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Microwave assisted biodiesel production from dairy waste scum oil using alkali catalysts

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Abstract: The high cost of biodiesel can be reduced by using dairy waste scum oil as a raw material. Conventional heating system employed in transesterification reaction is replaced by a microwave heating system which improves biodiesel yields. Catalytic activity of sodium hydroxide [NaOH] and potassium hydroxide [KOH] were compared which revealed that biodiesel yields produced with NaOH as a catalyst was higher than that of KOH. Studies were carried out to determine the optimum parameters such as catalyst type, catalyst amount, reaction time, methanol to oil ratio, stirring speed, and microwave power. The maximum yield was obtained with 0.75 wt% NaOH catalyst, reaction time 3 min, 6:1 methanol oil ratio, 350 rpm stirring speed, and a microwave power of 750 W.

Keywords: Dairy waste scum oil; Biodiesel; Microwave heating; Optimization.

1. Introduction

The need to reduce emissions from diesel engines has made the researchers to focus on alternative fuels which can be used without any engine modifications. Biodiesel, which is one of those types, can be produced from vegetable oils and animal fats. The main advantages of using biodiesel are renewability, lower greenhouse gas emissions, higher flash points, and biodegradability (1). Low temperature combustion and selective catalytic reduction system can reduce the nitrogen oxides (NOx) emissions from biodiesel (2-7). The cost of biodiesel is approximately 1.5 times higher than that of petroleum diesel. This is due to the use of vegetable oils for the production of biodiesel, which led to the search for other sources of biodiesel such as waste grease, waste cooking oil, waste tallow, dairy waste scum oil (8-11). The cost can also be reduced by increasing biodiesel yields. Parameters such as type of catalyst, amount of catalyst, reaction time, reaction temperature, alcohol to oil ratio, and stirring speed are very important in biodiesel production. Transesterification reaction is catalyzed by either acid catalyst or alkali catalyst or enzymatic catalyst. Acid catalysts require more alcohol-oil ratio and the reaction takes longer time which increases the production cost. Alkali catalysts are more preferred because of its lower alcohol-oil ratio and shorter reaction times to achieve better yields.

Microwave heating system has several advantages over conventional heating system. The drawbacks of conventional heating are surface heating, thermal conductivity, specific heat, and density of the material to be heated. The main reason that made researchers to focus microwave heating system is faster reaction rates and product yields.Leadbeater and Stencel conducted a batch process under atmospheric conditions for the preparation of biodiesel using monomode microwave unit for small scale reactions and multimode microwave unit for large scale reactions (12). They carried out the microwave-assisted transesterification of soybean oil in the presence of methanol and KOH, and found that a 1 min reaction time, a 50 °C temperature using 600 W, and a 1% catalyst-oil ratio were the optimal reaction parameters for microwave heating. Cottonseed oil was transesterified using microwave assisted heating and the optimum reaction parameters were 7 min reaction time, 60 °C temperature and 1.5% KOH-oil ratio. Whereas for conventional heating, the reaction time was 30 min to obtain 99.8% yield (13). Microwave heating was used to convert rapeseed oil into biodiesel via transesterification, with a yield of 88.3-93.7% (14). Lertsathapornsuk*et al.* modified 800 W household microwave system as a continuous reactor to produce ethyl ester from waste frying palm oil (9). A conversion over 97% was obtained with an ethanol-oil molar ratio of 12:1, 3.0% NaOH (in ethanol), a 30 s residence time. Suppalakpanya*et al.* identified the optimum conditions for the microwave heated transesterification process as molar ratio of palm oil to ethanol of 1:8.5, 1.5 wt% KOH/oil, a reaction time of 5 min, and a microwave power of 70 W (15). They also investigated the parametric studies of two-step reaction and concluded that a molar ratio of free fatty acid (FFA) to ethanol of 1:24 with 4 wt% H_2SO_4/FFA, a reaction time of 60 min, and a microwave power of 70 W are the optimal reaction parameters for the first step. 80% yield was obtained with oil to ethanol molar ratio of 1:4, 1.5 wt.% KOH, a microwave power of 70 W, and a reaction time of 5 min for the transesterification step (16). Patil *et al.* reported that the microwave-heating method consumes less than 10% of the energy to achieve the same yield as the conventional heating method (17). This study thus investigates the yields of biodiesel made from dairy waste scum oil with a microwave heating system. Additionally, the effects of catalyst type, amount of catalyst, reaction time, molar ratio of methanol to oil, and microwave power are investigated.

