

# Transesterification via Direct-Ultrasonic Irradiation of Rubber Seed Oil with Waste Materials Based Heterogeneous Catalyst

Maridah M. Amin, Suzana Yusup\*

<sup>a</sup>Biomass Processing Cluster, Centre for Biofuel and Biochemical Research, Green Technology MOR, Department of Chemical Engineering, Universiti Teknologi PETRONAS, 32610, Bandar Seri Iskandar, Perak Darul Ridzuan, Malaysia. [drsuzana\\_yusuf@petronas.com.my](mailto:drsuzana_yusuf@petronas.com.my)

Present process of transesterification faces various challenges. The most challenging is to obtain high conversion rate when using high free fatty acid (FFA) feedstock. The aim of this study is to investigate transesterification process of rubber seed oil (RSO) through direct-ultrasonic irradiation (UI) with addition of waste material based heterogeneous catalyst. The waste material based heterogeneous catalyst derived from empty fruit bunch (EFB) was prepared using incipient wetness impregnation method. System parameters such as reaction time, reactants molar ratio, ultrasonic amplitude and catalyst amount were studied. Properties of free fatty acid (FFA) content were measured for RSO and RSO-ester product. Characterization of catalyst was done using X-ray diffraction analyses and it was found that potassium was the primary component of the ash. Esterification with acid sulphuric ( $H_2SO_4$ ) catalyst using direct-ultrasonic irradiation successfully reduced the FFA value in rubber seed oil to less than 2 % with application of 30 % amplitude frequency in 20 min. However transesterification with waste material heterogeneous catalyst (KOH/EFB) under direct-ultrasonic irradiation showed low conversions of fatty acid methyl ester (FAME).

## 1. Introduction

Environment impact and degradation of fossil fuel has led to new research on environmental friendly fuel. Biodiesel has been the most interested green fuel that captured attention among researcher around the world. For years, biodiesel has been derived from edible feedstock which is no longer sustainable for long term usage. By substituting edible oil by non-edible feedstock seems a promising alternative. Despite its potential as non-edible feedstock for biodiesel, a high free fatty acid (FFA) amount in non-edible feedstock has been reported to be the major drawback in transesterification process (Widayat and Suherman, 2012). Ultrasonic-assisted is one of the techniques introduced to overcome the drawback in the process. This technique which its main characteristic is the cavitation effect will produce large amount of vibrational energy, thus increased the reaction rate of the transesterification process (Lee et al., 2011). Vynas et al, 2011 reported synthesis of biodiesel using ultrasonic irradiation of Jatropha oil reached maximum conversion in 30 min. In another similar study, maximum yield of more than 98.53 % was obtained with low frequency of ultrasound (Kumar et al., 2010). Efficiency of the reaction process using ultrasonic is influenced by its power intensity. Higher intensities of sonication were reported to have caused the reduction in polymer molecular weight (Gumel et al., 2014). As intensities have major effect in ultrasonic, application of this technique in transesterification process will reduce the effect of temperature. The effect of both parameters was observed in removal of free fatty acid (FFA) in fishmeal plant feedstock (Maghami et al., 2014). The authors in their report stated highest FFA removal was 93.8 % at 60 °C compared when using ultrasonic of 400 W which reported to be 79.86 %. In corresponding to the catalyst in transesterification process, heterogeneous catalyst are preferred due to their ability to be recycled and reused (Gimbun et al., 2013). Heterogeneous catalyst is also more tolerant to water and free fatty acid (Olutoye and Hameed, 2013). The present study involved the analysis of transesterification rubber seed oil

(RSO) with empty fruit bunch (EFB) waste materials based on a heterogeneous catalyst using direct-ultrasonic irradiation technique.

## 2. Experimental methods

### 2.1 Materials

The rubber seed oil was purchased through Kinetics Chemicals (M) Sdn Bhd. All analytical grades chemicals and reagents such as methanol (99.8 %), sulphuric acid (98 %), and potassium hydroxide (99 %) were purchased from Merck Chemicals. The FAME analytical standard was purchased from Sigma Chemicals (USA).

### 2.2 Ultrasonic equipment

Ultrasonic-assisted transesterification reaction was carried out in a 50 mL double jacket reactor in Cole-Parmer<sup>®</sup> 500-Watt Ultrasonic Homogenizer, 115 VAC, 20 KHz and standard probe (15 mm Titanium alloy Ti-6Al-4V) as shown in Figure 1. A temperature probe was inserted into and cooling water was flowing through the jacket to maintain the temperature inside the reactor. The temperature was fixed at  $50 \pm 2$  °C. Ultrasonic irradiation was introduced in a continuous mode with maximum ultrasonic amplitude of 40 %.

