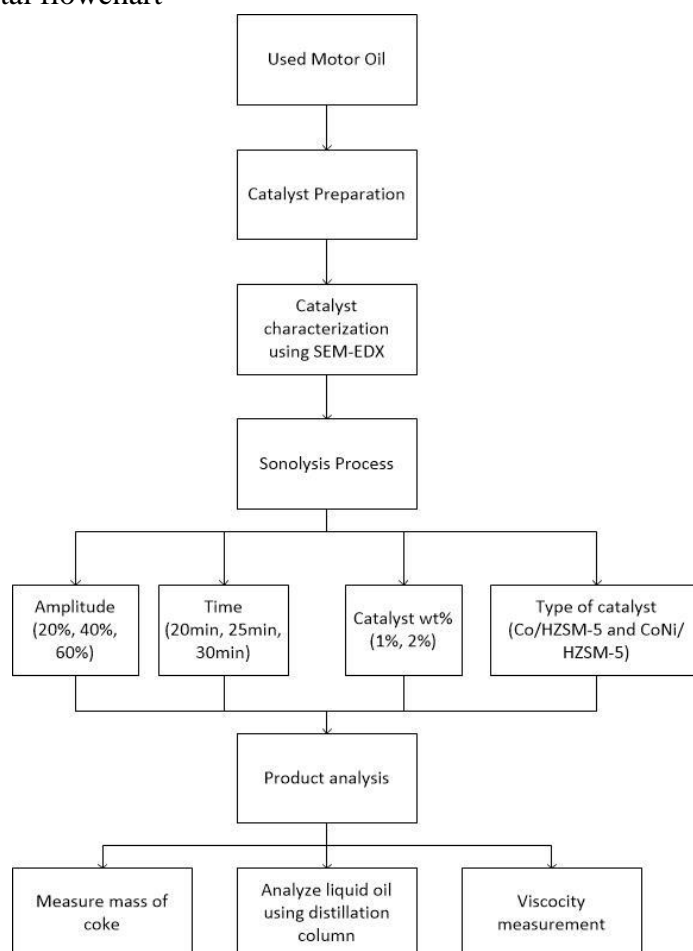


## CHAPTER 3

### MATERIALS AND METHODOLOGY

This chapter describes the materials and methodology that was be used in this study. The preparation of the catalysts and the characterization method used. After the analysis of the catalyst complete, the experiment proceeded to the experiments running. Ultrasonic homogenizer was used to carry out the sonication process. After the sonolysis cracked oil products collected, ASTM distillation analysis, was done for the liquid analysis, as well as viscosity analysis using viscometer (refer Figure 3.1).

#### 3.1 Experimental flowchart



*Figure 3.1: Experimental flowchart*

### 3.1 Materials

The feedstock used in the experiment was collected from the nearby motor workshop in Taman Pekaka workshop. The other chemicals that involved are listed below in Table 3.1.

*Table 3.1: Chemical used*

Chemical	Grade/Purity	Brand	Purpose
HZSM-5	CBV 2314	Zeolytst	Support for the catalyst
Cobalt(II) nitrate hexahydrate	98%	ACROS organics	To prepare catalyst
Nickel(II) nitrate hexahydrate	99%	ACROS organics	To prepare catalyst
Acetone	Analytical reagent	Fisher chemicals	Cleaning of the glassware
Dichloromethane	Analytical reagent	Fisher chemicals	Cleaning of the glassware

### 3.3 Catalyst preparation

The HZSM-5 was loaded with required amount of cobalt by incipient wetness impregnation method. Initially 6.53g of Cobalt(II) nitrate hexahydrate 98% was mixed with 50mL of distilled water and stirred using glass tube for half an hour. Then the aqueous solution was mixed with 15.0g of HZSM-5 powder and stirred for another half an hour. The resulted solid was filtered using filter paper, and it was dried in the oven at 110°C for 24h. After the drying process, the dried solids were crushed into powder using pestle and mortar. Then, it was calcined in a muffle furnace for 1h at 500°C with ramping rate 1°C per hour. The Co/HZSM-5 contain 8wt% of Co and it is as shown in Figure 3.2. To further load the Nickel on Co/HZSM-5, similar procedure

was carried out with the prepared Co/HZSM-5 as the initial material.  $\text{NiNO}_3(\text{H}_2\text{O})_6$  was used instead of  $\text{CoNO}_3(\text{H}_2\text{O})_6$  in the impregnation. At the end, the calcination process was carried out at  $500^\circ\text{C}$  for 4h. The amount of Nickel on NiCo/HZSM-5 is 6wt%.



*Figure 3.2: Cobalt loaded on HZSM-5*

#### 3.4 Characterization of catalyst: Scanning Electron Microscope/Energy Dispersive Using X- Ray (SEM-EDX)

To study the morphology and elements of the catalyst, Scanning Electron Microscope was used. The brand is Quanta FEG 450 (Figure 3.3). Sample was placed in the sample grid and vacuumed before analysis. Energy Dispersive X-ray will be used in determining the dispersion of the metal on the HZSM-5 catalyst.



