

ULTRASOUND-AIDED *IN SITU* TRANSESTERIFICATION OF OIL ADSORBED ON DECANter CAKE USING EFBA AND Na₂SiO₃ AS CATALYSTS

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SUMMARY: In the present study, renewable green fuel is produced using abundant biowaste from palm oil mill. The crude palm oil from decanter cake was transesterified using empty fruit bunch ash (EFBA) and waste marine sponge with sodium (Na₂SiO₃-WMS) under very mild conditions. The EFBA as a solid catalyst was calcined at 500 °C for 5 h, while Na₂SiO₃-WMS was prepared using impregnation method, then calcined at 500 °C for 3 h. Parametric study has been conducted and the optimal conditions were found to be: MeOH:oil mass ratio of 6:1 and 2.3 wt.% catalyst (based on DC weight) at 55 °C, yielding highest methyl ester conversion of 85.9 (under EFBA) and 90% (under Na₂SiO₃) within 1 h reaction time. Ultrasound undoubtedly assisted in transesterification achieving this remarkable result than mechanical stirring.

1. INTRODUCTION

The global oil demand increase sharply by 1.3 mb/d in 2014, to 92.8 mb/d, while the fossil fuel reserve is depleting rapidly (IEA, 2014). Furthermore, petroleum-based activities are one of the main causes of carbon dioxide (CO₂) emission to the atmosphere, and 13% of total greenhouse gas emissions is from transportation sector (EPA, 2014). The scenario drives countries like EU, USA, Brazil, and a part of Asia to import renewable energy. Now there are many studies being directed towards the exploitation of alternative renewable and environmentally friendly fuels. Biodiesel is one of the energy sources as an alternative fuels designed to extend the usefulness of petroleum, and the longevity and cleanliness of diesel engines. For many years, the cost of production has been the main barrier in commercializing biodiesel, globally. It has been well researched and established in the literature that the cost of feedstock is the major contributor. The use of edible feedstock sparks concern in terms of food security while the inedible feedstock needs additional pretreatment steps. In the other hand, the wide availability of edible feedstock guarantees the supply

while the choice of non-edible results in a non-continuous or non-ready supply. With these complications in mind, this study exploring the potential of waste edible oils and waste catalysts in biodiesel preparation. Biomass is a promising source of renewable energy that contributes to energy needs and is the best alternative for guaranteeing energy for the future. Malaysia, being one of the largest producers and exporters of palm oil for the last forty years (total Malaysian palm oil plantation approximately 5 million hectares in 2012), has an estimated total amount of processed fresh fruit bunches (FFB) of 7.8 tonnes/ha, 70% of which is removed as waste, and 3% is decanter cake (DC). As such, in the processing of 39 million tonnes of FFB annually (7.8 tonnes/ha x 5 million ha), 1.17 million tonnes of waste DC (3% of 39 million tonnes FFB) is generated in Malaysia alone. In view of this situation, in current work the use of waste crude palm oil (CPO) from decanter cake (DC) as a feedstock and empty fruit bunch ash (EFBA), as well as Na_2SiO_3 from waste marine sponge (Na_2SiO_3 -WMS) as catalysts is proposed.

The current work focuses on production of biodiesel using ultrasound as an eco-extraction process. Ultrasound-aided transesterification is reported previously in the production of biodiesel using vegetable oil, WCO and spent bleaching clay (Boey et al., 2011b; Choedkiatsakul et al., 2014; Hindryawati and Maniam) as feedstock. The use of ultrasound promises simpler process with higher product purity and the process can be completed in shorter reaction time as well as reducing the amount of solvent being used as compared to the conventional extraction methods and with lower energy consumption. This study demonstrates the potential of EFBA and Na_2SiO_3 -WMS as a low cost source of catalyst in a transesterification reaction aided by ultrasound. Waste marine sponge skeletons are high in natural silica (Ehrlich and Worch, 2007) and can be found at seaside area easily; unfortunately with no or less application. To the best of our knowledge, there is no published report on utilization EFBA and Na_2SiO_3 -WMS as a solid catalyst in transesterification oil adsorbed in DC using ultrasound as compared to mechanical stirring as a control.