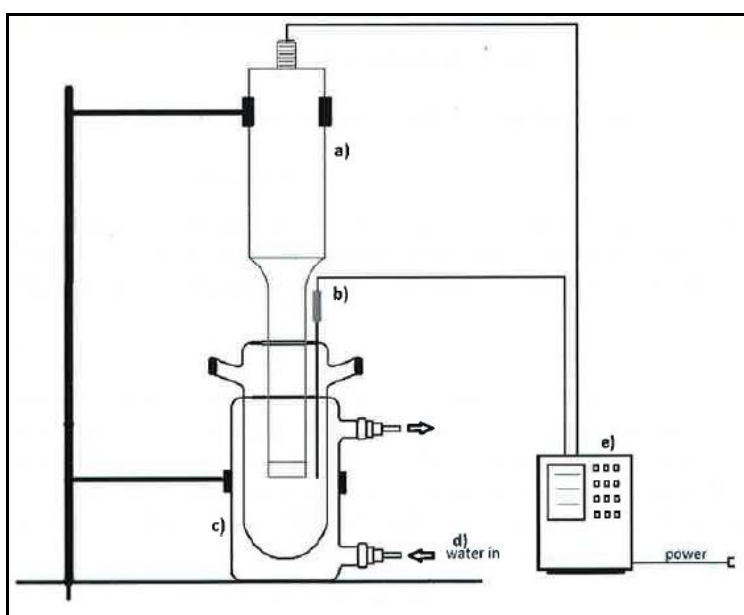


Figure 1: Ultrasonic system setup. a) transducer; (b) thermometer; (c) ultrasonic reactor; (d) cryostat; (e) ultrasonic generator

### 2.3 Ultrasonic power

The ultrasonic power released by irradiation in function of amplitude of the probe was determined using calorimetric method as shown in Eq(1).

$$P = m \times C_p \times \Delta T / \Delta t \quad (1)$$

Where P is the power (W), m is the mass of water (g), C<sub>p</sub> is the specific heat capacity of water (4.18 J g<sup>-1</sup> K<sup>-1</sup>), T is the temperature (K) and t is the insonation time (s). The calculated power is related to ultrasonic power intensity I (W m<sup>-2</sup>) as in Eq (2).

$$I = P / A \quad (2)$$

Where A represents the volumetric area (m<sup>2</sup>).

## 2.4 Methods

### 2.4.1 Catalyst preparation

Heterogeneous base catalyst was prepared with empty fruit bunch (EFB) as treated ash using wet impregnation method with potassium hydroxide (Yaakob et al., 2012). The characteristic of EFB used in this study is shown in Table 1. Wet impregnation method was prepared by heating a 20 g of empty fruit bunch (EFB) with small amount of potassium hydroxide (KOH) at high temperature till dry. Dry mixture was then kept in oven overnight to remove moisture. Prior to use the KOH/EFB was calcined at 550 °C for 4 h.

Table 1: Characteristics of empty fruit bunch

Analysis	Value (wt.%)
Moisture content	5.30
Volatile matter	71.00
Carbon (C)	45.01
Hydrogen (H)	4.88
Nitrogen (N)	0.78
Sulphur (S)	0.31
Oxygen (O)	49.02

### 2.4.2 Catalyst characterization

Analysis of X-ray powder diffraction (XRD) on prepared catalyst known as KOH/EFB was carried out in a Bruker D8 Advance diffractometer (Germany) using Cu K $\alpha$  radiation of wave length i.e.  $\lambda = 1.54 \text{ \AA}$ , generated with current of 40 mA and a potential of 40 kV. The XRD patterns were obtained on 2-theta scale in the angular range of  $0.5^\circ - 10^\circ$ .

### 2.4.3 Ultrasound-assisted transesterification reactions

Rubber seed oil used in this study contained high acid and FFA values of  $83.51 \pm 0.02$  and  $41.76 \pm 0.03$ . This high free fatty acid (FFA) can be converted to methyl ester via esterification process. Esterification was done with 40 g oil and 9:1 methanol to oil ratio with 1 wt.% of sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) as acid catalyst. Stirring was applied for 10 min before the reaction mixture was placed under ultrasonic irradiation for 20 min. After reaction was completed, the mixture was separated in separating funnel to separate the pre-treated oil and excess methanol and catalyst. The treated oil was further processed for base transesterification. In base transesterification the same amount of oil with 3:1 methanol to oil molar ratio and KOH/EFB catalyst concentration of 0.3 %, 0.5 % and 0.7 % were used.