2. Materials and methods

2.1. Materials

Dairy waste scum was collected from scum removing tank of the effluent treatment plant in a fresh condition. It was processed immediately to avoid further biological actions which in turn increase free fatty acid (11). Scum is turbid white and semi-solid in texture. Collected scum was heated to the temperature of 50-60 °C to melt into liquid condition. It was then centrifuged to remove unwanted suspended materials and waste water. The top layer was then heated to the temperature of 110 °C until the oil becomes substantially anhydrous for transesterification (18). Oil yield from scum was 60-70%. The acid value of dairy waste scum oil was less than 2 mg of KOH g^{-1}. Other chemicals used in this study namely sodium hydroxide, potassium hydroxide, and methanol (99.8% pure) were purchased from Merck. All chemicals and reagents used in this study were of analytical grade.

2.2. Transesterification setup

A household microwave heating system equipped with a teflon coated mechanical stirrer and reflux condenser was used for microwave assisted reactions as shown in Fig. 1. For conventional heating reactions, microwave heating was replaced by a heating mantle.

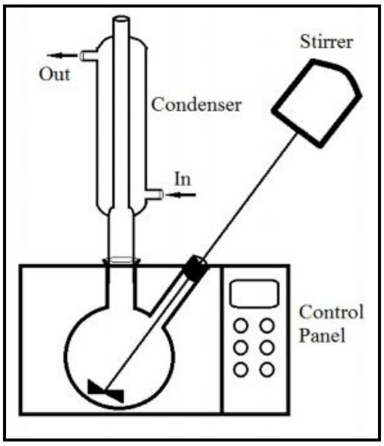

Figure 1. Microwave heated transesterification setup

2.3. Optimization studies

Optimization studies were carried out to obtain maximum yields of biodiesel. Parameters such as catalyst type and quantity, reaction time, methanol-oil ratio, stirring speed, and microwave power were optimized. The optimum of each parameter involved in the process was determined while the other parameters were set constant. After optimizing one parameter, the optimum value was set constant during the optimization of next parameter. Biodiesel yields (given as percentages) were calculated with respect to the weight of oil taken (weight of biodiesel/weight of oil).

2.4. Separation and purification

If biodiesel content is higher than 85% we thought that tranesterification reaction is complete. The resultant mixture was phase separated with the help of a centrifuge operated at 3000 rpm for 10 min. Since excess methanol was used, the unconverted triglycerides should be probably zero. Ma *et al.* reported the presence of traces of mono-glycerides and di-glycerides (19). Due to their polarity these glycerides are attracted to the glycerol phase. Excess methanol in biodiesel was evaporated by heating at 80 °C. Catalyst was removed using silica gel and then washed with hot water for three times.

2.5. Product analysis

A GC (gas chromatography; CLARUS 680, Perkin Elmer) system equipped with a FID (flame ionization detector) was used to determine methyl ester content. The temperature of the injection port and detector were set at 250 and 260 °C, respectively. The oven temperature was programmed to initiate at 50 °C for 2 min, then the temperature was raised to 150 °C at a rate of 10 °C min^{-1}, held there for 2 min. Then the temperature was raised to 200 °C at a rate of 4 °C min^{-1}, held there for 4 min, and finally increased to 230 °C at a rate of 1 °C min^{-1} and held there for 5 min. The injection volume was 1 mL in the split-less injection mode. The capillary column was an Elite 5 MS, 30 m x 0.25 mm I.D, and 0.25 mm film thickness. The chemical composition of dairy waste scum oil is given in Table 1.