2. MATERIAL AND METHODS

2.1. Materials

Waste marine sponge (WMS) was collected from Tanjung Lumpur shore in Kuantan, Malaysia, and were cut into small pieces (0.5–1.0 cm^3), cleaned with water several times and air-dried for 24 h. The WMS fragment was then calcined at 500 °C in air. The chemicals were purchased from Sigma-Aldrich (Switzerland) include sodium hydroxide (analytical grades), phenolphthalein ($H_{\text{pH}} = 8.2$), 2,4-dinitroaniline ($H_{\text{pH}} = 15.0$) and 4-nitroaniline ($H_{\text{pH}} = 18.4$), and methyl heptadecanoate (as an internal standard) GC grades (> 99.1%). Methanol (anhydrous, $\geq 99.8\%$), and hexane (anhydrous, $\geq 99.8\%$) were purchased from Hamburg (Germany).

2.2. Preparation of catalysts and decanter cake

The EFBA was prepared following the procedures published elsewhere (Boey et al., 2011; Boey et al., 2012). EFBA was prepared by oven drying at 105 ± 2 °C until constant weight, then calcined at 500 °C for 5 h. Waste sponge with sodium (Na_2SiO_3 -WMS) was prepared using impregnation method. WMS was suspended in water in the first step. An aqueous solution of sodium hydroxide was then slowly added to the suspension. All reactions were performed at $\text{Na}^+:\text{Si}$ molar ratio of 2:1. The mixture obtained was then stirred and heated at 90 °C for 2 h. Lastly, the mixture was dehydrated at 200 °C for 30 min, and then calcined at 500 °C for 3 h. The catalysts was characterized by X-ray diffraction (Rigaku) with Cu $K\alpha$ as a source, 2θ range from 25° to 125° with step sizes of 0.1°, at a scanning speed of 1° min^{-1} . Surface analysis of the catalyst was examined by using Micromeritics ASAP 2000. Prior to the analysis all the samples were degassed at 105 °C and

the adsorption of N₂ was measured at 196 °C. The morphology of catalyst was observed by FE-SEM with electron dispersive X-ray (EDX) (JSM-7800F). The basicity of catalyst (H₊) was determined by using Hammett indicators. The following Hammett indicators were used: phenolphthalein (H₊ = 8.2), 2,4-dinitroaniline (H₊ = 15.0) and 4-nitroaniline (H₊ = 18.4). About 5.0 mL of a solution of Hammett indicator diluted with methanol and mixed with 25 mg of catalyst, and left to equilibrate for 2 h. After the equilibration, the colour change of the solution was noted.

The DC was dried in an oven at 105 °C for 2.5 h. Subsequently, the dried DC was ground and sieved to obtain a smaller particle size. The oil recovered from DC (O-DC) was 11.5 ± 0.18 wt.% (on dry basis) and its acid value is 13.8 ± 0.02 mg/KOHg (equivalent to 6.3% FFA as palmitic acid). The properties and elemental analysis of decanter cake was published in our previous work (Maniam et al., 2013).

2.3. *In situ* transesterification reaction

The transesterification reaction was carried out in a 250 ml two neck round-bottom glass flask equipped with a condenser to reduce the losses of methanol due to the evaporation and thermocouple thermometer. The ultrasonic reaction was performed using Branson (USA) ultrasonic bath (42 kHz) with the power dissipation 100 W and the exact power dissipation at 40 W determined calorimetrically (Gole and Gogate, 2012; Liu et al., 2013; T. Sivasankar et al., 2007). The bath was filled with distilled water up to 1/3 of its volume. The temperature was controlled and maintained at desired level (±0.1 °C) by water circulating from a thermostated bath by means of a pump. A constituent of 50 g of DC, catalyst (0.3-3.5 wt.%), methanol (2:1 – 8:1 wt/wt) and 1 g co-solvents (PE and hexane in equal ratio) to give 1:2 co-solvents:DC mass ratio, was immersed in an ultrasound (US) waterbath with the temperature set at 55 °C for 1 h. Then the flask was removed and centrifuged at 1000 rpm for 5 min. Three layers were formed; the top was co-solvents, followed by methanol and the DC layer at the bottom. The co-solvents and methanol layers were pipetted out separately, then about 3 ml of each PE and hexane were added into the test tube, homogenized and centrifuged, then the resultant top co-solvents layer was added to the portion of co-solvents that was pipetted out earlier. The step was repeated twice to obtain a total amount of about 14 ml of accumulated co-solvents. The conversion of Oil-DC to methyl esters (ME) by mechanical stirring (MS) was performed in a 250 ml 2-neck round bottom flask equipped with a reflux condenser and magnetic stirrer at 300 rpm. After the transesterification, the reaction mixture was allowed to cool. Then, to further separate the product (ME and glycerol) and the catalyst centrifugation at 4000 rpm for 5 min was performed. The excess methanol was evaporated before the chromatographic analysis. The reaction was carried out three times in order to reflect the precision and errors of the results.

