

Microwave Assisted Energy Efficient Biodiesel Production from Crude *Pongamia pinnata* (L.) Oil Using Homogeneous Catalyst

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Abstract

Microwave assisted biodiesel production from crude *Pongamia pinnata* oil using homogeneous base catalyst (KOH) was unsuccessful because of considerable soap formation. Therefore, a two step process of biodiesel production from high free fatty acid (FFA) oil was investigated. In first step, crude *P. pinnata* oil was acid catalyzed using H₂SO₄ and acid value of oil was reduced to less than 4 mg KOH/g. Effect of sulfuric acid concentration, alcohol-oil molar ratio and microwave irradiation time on acid value of oil was studied. Result suggested that 1.5% H₂SO₄ (w/w), 6 : 1 methanol oil molar ratio and 3 min microwave irradiation time was sufficient to reduce the acid value of oil from 12 and 22 mg KOH/g to 2.9 and 3.9 mg/KOH/g, respectively. Oil obtained after pretreatment was subsequently used for microwave assisted alkali catalyzed transesterification. A higher biodiesel yield (99.0%) was achieved by adopting two step processes. Microwave energy efficiency during alkali catalyzed transesterification was also investigated. The results suggested a significant energy saving because of reduced reaction time under microwave heating.

Key Words: microwave, pongamia pinnata, biodiesel, acid value, energy efficiency

Introduction

Presently the world's energy requirement is met through non-renewable resources such as petrochemicals, natural gas and coal. It is reported that with an existing rate of petroleum consumption, the world's fossil fuel reserves will diminish by 2050 (Demirbas 2009). Fossil fuels add carbon dioxide, sulfur dioxide and other green house gases into the atmosphere raising environmental concerns. Hence, efforts are being made to explore the alternative sources of energy. Biodiesel obtained from vegetable oils (VOs) is a suitable alternative to diesel fuel. It is renewable, cost effective and eco-friendly fuel (Ma and Hanna 1999). Many non-edible oil yielding species such as *Pongamia pinnata*, *Jatropha cur-*

cas, *Madhuca indica*, *Azadirachta indica*, *Simarouba glauca*, *Hevea brasiliensis* etc have been identified as potential biodiesel species (Tewari 2003). Seeds of *P. pinnata* contain 30 to 40% oil, which is used for biodiesel production, lighting lamps, soap making, and as a lubricant.

Annual production of *P. pinnata* oil in India is more than 200 metric tons. Crude *P. pinnata* oil contains variable amounts of nonglyceride impurities such as free fatty acids, gums, color pigments etc which are detrimental to end product. Quality of oil in terms of acid value is an important qualitative parameter noted for biodiesel production (Freedman 1984; Marinkovic and Tomasevic 2003). High acid value oil results in soap formation during alkali catalyzed transesterification (Sharma and Singh 2008). It re-

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duces yield and makes biodiesel separation and purification process extremely difficult (Ma et al. 1998). For successful biodiesel production, acid value of the oil is required to be < 4.0 mg KOH/g (Ghadge and Raheman 2005; Karmee and Chadha 2005). *P. pinnata* oil generally has higher acid value (> 4.0 mg KOH/g) and therefore, it requires pre-treatment before biodiesel production (Sharma and Singh 2008). Studies in the past have suggested a two step process i.e., acid catalyzed esterification followed by alkali catalyzed transesterification for production of biodiesel from high acid value oils (Ramadhas et al. 2005; Sharma and Singh 2008).

During past few years, there has been an increasing interest in the use of microwave energy for chemical synthesis (Leadbeater and Stencel 2006; Liu et al. 2010). Short reaction time, clean reaction products and uniform heating are the main advantages of microwave (Lidstrom et al. 2001; Bouaid et al. 2005; Hernando et al. 2007). Use of microwave energy for biodiesel production has received increased attention in recent years mainly due to its ability to complete reaction in very short time (Liu et al. 2010; Kumar et al. 2011). Effectiveness of microwave for chemical synthesis is well established, however, its usefulness in terms of energy intensiveness is current area of research (Barnard et al. 2007; Kim et al. 2011).

In the present work, microwave assisted esterification of crude *P. pinnata* oil was carried out. Effect of H_2SO_4 concentration (0.5%, 1.0% and 1.5% w/w), methanol-oil molar ratio (1 : 6, 1 : 9 and 1 : 12) and microwave irradiation time (3, 9, 15, 20, 30 and 60 min) on acid value of oil was studied. Low acid value oil (< 4.0 mg KOH/g) obtained after esterification reaction was subsequently used for microwave assisted alkali catalyzed transesterification. Energy efficiency of microwave during alkali catalyzed transesterification was also investigated.