Table 1. Chemical composition of dairy waste scum oil

Compound	Carbons	Fatty acid%
Butyric acid	04:00	1.344
Caproic acid	06:00	2.21
Caprylic acid	08:00	2.154
Capric acid	10:00	6.599
Lauric acid	12:00	7.043
Tridecanoic acid	13:00	5.147
Myristic acid	14:00	9.893
Myristoleic acid	14:01	2.781
Pentadecanoic acid	15:00	5.484
Palmitic acid	16:00	19.519
Hexadecenoic acid	16:01	2.457
Heptadecanoic acid	17:00	2.129
Stearic acid	18:00	12.976
Oleic acid	18:01	13.45
Linoleic acid	18:02	1.413
Linolenic acid	18:03	3.075
Arachidic acid	20:00	1.333
Behenic acid	21:00	0.992

3. Results and discussion

3.1. Comparison of yield for conventional and microwave heating

The conventional heating was carried out at 65 °C, with a methanol-to-oil molar ratio of 6, stirring speed 300 rpm, and 0.75 wt% NaOH. The microwave heating was carried out at 750 W, with a methanol-to-oil molar ratio of 6, stirring speed 350 rpm, and 0.75 wt% NaOH. As shown in Table 2, the biodiesel yield increased with reaction time for conventional heating. The maximum yield of biodiesel made from dairy waste scum oil under conventional heating was 93.6%. For the microwave system, the biodiesel yield increased with reaction time from 1 to 3 min, but then decreased from 3 to 5 min. The maximum yield of biodiesel made from dairy waste scum oil was 96.72%. The above results indicate that microwave heating has a significantly shorter reaction time and a higher yield of biodiesel compared to those for convention heating. The highly effective transesterification in the microwave heating system is attributed to the direct adsorption of the radiation by the OH group of the reactant. The OH group is directly excited by microwave radiation, causing the local temperature around the OH group to be much higher than that of its environment, far exceeding the activation energy needed for transesterification (9). Methanol is a good microwave radiation absorption material as its dipole reorients, which can destroy the two-tier structure of the interface of methanol and oil, improving the solubility of methanol and oil and thus enhancing the transesterification reaction (20,21). The above experimental results may be attributed to microwave localized temperature and pressure, and the microwave absorbing character to penetrate materials and to produce a volumetrically distributed heat source (9, 22-25). Microwave heating thus outperforms conventional heating, offering a fast, easy route for biodiesel production.

Table 2. Comparison of biodiesel yields from dairy waste scum oil under conventional heating and microwave heating systems

Method	Reaction time (min)	Yield (%)
Conventional heating	20	83.74
	30	87.60
	40	92.38
	50	92.40
	60	93.00
Microwave heating	1	85.89
	2	90.17
	3	94.57
	4	92.84
	5	90.18

3.2. Effects of catalyst type and amounts of catalyst on the yield of biodiesel under a microwave system

Experiments were carried out using different catalysts in order to investigate their influence on yield. The microwave system was operated with a reaction time of 5 min, a microwave power of 750 W, stirring speed 300 rpm, and a methanol-to-oil molar ratio of 6. NaOH and KOH were used as the catalysts. The fractions of the catalysts were 0.50, 0.75, 1.00, 1.25, and 1.50 wt%, respectively. As shown in Fig. 2, the yields of biodiesel were 83.46%, 86.97%, 89.31%, 85.34%, and 83.95% for 0.50, 0.75, 1.00, 1.25, and 1.50 wt% KOH catalyst, respectively. The yield increased with increasing amount of catalyst for catalyst concentrations of 0.50 wt% to 1 wt%, and then decreased from 1 wt% to 1.50 wt%. The best yield was obtained with 1 wt% KOH. Similar results were found for the NaOH catalyst, as shown in Fig. 2. The biodiesel yields were 85.73%, 90.18%, 89.63%, 87.04%, and 85.3% for 0.50, 0.75, 1.00, 1.25, and 1.50 wt% NaOH catalyst, respectively. These results indicate that although excess catalyst might increase the biodiesel yield, the amount of glycerol formed is also increased due to saponification, causing a decrease in biodiesel yields. A further increase in catalyst concentration did not increase the conversion, but increased production costs due to its removal from the reaction medium at the end of the process (26-28). Furthermore, Dorado *et al.* concluded that the addition of an excessive amount of alkali catalyst gives rise to the formation of an emulsion, which increases viscosity and leads to the formation of gels (26). These hinder glycerol separation, and as a result there is a dilution of the ethyl esters; the apparent ester yield diminishes. In this study, the best yields were achieved with 0.75wt% NaOH and 1 wt% KOH for dairy waste scum oil. The yields of biodiesel with NaOH catalyst were higher than those for KOH catalyst. Azcan and Danisman found that the yields of corn biodiesel with 1 wt% NaOH catalyst (92.7%) were higher than those with 1 wt% KOH catalyst (90.9%) with a methanol-to-oil molar ratio of 6 and a reaction time of 3 min (14). Leadbeater and Stencel found that the yields of corn biodiesel increased with increasing amounts of KOH catalyst, achieving yields of 93.0%, 96.0%, and 97.0% for 1 wt%, 5 wt%, and 10 wt% KOH catalyst, respectively (12).