2.4. Analysis

The concentration of ME in the sample was determined by following the European regulation procedure EN 14103. In this study, GC-MS (Agilent Technologies, 7890A GC-System) with capillary column DB-wax (length 30 x diameter 0.25 mm x film thickness 0.25 µm) using methyl heptadecanoate as an internal standard. Helium was used as a carrier gas with a linear velocity of 40 cm/s. The oven temperature was programmed at 190 °C, held for 2 min, then ramped at 10 °C per min until it reached 230 °C, and with a final hold time of 8 min. The sample volume of 0.6 µL was injected into GC. The peaks of ME were identified by comparing them with their respective ME standards and the ME content was quantified using the following formula:

$$\text{Content (\%)} = \frac{(\sum A) - A_{\text{ISTD}}}{A_{\text{ISTD}}} \times \frac{C_{\text{ISTD}} \times V_{\text{ISTD}}}{m} \times 100$$

where

$\sum A$ = total peak area of ME from C_{12:0} to C_{18:3}

A_{ISTD} = peak area of methyl heptadecanoate

C_{ISTD} = concentration, in mg/mL, of the methyl heptadecanoate solution

V_{ISTD} = volume, in mL, of the methyl heptadecanoate solution

m = mass, in mg, of the sample

The concentration of methyl heptadecanoate solution (C_{ISTD}) is at 10 mg/ml (in heptane) whereas the volume (V_{ISTD}) is at 0.5 ml.

3. RESULT AND DISCUSSION

3.1 Characterization of catalyst

The powder XRD pattern of WMS and Na₂SiO₃-WMS are shown in Figure 1. The diffractograms of WMS (Fig. 2a) showed a hump at 2 θ ranging from 16° to 40°, and the presence of large reflection at 22.45°, indicates the presence of amorphous silica particles. The results are similar with reported work by Kalapathy and Proctor (2000) indicating the disordered structure mainly due to amorphous SiO₂. In Fig. 2(b), the intense diffraction peaks found at 25.26°- 65.93° correspond to the Miller indexes (100), (101), (110), (200), (111), (002), (112), (300) and (302) were confirmed as Na₂SiO₃ (Na₂SiO₃-WMS).

X-ray diffraction (XRD) was used to determine the crystal structure of the EFBA, which is shown in Figure 1. The diffractograms of EFBA-dried showed a minor amorphous structure and the trait peaks for EFBA-dried are examined at 2 θ = 28.40°, 29.70°, 34.06°, 50.28°, 57.63°, and 74.10°, the dominant is potassium; magnesium; calcium silicate structure. Calcination of EFBA at 500 °C may have caused increasing bond formation between potassium, magnesium calcium and silicone oxide. The EFBA-calcined peaks at 2 θ = 28.58°, 29.93°, 31.33°, 31.91°, 32.35°, 39.78°, 50.38°, 58.89°, 66.60° and 73.86°. The mayor peaks of the XRD patterns were potassium calcium silicate (K₄CaSi₃O₉) is indicated by 2 θ at 28.6, 31.3, 31.9, 32.3, 40.7, 41.9, 50.4, 66.1°, and potassium calcium silicate (K_{9.6}Ca_{1.2}Si₁₂O₃₀) at 2 θ at 29.9, 39.8, 58.9, 73.9°. SiO₂ in this XRD pattern which is crystalline phase and perform as sustain for the metal oxides in the catalyst. The development between silicone oxide and metal oxides was caused by calcinations. Examples are potassium, magnesium and calcium. Since XRD is for the qualitative detection of minerals, other amorphous compounds may not be clear in this particular identification.