## 3. Results and discussion

### 3.1 Catalyst characterization

In this study heterogeneous catalyst derived from empty fruit bunch (EFB) was designated through wet impregnation method. The calcination temperature of 550 °C was selected as it has been reported to be the best temperature for ash that can be used as heterogeneous catalyst (Yaakob et al., 2012). Incorporation of EFB with KOH contributed the strong base sites. This is shown in Figure 2 where the x-ray diffraction analyses indicate potassium as the main contributor in the catalyst. Component of ash content in KOH/EFB catalyst were potassium aluminium silicate, sylvite, sodium hydrogen lutetium aluminium when compared with JCPDS data.

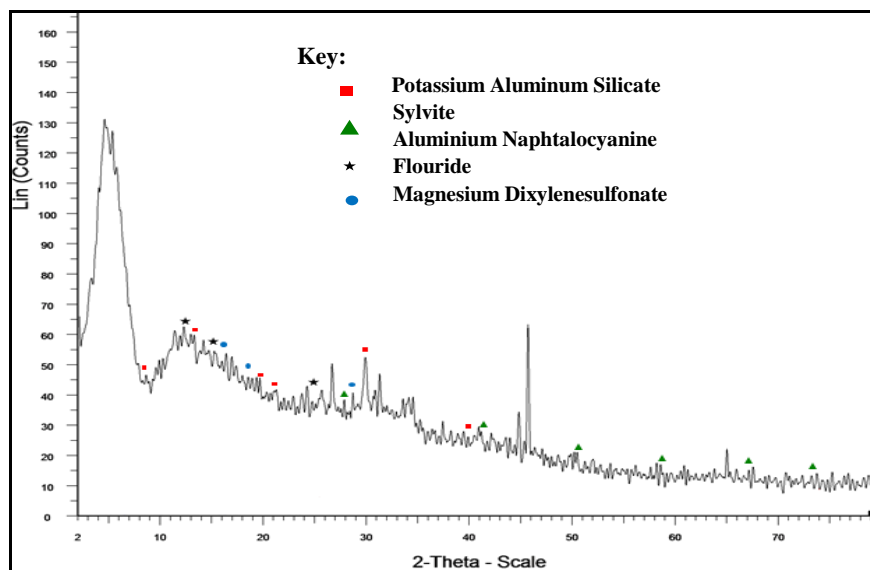


Figure 2: X-ray diffraction patterns of empty fruit bunch ash at 550 °C

### 3.2 Transesterification process of RSO

#### 3.2.1 Effect of ultrasonic intensity

Figure 3 shows the amplitude effect of the probe to the ultrasonic intensity. It can be seen from the figure that increases of amplitude frequency increases the ultrasonic power intensity. The increased of amplitude frequency produced a large cavities in the system. Large cavities produced higher energy during isothermal growth resulting in shock waves with high energy density (Vichare et al., 2000). In biodiesel synthesis large number of cavitations bubbles is the main contributor both in reducing the FFA amount and achieving high yield of FAME. Conversion efficiency using ultrasonic was found to be higher than mechanical stirring using waste oil (Babajide et al., 2009), palm oil (Ho et al., 2015) and Jatropha oil (Vynas et al., 2011). It can be observed in this study, lower amplitude frequency reduced the FFA amount of RSO more efficiently compared to higher amplitude frequency (Figure 4). The result shows at 20 %, 30 % and 40 % of amplitude frequency the FFA reduction was 0.4 %, 0.2 % and 0.5 %. An increase of frequency in acoustic cavitation generally reduces the time of bubble growth. This resulted in decreasing of water vapour amount and caused the collapsed of the intensity (Capocelli et al., 2014). It can be observed from the results higher amplitude frequency produced 0.5 % FFA compared to lower amplitude frequency. This can best be explained by the intensity rate of irradiation produced by the horn tip. It was reported large horn tip generally produced higher decomposition rate at lower intensities under ultrasound (Vichare et al., 2000). As this study used large horn tip, the lower intensities occurred during esterification process contributed to the increase rate of FFA reduction at higher amplitude. Based on this fact 30 % of amplitude frequency was chosen for the following transesterification process to produce effective cavitation effect thus obtaining a high yield of methyl ester conversion.

