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Research note

Continuous-flow transesterification of crude jatropha oil with microwave irradiation

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Abstract Biodiesel is one of the major renewable energy sources, produced from vegetable oils. *Jatropha curcas* L. is considered as a promising energy crop for biodiesel production in Thailand. This study is about continuous biodiesel production from jatropha oil by transesterification in a flow process with microwave heating. Sodium methoxide was used as a catalyst at concentrations between 0.25%–1.5%, with microwave power of 800 W, irradiation time between 10–40 s, and oil to methanol molar ratio of 1:3–1:9, respectively. Results showed that jatropha oil can be converted to biodiesel (96.5%) within 30 s under oil/methanol molar ratio of 1:6 and 1.0% catalyst. The findings indicated that this method can offer alternative means to produce biodiesel continuously.

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1. Introduction

At present, energy issue is one of the main concerns in the Thai society. Owing to the shortages of petroleum production and increased consumption, the price of petroleum fuel has continued to rise. Diesel engines are very important prime movers in transportation and agricultural sectors, especially for Thailand. Looking for alternative energy sources to develop as a substitute for diesel fuels is crucial. Vegetable oils and animal fats are obvious feedstock used as alternative fuels for diesel engines [1,2]. Short term engine tests indicated that it can be used directly in the diesel engines, but many problems arose for long term uses. The central problem is associated with high viscosity and impurity in these biological oils, leading to poor performance, high exhaust emissions and reduced engine life.

Biodiesel is a renewable energy source that can be used as replacement or an additive to diesel fuel. Generally, it is produced by transesterification, a reaction of triglycerides with an alcohol using alkali, acid or enzyme as catalysts to form esters and glycerin. Alcohols such as methanol and ethanol are

the most frequently employed [3,4]. Most raw materials used are edible vegetable oils or animal fats. Using edible oils is in direct competition with consumption. Non-edible triglycerides such as jatropha oils, cotton seed oils, used cooking oils, and rubber seed oils offer alternative raw materials for biodiesel production [5].

Jatropha curcas L. has been considered as a promising energy crop for biodiesel production in Thailand [6]. It is a tropical plant that can be grown in poor land, requiring small amount of water, fertilizers and pesticides. It was also reported to improve soil quality and offer other ecological benefits [7]. The seeds of jatropha can be extracted for oil with 30%–40% recovery. Large volumes of literature exist with regards to biodiesel production from *Jatropha* oil. Recent reviews can be found in the literature [8–11].

Typically, biodiesel is produced in a discontinuous batch reactor with conventional heating from burning of fuels or electrical heating coils to provide process heat. This method consumes large amount of energy and requires long reaction time to produce high yields of biodiesel product. Microwave irradiation can offer an alternative means of heating that potentially improve energy consumption and increase efficiency. A number of works on microwave heated transesterification have been reported in [12–15] which used batch process. Several reports described the use of domestic microwave ovens as continuous-flow process [16–18]. It was shown that microwave irradiation accelerated the chemical reaction and high product yields were achieved within a short time.

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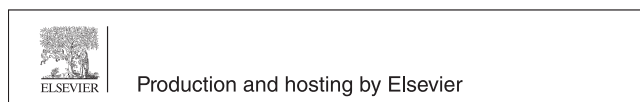


Table 1: Composition of jatropha oil.

Fatty acid	Structure	wt%	
		[19]	[20]
Palmitic	16:0	11.3	14.1–15.3
Palmitoleic	16:1	–	0–1.3
Stearic	18:0	17	3.7–9.8
Oleic	18:1	12.8	34.3–45.8
Linoleic	18:2	47.3	29.0–44.2
Linolenic	18:3	–	0–0.3
Arachidic	20:0	4.7	0–0.3

To our knowledge, biodiesel production from continuous-flow transesterification of jatropha oil with microwave heating has not yet been reported. This work is an attempt to bridge this gap. The objective of this research was to develop a process with enhancement of transesterification of jatropha oil under the continuous microwave reactor modified from domestic microwave oven. Parametric investigation for catalyst concentration, reaction time in microwave irradiation and oil to methanol molar ratio were carried out, and optimal conditions for biodiesel yields were determined.