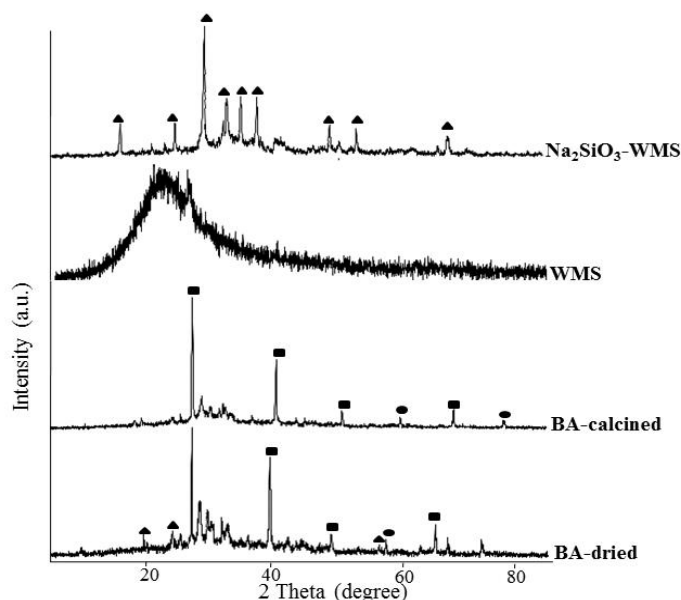


Figure 1. XRD pattern of BA-dried, BA-calcined, WMS and Na₂SiO₃-WMS; ■: K_{9,6}Ca_{1.2}Si₁₂O₃₀, ●: K₄CaSi₃O₉, □: KAlO₂, and ▲: Na₂SiO₃

The values of specific surface area and pore volume considerably decrease after modification of sodium with WMS. The loading of the sodium with WMS resulted in decrease in both the BET surface area from 11.77 to 5.08 m²/g and the pore volume from 0.15 to 0.08 cm³/g of the WMS and Na₂SiO₃-WMS, respectively. The decrease in surface area and pore volume has been observed for sodium silica by the corporation of sodium in pore of waste marine sponge conforming the impregnation. The EFBA-dried has total surface area is 106.6 (m²/g) and pore volume is 0.032 cm³/g. The calcination may have collapsed in the surface area and pore volume of EFBA-calcined. However a slight increase was observed for the average pore diameter of the calcined EFBA. The major pore distribution in EFBA-dried and EFBA-calcined is between 20 and 25 nm, which can be classified as mesopores.

The micrograph of EFBA-dried and EFBA-calcined has shown similar spongy and porous structure in nature (Figure 2). This shows the common catalytic activity if BA-dried and EFBA-calcined. EFBA-calcined explains the presence of metals such as potassium, calcium, magnesium, aluminum and phosphorus. The metals are in the form of oxides because the high oxygen content presence in the EFBA-calcined. The basicity of EFBA-calcined comes from the mixture of these metal oxides. This was confirmed by Chin et al., 2009. There are different metal oxides in EFBA, this maybe because the different sources of EFBA. The difference fertilizers used for palm oil plantation, the different types of metal oxide present in the EFBA. The micrograph of the Na₂SiO₃-WMS catalyst (with Na⁺: Si stoichiometry ratio 2:1 at 500 °C) demonstrated the crystal morphology. The morphology of Na₂SiO₃-WMS shows the homogenous surface (Figure 2.e), having a smooth surface and similar to each other. In contrast, the WMS (Figure 2.d) showed a bulky substance. The skeleton consisted of needle shaped spicules that are bundled together.