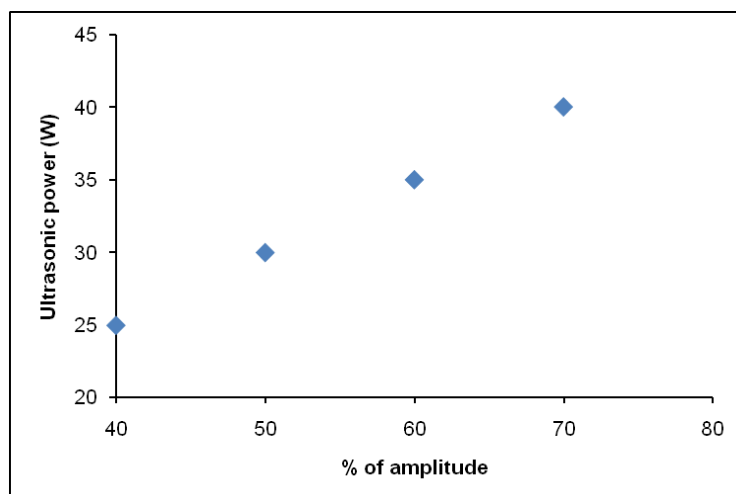


Figure 3: Ultrasonic power as function amplitude of the probe

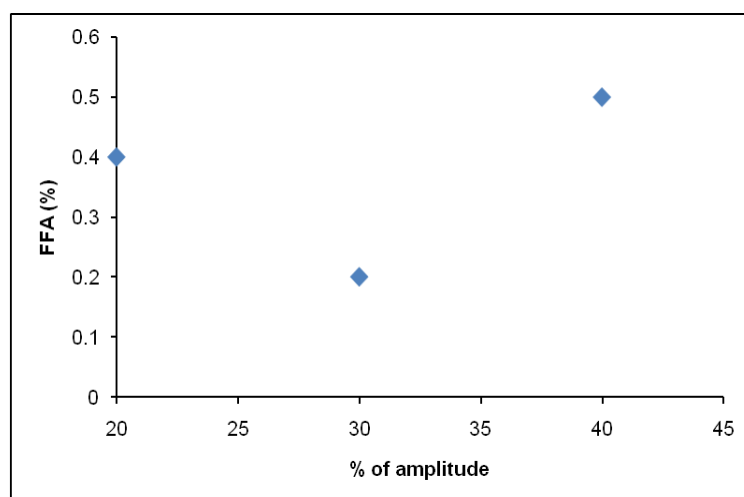


Figure 4: Effect of ultrasonic amplitude on FFA value

### 3.2.2 Direct-ultrasonic irradiation transesterification of RSO

The overall reaction process in this study consists of three steps. In the first step, triglyceride (TG) reacts with methanol to produce diglycerides (DG). Additional reaction with methanol produced monoglycerides (MG) and at final stage MG will react with methanol to produce methyl ester and glycerol. Combining the whole reaction process, the transesterification in this study can be written as Eq(3).



Various critical parameters influenced the transesterification process. One of them is catalyst type. Heterogeneous base catalyst with direct-ultrasonic using Jatropha oil was reported to produce high conversion rate above 85 % (Vynas et al., 2011). Higher conversion of 98.53 % was reported when using solid catalyst with Jatropha curcus oil under atmospheric condition (Kumar et al., 2010). Intensity of ultrasonic power also influenced the conversion rate of transesterification process (Lee et al, 2011). The successful of transesterification process depends on the basic strength of the heterogeneous solid catalyst used in the reaction. This excess basic strength is responsible to shift the reversible esterification and transesterification forwards. In this study, it was observed that integration of solid base catalysts derived from EFB with ultrasonic was not successful in producing higher yield of RSO-methyl ester. The used of 3:1 methanol to oil molar ratio and catalyst loading of 0.3 % to 0.7 % with 30 % amplitude frequency in 20 minutes successfully decreased the FFA amount, however it failed to shift the transesterification forward. A possible explanation could be as the FFA decreased, the products of ester and water increased. This

could be due to the loss of methanol by evaporation at 20 min that caused the reversed reaction. It can be stated that the used of solid base catalyst derived from EFB using ultrasonic is not in good agreement with the report by Yaakob et al., 2012. The authors in their study stated maximum conversion of more than 98 % was obtained from transesterification using conventional method. Although sonification intensifies the mass transfer in heterogeneous catalyzed transesterification, the properties of the prepared catalysts (KOH/EFB) might not be stable in thermal-driven reaction. Parker, 2012 listed few factors that could be the contributed factors to the findings in this study. First the EFB/KOH catalyst that was used in the process was not thermally stable in the presence of ultrasound. The thermal instability could be influenced by the support factor of the catalyst, in this case (EFB). Combination of the support (EFB) and catalyst (KOH) produced strong interaction thus affecting the catalytic reaction.

#### 4. Conclusions

Direct-irradiation ultrasonic transesterification reaction for the production of biodiesel was found to be very promising in reduction of FFA content of RSO. The 1wt. % acid pre-treatment and 9:1 methanol to molar ratio in 20 min successfully reduced the FFA content from 42 % to 0.2 %. The application of waste material based heterogeneous catalyst (KOH/EFB) under ultrasonic-irradiation of transesterification process showed low conversion of FAME.

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