2. Methodology

2.1. Materials

In this study, crude jatropha oil was used as raw starting material, purchased from a local vender in Chiang Mai. It was dark yellow in color. Profile of its typical composition is given in Table 1. The molecular weight of jatropha oil was approximated to be about 900. Prior to experiments, a sample of the vegetable oil was collected to determine Free Fatty Acid (FFA) content using standard titration technique. Its initial acid value was found to be 6.75–7.83 mg KOH/g, corresponding to an FFA content of 3.40%–3.93%. The oil was subsequently pretreated to remove moisture and FFA by slowly being heated up to 120 °C and reacting with NaOH at 1% w/w for 30 min to encourage soap formation; similar technique was used by Chitra et al. [21]. The mixture was allowed to settle for 1 h and the residual soap was removed. The pretreated oil with less than 1.0% FFA content was stored in an air tight container to minimize oxidation. Laboratory grade methanol (100%) and sodium methoxide (95% purity) were used without any purification. They were obtained from a local chemicals supplier (O. V. Chemicals, Co., Ltd.).

2.2. Apparatus

A Samsung model M1712N commercially available, domestic microwave oven was used. It consists of a continuously focused microwave power delivery system with an operator selectable power output from 0 to 800 W. A Teflon tubing with 8 mm internal diameter was coiled into the oven and connected to the inlet mixture tank and the outlet reservoir at the back of the oven (shown in Figure 1). A thermocouple (type K) was inserted at the outlet and connected to a digital thermometer for monitoring the reaction temperature. Prior to the experimental runs, the modified microwave oven was tested and checked that no irradiation leakage occurred.

2.3. Procedure

Transesterification reactions were carried out under microwave heating in order to see the effect of microwave irradiation on the transesterification process. Transesterification

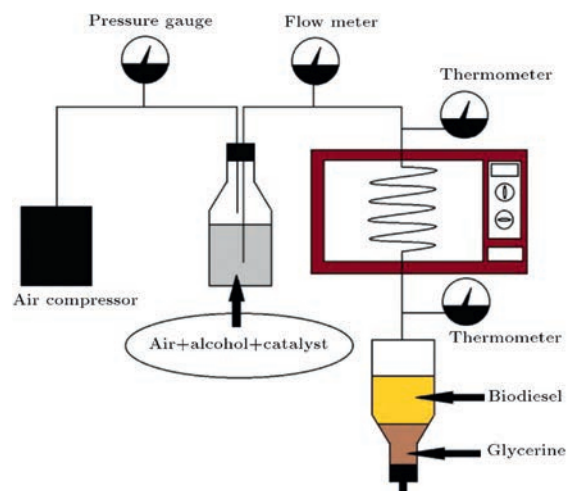


Figure 1: Experimental setup of the continuous-flow, microwave heated reactor.

reactions were done in the presence of NaOCH₃ catalyst (0.25, 0.5, 0.75, 1, 1.25 and 1.5% w/w), oil to methanol molar ratio of 1:3, 1:6, and 1:9 under different reaction time in microwave (10, 20, 30 and 40 s). The pretreated jatropha oil, methanol and catalyst were mixed in a tank. The mixture was fed via to microwave reactor. Reaction times were controlled from the flow rate driven by a pressure of air. The outlet was slightly bended upward to keep the reactor filled at all flow rates and the reaction was acidified immediately with H₂SO₄ to stop the reaction. The esters fraction (upper layer) was separated and washed until its pH neutral. Biodiesel yield, defined as the weight percentage of the final product relative to the weight of jatropha oil at the beginning, was estimated. The extent of the transesterification of the oil was also determined by an Agilent Technology gas chromatograph model GC 7890, as well as thin layer chromatography with densitometry. The biodiesel product was analyzed for viscosity (ASTM D88), higher heating value (ASTM D240), flash point (ASTM D93), pour point (ASTM D97), cloud point (ASTM D2500) and specific gravity (ASTM D1298) to assess their quality. All experiments were carried out in triplicate and mean values were reported.

3. Results and discussion

After pretreatment, only 1.5% loss in original mass of the vegetable oil was observed. The pretreated oil was found to have average FFA content of 0.11%, and was used for biodiesel production. The experimental setup adopted here was found to produce reliable, and reproducible conditions.

3.1. Effect of reaction time

It is necessary to evaluate a proper transesterification time to guarantee completion of the reaction. In this work, reaction was assumed to occur during microwave irradiation. Hence, reaction time was equal to irradiation time. It is well known that microwave irradiation activates variance of polar molecules and ions such as methanol. The continuously changing electromagnetic field interacts with molecular dipoles and charged ions, causing them to oscillate and generate heat rapidly. Studies were carried out at different irradiation times, e.g. 10, 20, 30 and 40 s with 1.0% NaOCH₃ as catalyst, irradiation power of 800 W and oil/methanol molar ratio of 1:6. The results