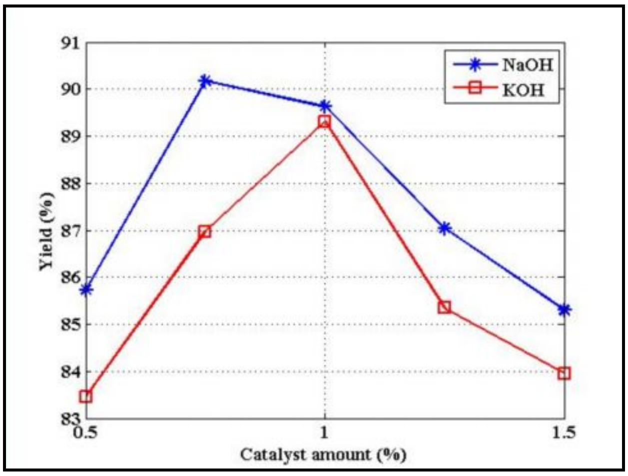

Figure 2. Optimization of catalyst type and amount

3.3. Effects of reaction time

Experiments were carried out with 0.75 wt% NaOH catalyst, a microwave power of 750 W, a methanol-to-oil molar ratio of 6, stirring speed 300 rpm, and various reaction times (1, 2, 3, 4, and 5 min) to investigate the effects of reaction time on yield. As shown in Fig. 3, the yields of dairy waste scum oil biodiesel were 85.89%, 90.17%, 94.57%, 92.84%, and 90.18% for reaction times of 1, 2, 3, 4, and 5 min, respectively. An increase in reaction time from 1 to 3 min caused a significant increase in biodiesel yield, which then decreased with a further increase to 5 min. These results may be attributed to the incomplete transesterification reaction between methanol and oil in the shorter reaction; the longer reaction had a higher reaction temperature, resulting in greater solubility of glycerol. Similarly, Azcan and Danisman found that the yields of rapeseed oil biodiesel were 92.2%, 92.7%, and 92.0% for reaction times of 1, 3, and 5 min, respectively, with 1.0 wt% NaOH, a methanol-to-oil molar ratio of 6, and a microwave power of 1200 W (14).