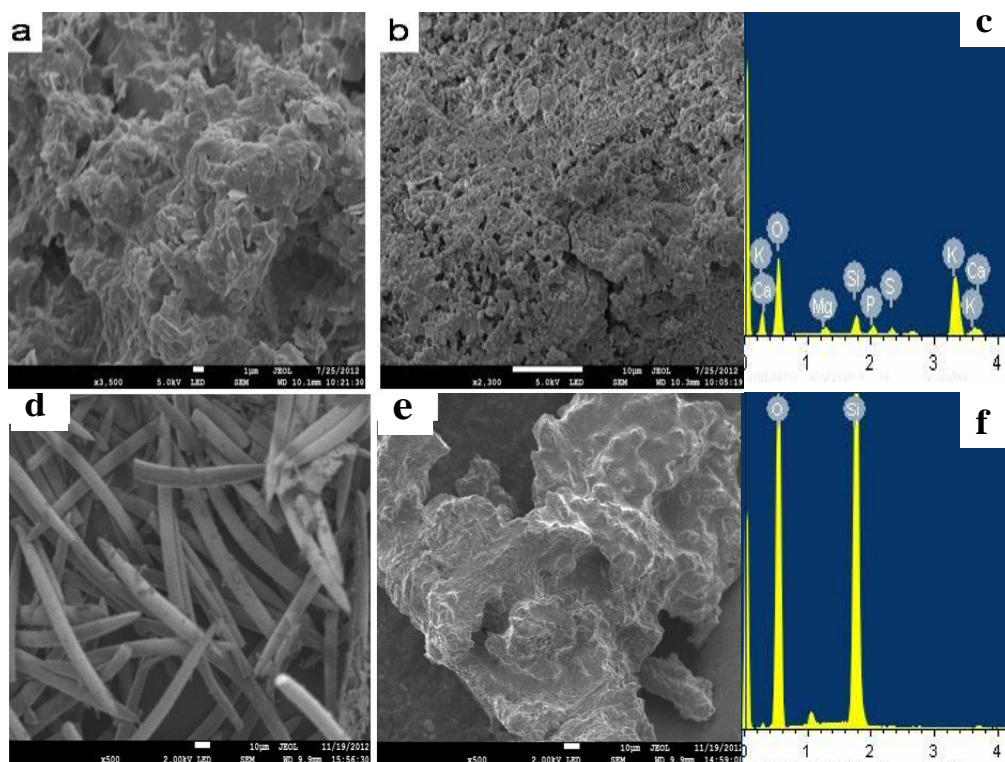


Figure 2. SEM micrograph of (a) EFBA-dried, (b) EFBA-calcined, (c) EDX EFBA-calcined, (d) WMS, (e) Na_2SiO_3 -WMS and (f) EDX Na_2SiO_3 -WMS

3.2 Catalyst amount

The amount of catalysts (EFBA-calcined and Na_2SiO_3 -WMS) was varied in the range of 0.5-3.5 wt.% (based on oil weight). As shown in Figure 3, the transesterification was dependent on the amount of catalyst used. Increasing the amount of catalyst from 0.3 to 3.5 wt.%, the methyl esters content increases from 18.5 to 85.9 wt.% and 90 wt.% for EFBA-calcined and Na_2SiO_3 -WMS, respectively. The ME content reaches the highest value at the catalyst concentration of 2.3 wt.%, due to the contact opportunity between catalyst and the reactants hence propels the reaction kinetics. The maximum ME content was observed at 2.3 wt.% for both catalysts, although Na_2SiO_3 -WMS was more high than EFBA-calcined but the differences is not significant. Based on the oil weight, the amount of catalyst used in this work seems to be higher due to several reasons; part of the catalyst could be entrapped in the clay matrix; this portion of the catalyst may not have any contribution in catalytic activity. In addition, a part of the catalyst (basic) is also used to neutralize the acids in CPO (acid value = 13 mg KOH g^{-1}). Ultrasonic that used in this work can affect the catalyst reactivity, positively, by enhancing the mass transfer between clay-catalyst-reactants as well as promising the presence of kinetic energy in the reaction media. Dispersion due to ultrasonic increases the surface area available to the reactants. As such, the use of ultrasound promotes the efficiency of acyl conversion in a shorter reaction time.

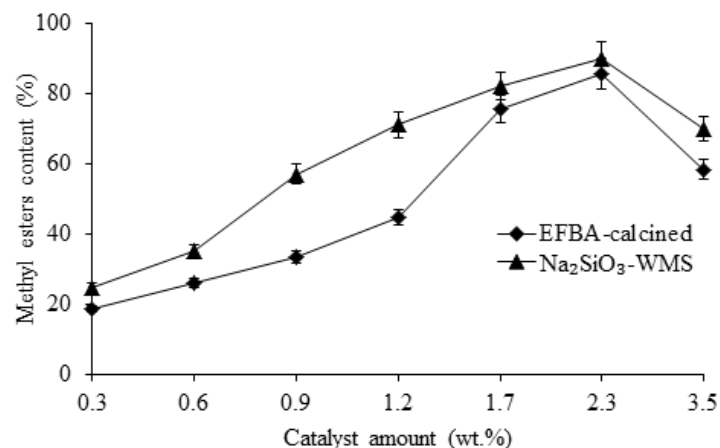


Figure 3. Effect of catalyst amount in methyl esters content (reaction conditions: temperature 55 °C; reaction time, 1 h).