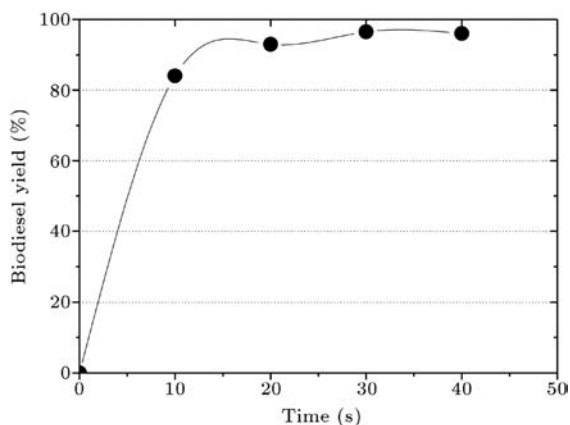


Figure 2: Effect of reaction time on biodiesel yields with 1:6 molar ratio of oil to methanol, 1.0% NaOCH₃, and microwave power of 800 W.

are shown in Figure 2. It was found that within the first 20 s, the biodiesel yields increased rapidly with the reaction time. After 30 s, they increased only slightly, reaching a conversion over 96%. Further increase in reaction time did not lead to more conversion. It was noteworthy that observed exit temperatures of the mixture were in range of 59–61, 63–66, 67–70, and 70–73 °C for 10, 20, 30 and 40 s, respectively. As expected, longer irradiation time led to higher temperature. Reaction temperature was known to have positive influence on the reaction and yields of biodiesel. However, close to the boiling point of methanol, soap formation reaction was accelerated, resulting in yield reduction.

3.2. Effect of oil/methanol molar ratio

The molar ratio is an important factor for successful transesterification. According to the chemical reaction rate, the transesterification can be accelerated by increasing amounts of methanol. The high molar ratio of oil to methanol can enhance the conversion yield of biodiesel. The required molar ratio of oil to methanol is 1:3 in order to generate three moles of biodiesel from one mole of oil. The molar ratio used in practical production has to be higher than the stoichiometric value in order to increase the degree of reaction completion. On the other hand, excessive amounts of methanol can reduce the concentrations of catalyst and reactant, slowing the reaction and aggravating the recovery of solvents. In our study, the oil to methanol molar ratio used was 1:3, 1:6 and 1:9 at catalyst concentration of 1.0% and residence time of 30 s. Effect of the molar ratio on yields was shown in Figure 3. The yield of biodiesel with oil/methanol molar ratio of 1:6 after 30 s was 96.5%. The reaction was found to be faster with higher molar ratio. Longer time was required for lower molar ratio to obtain similar conversion yields. However, the high molar ratios of oil to methanol can make solvent recovery more difficult, and emulsification can occur on washing of products.

3.3. Effect of catalyst concentration

It is generally accepted that use of higher catalyst concentration results in faster reaction rate. However, excessive amounts of catalysts will lead to soap formation, which increased the viscosity of the reactants and difficulty in separating the products. Therefore, the amount of catalyst represents a critical parameter in obtaining a high conversion yield. In this study, transesterification was carried out using NaOCH₃ as a catalyst at a

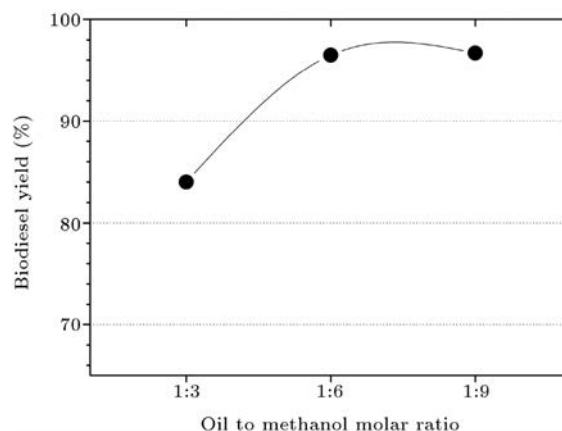


Figure 3: Effect of molar ratio of oil to methanol on biodiesel yields with reaction time of 30 s, 1.0% NaOCH₃, and microwave power of 800 W.

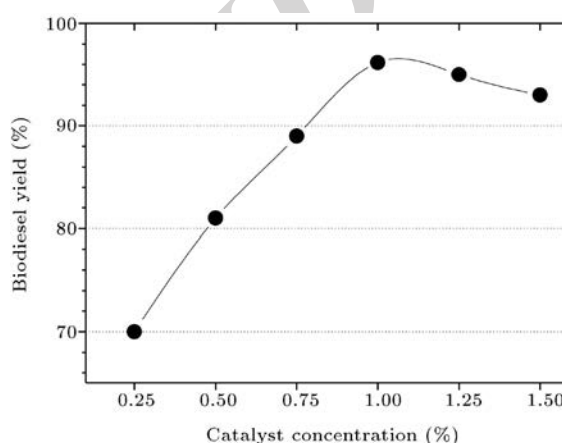


Figure 4: Effect of NaOCH₃ concentration on biodiesel yields with reaction time of 30 s, 1:6 molar ratio of oil to methanol, and microwave power of 800 W.

concentrations between 0.25%–1.5% with the oil/methanol molar ratio of 1:6, reaction of 30 s and the microwave irradiation power of 800 W. Figure 4 shows that the yields of biodiesel was very low when the catalyst concentration was 0.25%. The highest yield (96.5%) was obtained at 1.0%. However, when a catalyst concentration of over 1.0% was employed, no difference in biodiesel yields was observed. This was due to soap formation in the presence of high catalyst amounts.