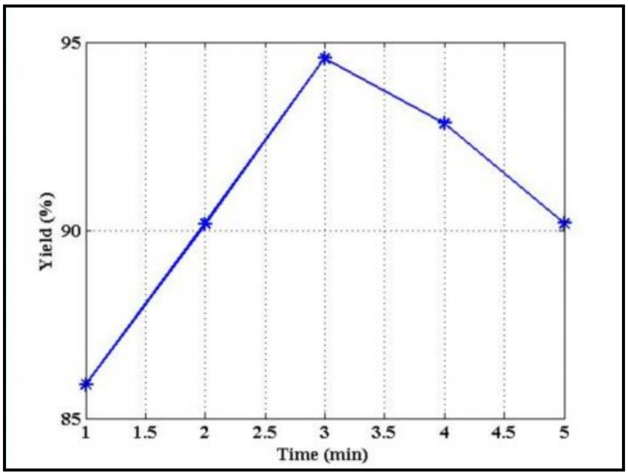

Figure 3. Optimization of time

3.4. Effects of molar ratio of methanol to oil

Experiments were carried out with 0.75 wt% NaOH catalyst, a microwave power of 750 W, a reaction time of 3 min, stirring speed 300 rpm, and various methanol-to-oil molar ratios (3, 6, 9, 12, and 15) to investigate the influence of this ratio on yield. As shown in Fig. 4, an increase in the molar ratio from 3 to 6 caused a significant increase in yield from 55.38% to 94.64%; when the molar ratio was further increased to 9, the yield decreased from 94.64% to 90.77%. Therefore, a molar ratio of 6 is most suitable for the synthesis of dairy waste scum oil biodiesel. Theoretically, each mole of biodiesel is made from 1 mol of methanol and one-third of a mole of triglyceride in the transesterification reaction. However, in practice a higher molar ratio is needed for the reaction, because the transesterification reaction is reversible. Furthermore, biodiesel and glycerol are miscible due to the use of excess methanol (21, 19). In addition, methanol is a strong medium for absorbing microwaves, and thus the excess methanol may absorb microwave energy and reduce the microwave power. Consequently, the molar ratio of methanol to oil should not be excessive, and 6 was considered the most suitable level in this experimental system.

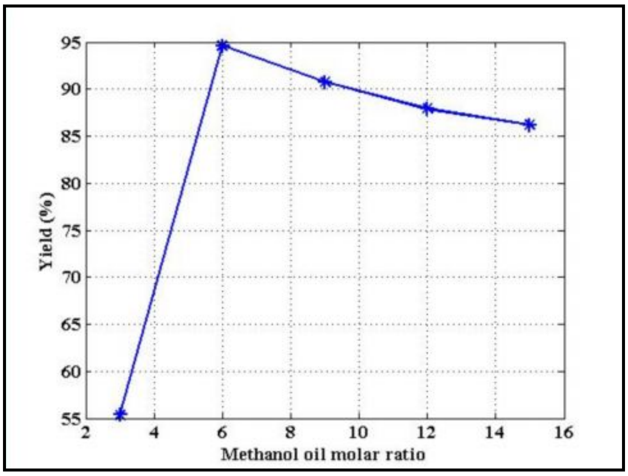

Figure 4. Optimization of methanol-oil molar ratio

3.5. Effects of stirring rate

Experiments were carried out with 0.75 wt% NaOH catalyst, a microwave power of 750W, a reaction time of 3 min, a methanol-to-oil molar ratio of 6 and various stirring rates (200, 250, 300, 350, 400 rpm) to investigate the effect of stirring rate on yield. The yields of dairy waste scum oil biodiesel were 80.24%, 84.48%, 92.66%, 96.7%, and 96.81% for stirring speeds 200, 250, 300, 350, and 400 rpm, respectively. As shown in Fig. 5, the yields of biodiesel increased with increasing stirring rate. The reaction is incomplete at the rate of 200 and 250 rpm and rate of mixing was insignificant for methanolysis. The yield of bio-diesel at 350 and 400 rpm was same after 3 min i.e. 96%. The optimum of 350 rpm is suggested.