*Figure 3.3: Scanning Electronic Microscope*

### 3.5 Sonication experiment

The sonolysis reaction were carried out in a system ultrasonic homogenizer, (Sonics Vibra-cell). For each batch of reaction, 150mL of the used motor oil was added into a 3-neck glass reactor (Figure 3.4). The mass of the 3-neck reactor was measured before and after to find the mass of gas released during the experiment. The sonication system was set at 01 01 pulses, where the ultrasonic probe would vibrate for 1 second, and stop for one second. Initially, the time was set at 25 minutes, and the amplitudes were set to 20%, 40% and 60%. The energy limit was set to 6,000,000 J. The probe was inserted at the middle neck of the glassware, and thermocouple at any one of the other neck. After all setting was fixed, the machine was turned on until the reaction time limit. The power used during the experiment was recorded, as well as the energy consumption. The temperature was recorded every minute as read from the control panel (Figure 3.5). After experiments using different amplitudes were completed, the reaction amplitude setting with best liquid yield was used to study the reaction with different time. The liquid yield was obtained by measuring its weight (Figure 3.6).



Figure 3.4: Ultrasonic Probe



Figure 3.5: Control panel of ultrasonic homogenizer



*Figure 3.6: Weigh the mass of sample after a run*

### 3.6 Product analysis

#### 3.6.1 Coke yield measurement

Coke yield was obtained via the measurement of coke recovery from the experiment. The product was filtered using a filter paper (Figure 3.7), assisted by filter pump to further accelerate the filtration process. The initial mass of the filter paper was measured. Because some on the oil was absorbed by the filter paper after filtration, the filter paper was dried in oven at 100°C overnight. The dried filter paper was weighed again (Figure 3.8) and mass of coke produced was recorded.



*Figure 3.7: Filtration of the oil*



*Figure 3.8: Weigh the filter paper after filtration and drying*

### 3.6.2 Viscosity analysis

The viscosity of end oil product was recorded using viscometer Brookfield DV III Ultra (Figure 3.9). Spindle 27 was selected due the recommendation of the technician in charge. Clean motor oil was used to calibrate the rpm setting, and rpm 200, 225, and 250 were chosen. The shear rate, shear stress and torque were also recorded.

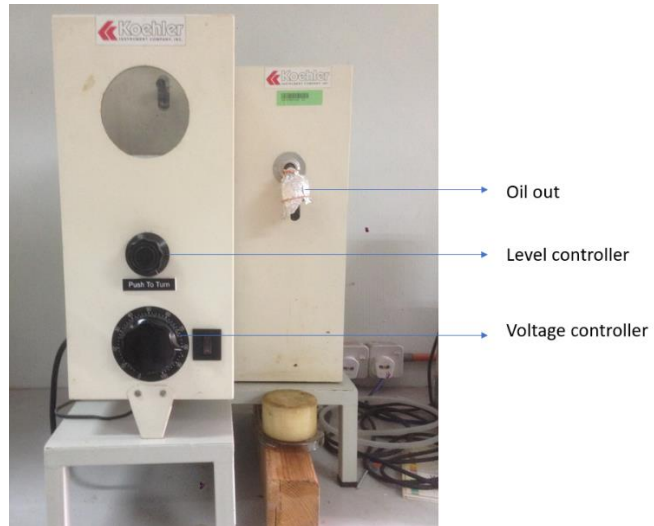


*Figure 3.9: Viscometer used*

### 3.6.3 Liquid analysis: ASTM distillation analysis

ASTM D86 was used to analyse the liquid oil products, using a Koehler 45390 distillation unit (Figure 3.10) to determine the oil product boiling range distribution and to investigate the yield of lighter product after the sonolysis. The mass of clean flask was measured before the distillation process starts. 100mL of product sample was loaded into the distillation flask. For every batch analysis, thermometer was inserted into the flask to measure the temperature of the oil. Once the heater was turned on, the initial temperature was recorded, and it was recorded for every 5 minutes. The volume also recorded every 5 minutes. As soon as the first drop of oil dropped (initial boiling point, IBP), the respective time and temperature was recorded. The volume of the oil fraction was recorded based on the category of gasoline (b.p. <150°C), kerosene (b.p. 150-250°C), diesel (b.p. 250-340°C) and residue (b.p. >340°C) fractions. The recording stops after the temperature was above 340°C. The flask was allowed to cooldown for few hours, and its mass was recorded before cleaning (Figure 3.11).





*Figure 3.10: Distillation equipment*



*Figure 3.11: The flask weigh was recorded after distillation*

## CHAPTER 4

### RESULT AND DISCUSSION

In this chapter, the result obtained from the experiments described in Chapter 3. Effect of amplitude, residence time and catalyst type to the yield, components and viscosity have been tested, analyzed and discussed here. This chapter consists of two parts, which is the effect of operating parameter in catalytic sonocracking of used motor oil and the characterization of catalyst. For the first part, the effects of three parameters are discussed and the best value obtained from the previous study was selected to be used for the next parameter study.

#### 4.1 Effect of operating parameters in catalytic sonocracking of used motor oil

##### 4.1.1 Effect of amplitude

For the amplitude test, there are three amplitudes tested, which is 20%, 40% and 60% without catalyst. The experiments conducted were set at 25 minutes, pulse 01 for all run. Based on the result obtained in the experiments, there are three yields that can be observed, which is the liquid yield, solid yield and gas yield are analysed. For the liquid yield, it decreases as the amplitude increase. At 20% and 40%, the decrement is observable but from 40% to 60%, the decrement is not significant (Figure 4.1). The decrement is due to the increment in the temperature of the glass reactor during the reaction. With high amplitude, more energy was released by the probe, leading to more cavitation of microbubbles, and eventually increase the temperature of the glass reactor. The temperature increases until around 42°C for 20% amplitude, 73°C for 40% amplitude and 90°C for 60% amplitude. As the temperature increase, components with low boiling point are released to the surrounding as gas and increase