3.4. Comparison with literature

Biodiesel yields from jatropha oil and other vegetable oils at optimum conditions were listed in Table 2. Chitra et al. [21], and Berchmans and Hirata [19] studied transesterification of jatropha oil under conventional heating in the presence of NaOH. It was concluded that 90%–98% of biodiesel yield at similar molar ratios and catalyst concentrations was achieved after 90–120 min of reaction time. Tiwari et al. [20] reported that 99% yield was obtained after only 24 min for conventional heating with 0.6% KOH. With respect to other vegetable oils, works on microwave assisted transesterification with NaOH or KOH were reported in [12,13,15,18,22–24], achieving 98–99.8% yields in 1–7 min.

From the comparison, it was clear that biodiesel yields obtained in this work were comparable to those reported in the literature. Against conventional heating, it was also confirmed

Table 2: Comparison of optimum conditions and corresponding yields of biodiesel.

Raw materials	Reference	Process type	Heating	Catalyst type and concentration (%)	Oil/methanol molar ratio	Reaction time (min)	Yield (%)
Jatropha oil	This work	Continuous	Microwave	NaOCH ₃ 1.0	1:6	0.5	96.5
Jatropha oil	[21]	Batch	Conventional	NaOH 1.0	1:6	90	98.0
Jatropha oil	[19]	Batch	Conventional	NaOH 1.4	1:7	120	90.0
Jatropha oil	[20]	Batch	Conventional	KOH 0.6	1:4	24	99.0
Cotton seed oil	[12]	Batch	Microwave	KOH 1.5	1:6	7	99.8
Soybean oil	[13]	Batch	Microwave	KOH 5.0	1:6	1	98.0
Sunflower oil	[15]	Batch	Microwave	KOH 1.0	1:6	2	99.6
Used vegetable oil	[18]	Continuous	Microwave	KOH 1.0	1:6	1	98.9
Rapeseed oil	[22]	Batch	Microwave	NaOH 1.0	1:6	1	99.4
Maize oil	[23]	Batch	Microwave	NaOH 1.5	1:10	5	>98
Safflower oil	[24]	Batch	Microwave	NaOH 1.0	1:10	6	98.4

Table 3: Fuel properties of jatropha biodiesel.

	Method	Biodiesel	Thai specification	EN 14214
Viscosity at 40 °C, cSt	ASTM D88	4.2	3.5–5.0	3.5–5.0
Higher heating value, MJ/kg	ASTM D240	37.8		
Flash point, °C	ASTM D93	154	Min 120	> 101
Pour point, °C	ASTM D97	1		
Cloud point, °C	ASTM D2500	4		
Specific gravity	ASTM D1298	0.87	0.86–0.90	0.86–0.90
Ester content, % w/w	EN 14103	>97	Min 96.5	Min 96.5
Acid number, mg KOH/g	ASTM D664	0.22	Max 0.5	Max 0.5

that the microwave heating can enhance transesterification of jatropha oil with methanol, allowing high yields and conversions into esters at a short time.

3.5. Biodiesel properties

The quality of biodiesel is important for usage in a diesel engine. In this work, biodiesel from jatropha oil produced at the optimum condition was sent for quality testing using standard methods. Results are shown in Table 3, against the Thai and European biodiesel specifications. For the properties considered, it can be seen that the jatropha biodiesel obtained met the required specifications.

4. Conclusions

Production of biodiesel from jatropha oil with microwave heating was investigated in this study. It was demonstrated that microwave irradiation can enhance transesterification of the vegetable oil. High yield of over 96% can be obtained in a relatively short reaction time and at a small amount of catalyst. Microwave heating was found to give efficient heating for rapid conversion of jatropha oil to biodiesel. The optimal transesterification conditions were found to be reaction time of 30 s, a molar ratio of oil to methanol 1:6, and 1.0% NaOCH₃ as catalyst to give a conversion yield higher than 96%. This continuous transesterification process is simple, practical and time-saving, offering alternative production method to increase the reaction rate and decrease energy for producing biodiesel.

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