3.3 Effect of methanol to oil mass ratio

The molar ratio of methanol to oil is one of the important variables that affect the transesterification reaction. Stoichiometrically, the reaction requires three moles of methanol for each mole of oil (MeOH:oil=3:1), and with excess methanol it would shift the equilibrium towards the direction of ME production. As observed from Figure 4, four different mass ratios of MeOH:oil were tested; 2:1, 4:1, 6:1 and 8:1. The ME content is increased as the MeOH:oil was raised from 2:1 to 4:1. A very sharp increase is observed between 2:1 and 4:1, and then reaches the maximum performance at 6:1 for both catalysts. However further increases to 8:1 has negative effect on ME conversion. Furthermore, there is no significant difference in ME content between EFBA-calcined and Na₂SiO₃-WMS. Too much of methanol could dilute the oil and as a result slowing the reaction rate (Gao et al., 2008), as a result, lower conversions were recorded with higher amount of methanol. Additional to that, high mass ratio of alcohol to oil increases the solubility of glycerol, and as a result, the separation of glycerol becomes more difficult and retards the forward reaction by promoting the backward equilibrium (Meher et al., 2006). Relatively larger amount of methanol was used in this work mainly to cater the solvent-absorbing and solvent-retaining characteristics of the DC during the reaction. Nevertheless, the excess amount of methanol can be readily recovered at the end of the reaction. Ultrasound radiation makes methanol to disperse into the oil, thus increases the contact surface between reactant and consequently accelerating the reaction. The effect of cavitations created by ultrasonic supplies sufficient energy into the immiscible medium and the continuous formations and collapses of micro bubble accelerates the miscibility of reactants in addition to chemical and mechanical effects.

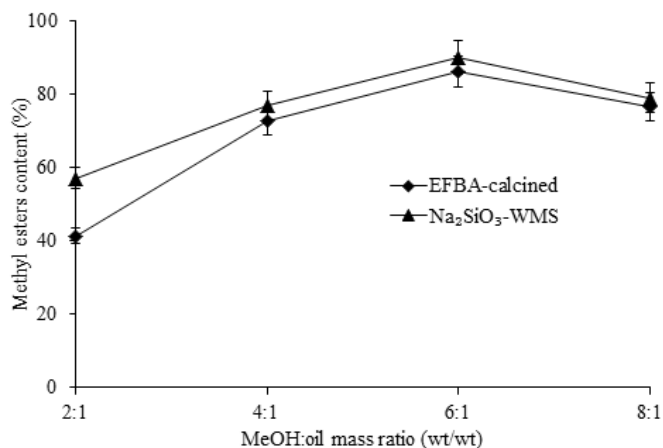


Figure 4. Effect of methanol to oil mass ratio (reaction conditions: temperature 55 °C; reaction time, 1 h).

3.4 Effect of co-solvents

In this work, co-solvents (PE and hexane) are used to aid *in situ* oil extraction as well as oil solubility in the reaction media. Figure 5 shows the influence of the co-solvents in the transesterification of the DC where approximately ME content of 80% and 84% is achieved by using PE and hexane alone, respectively. Higher conversion value for hexane is understandable as hexane (dielectric constant, 1.89) is less polar than PE (dielectric constant, 2.0-2.2), thus makes hexane to easily soluble in oil. On the other hand, the higher polar PE has better methanol soluble characteristic. This implies that by combining these two solvents, a better solubility between oil and methanol can be achieved as an evident of highest ME content (86%) is achieved at the combination ratio of 1:1 PE:hexane. The reduction of energy consumption is one of the advantages of the ultrasound technique in methyl esters production. A study on the energy requirement for transesterification using ultrasound and hotplate (mechanical stirring) methods revealed that, transesterification using hotplate requires very much more energy than ultrasonic process (Gude et al., 2012). This shows that with appropriate reactor design, non-conventional techniques have potential to reduce the process energy requirement significantly.