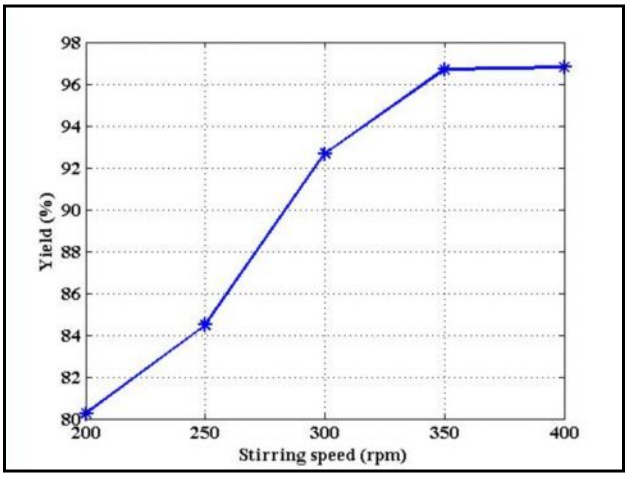

Figure 5. Optimization of stirring speed

3.6. Effects of microwave power

Experiments were carried out with a 0.75 wt% NaOH catalyst, a reaction time of 3 min, a methanol-to-oil molar ratio of 6, stirring speed 350 rpm, and various microwave powers (200, 350, 500, 650, and 750 W) to investigate the effect of microwave power on yield. As shown in Fig. 6, the yields of dairy waste scum oil biodiesel were 86.48%, 88.94%, 91.42%, 95.66%, and 96.72% for microwave powers of 200, 350, 500, 650, and 750 W, respectively. The yields of biodiesel increased with increasing power. Similar results were found in earlier works (17,29). For example, Groisman and Gedanken also concluded that the efficiency of a continuous flow system is lower than that of laboratory batch ovens at various microwave intensities (29). However, the microwave output must not be too high, as it may cause damage to organic molecules such as triglycerides, which are cleaved to FFA (30). In addition, Patil*et al.* have reported that the energy required for the microwave heating method is 23 times lower than that required for the conventional method. These results suggest that appropriate power dissipation control will result in effective use of microwave energy and reduce energy requirements (17).

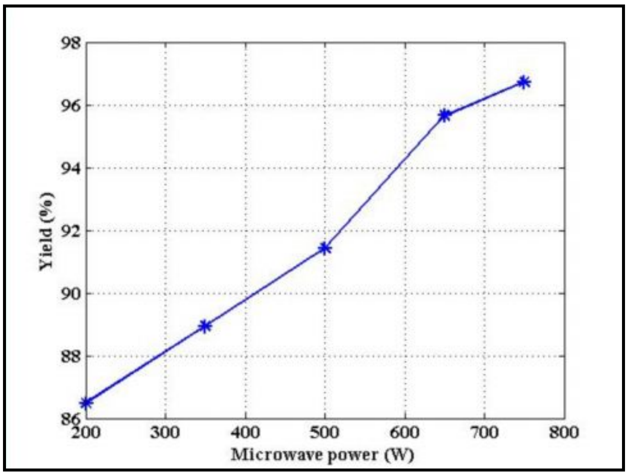

Figure 6. Optimization of microwave power

4. Conclusion

Experimental results indicate that the reaction time was reduced significantly and yield of biodiesel was improved due to the use of microwave heating. Microwave heating can achieve better performances compared with conventional heating. Biodiesel yields increased with increasing catalyst amount from 0.50 wt% to 0.75 wt% then decreased with increasing catalyst amount from 0.75 wt% to 1.50 wt%. The best performances were both under 1 wt% KOH and 0.75 wt% NaOH for dairy waste scum oil. The yields of biodiesel under NaOH catalyst were higher than those under KOH catalyst. Although excess catalyst might increase the biodiesel yield, glycerol increased as well due to saponification causing the reduction of biodiesel yields. An increase of reaction time from 1 to 3 min caused a significant increase in biodiesel yield, which decrease with a further increase to 6 min. The above results may be attributed to the incomplete transesterification reaction between methanol and oil in a shorter reaction, whereas a longer reaction had a higher reaction temperature, resulting in higher solubility of glycerol. An increase in the methanol-to-oil molar ratio from 3 to 6 caused a significant increase in biodiesel yield, with then decreased with a further increase to 9. A methanol-to-oil molar ratio of 6 is thus suitable for the synthesis of biodiesel. An increase in stirring speed from 200-400 rpm caused a significant increase in biodiesel yield. The biodiesel yield also increased with increasing reaction power, although the microwave output must not be too high as it may damage the organic molecules. The optimal reaction conditions are 0.75 wt% NaOH catalyst, a methanol-to-oil molar ratio of 6, a reaction time of 3 min, stirring speed 350 rpm and a microwave power of 750 W.

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