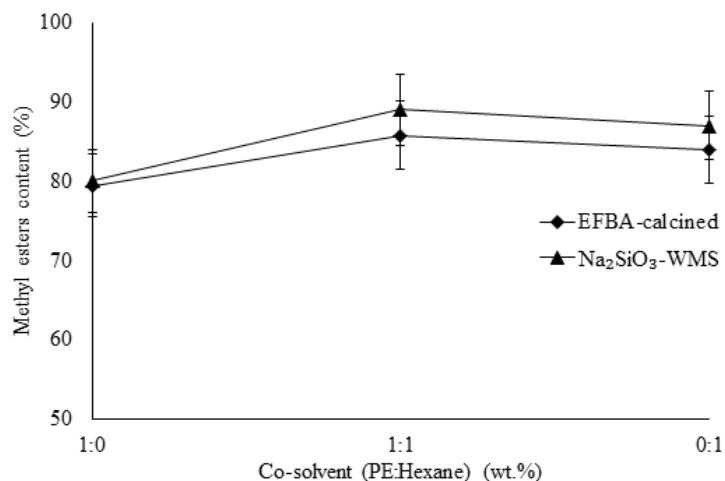


Figure 5. Effect of co-solvents to DC ratio on the methyl ester content (reaction conditions: temperature 55 °C; reaction time, 1 h).

3.5 Comparison between ultrasonic and mechanical stirring

A comparison of the effect of ultrasound in the transesterification reaction was carried out at the optimal operating conditions (methanol to oil mass ratio (3:1), catalyst amount (1.7 wt.% at 55°C for 1 h) shown in Figure 6. It can be seen from the figure that ultrasonic cavitations results in 85 and 87% conversion for EFBA-calcined and Na₂SiO₃-WMS, respectively, whereas the conventional stirring method results in lower extent of conversion 60 and 63% ME conversion for EFBA-calcined and Na₂SiO₃-WMS, respectively. This can be attributed to the fact that as the reaction is mass transfer controlled, the micro level turbulence generated due to cavitations bubbles results into the higher availability of the interfacial area and hence higher conversion. Thus, the use of ultrasonic irradiation to be in both enhances the rate of reaction as well as shifting the equilibrium and resulting in higher product yield. In agreement with Worapun et al. (2010), effect ultrasonic irradiation will inducing an effective emulsification and mass transfer so that the rate of ester formation is significantly enhanced.

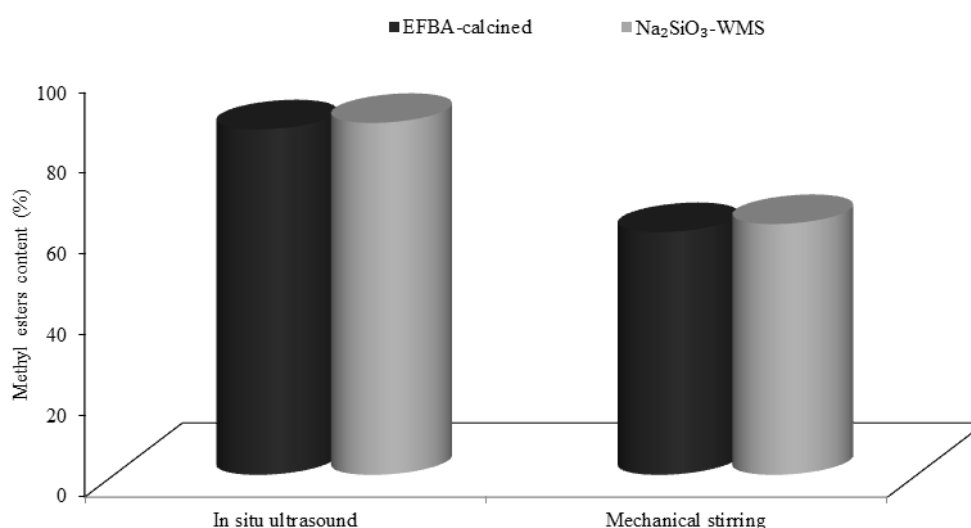


Figure 6. Comparison *in situ* ultrasound and mechanical stirring (reaction conditions: temperature 55 °C; reaction time, 1 h).

4. CONCLUSIONS

In this work, decanter cake (DC) was successfully utilized as a low-cost feedstock to produce methyl ester (biodiesel) via ultrasound aided *in situ* transesterification. Highest ME content of 85.9 wt.% was obtainable in an hour reaction time at 55 °C. Optimization of reaction parameters revealed that MeOH:oil, 6:1; catalyst, 2.3 wt.% (based on DC weight) and co-solvents to DC mass ratio of 1:2 as the optimal reaction conditions. The use of ultrasound undoubtedly assisted in achieving this remarkable result in 1 h reaction time. Materials derived from waste sources, as used in this work, should be given a priority for sustainable production of biodiesel.

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