Materials and Methods

Materials

P. pinnata oil was obtained from Mahatma Gandhi Institute of Rural Energy and Development, Bangalore. Reference standards of fatty acid methyl ester were procured from M/s Sigma-Aldrich. Analytical reagent grade chemicals such as methanol, sulphuric acid and potassium hydroxide pellets were obtained from M/s Himedia.

Microwave assisted esterification and transesterification was carried out using Start Synth Model microwave unit (Milestone company-Italy), which is equipped with reflux condenser, magnetic stirrer bar and non-contact infrared continuous feedback temperature system.

Microwave assisted acid esterification

P. pinnata oil had an initial acid value of 12 and 22 mg KOH/g, which corresponds to a FFA value of 6% and 11%, respectively. Acid value was determined using standard method (Helrich 1990). Microwave assisted esterification was carried out at $62^\circ C$ reaction temperature. Effect of H_2SO_4 concentration (0.5%, 1.0% and 1.5% w/w), methanol-oil molar ratio (6 : 1, 9 : 1 and 12 : 1) and microwave irradiation time (3, 9, 15, 20, 30 and 60 min) on acid value of crude oil was studied. After completion of reaction time, solution was poured into separating funnel for separation. Surplus alcohol along with water and other impurities moves to the top layer of separating funnel. The lower layer of oil was separated and analysed.

Microwave assisted transesterification

P. pinnata oil obtained after esterification was used as raw material for alkali catalyzed transesterification. Catalyst concentration (1% KOH), stoichiometry (6 : 1 alcohol to oil) and reaction temperature ($62^\circ C$) were kept constant for all experiments. The reaction was continued for different microwave times i.e., 3, 5, 7 and 10 min. After completion of reaction, the mixture was transferred to a separating funnel for separating biodiesel and glycerol. Biodiesel was initially washed with glacial acetic acid mixed in hot water followed by plain hot water washing for two times. Moisture from the washed biodiesel was removed by using anhydrous sodium sulphate. Biodiesel yield was calculated relative to the initial amount of *P. pinnata* oil by weight. Biodiesel purity was determined according to the relative methyl ester content obtained by gas chromatography analysis. For each reaction conditions the experiment was repeated for three times and average value was obtained.

Ester content and fuel properties of biodiesel

The purity of biodiesel i.e., relative methyl ester content, was determined using Gas Chromatography (AIMIL Nucon 5765) equipped with Flame Ionization Detector

(FID). The column used for analysis was DB-30 column (30 m x 0.25 mm x 0.15 μ m). Nitrogen was used as a carrier gas at a flow rate of 40 mL/min. Oven temperature was maintained at 160°C. Relative density at 15°C was determined according to ASTM D-4052, using Anton Paar density meter (DMA 4500 M). Fuel properties of methyl ester were determined using ASTM (D6751) standards.

Determination of specific heat of *P. pinnata* oil

Specific heat of *P. pinnata* oil was determined using Differential Scanning Calorimeter (DSC). A known quantity of oil sample was placed in an aluminum crucible and heated from ambient to 65°C at a heating rate of 10°C min⁻¹. Two replicates of the oil sample were analyzed and average values are reported.

Estimation of electrical energy consumption

Microwave reactor used in this study does not directly give the total energy consumption; however, it provides necessary information on power consumption with time. Power consumed during the reaction was recorded at every 5 second interval. Overall electrical energy consumed during transesterification reaction was calculated using equation 1 (Halliday and Resnick 1977).

$$E_{mw} = P_{mw} * t \quad (1)$$

where E_{mw} is the energy (joules), P_{mw} is power (watt) and t is time (sec).

Overall electrical energy consumed (equation 1), includes energy utilized during transesterification, energy losses due to heat dissipation etc. The theoretical energy required to raise the temperature of oil methanol mixture by 32°C (29 to 62°C) was determined using equation 2 (Halliday and Resnick 1977).

$$Q = m C \Delta T \quad (2)$$

where Q is heat (joules), m is mass (grams), C is specific heat capacity of material (J g⁻¹ K⁻¹) and ΔT is change in temperature (K). Efficiency of microwave reactor was determined by comparing theoretical energy consumption with overall electrical energy consumption.

Results and Discussion

Physical and fuel properties of *P. pinnata* oil

Kinematic viscosity at 40°C and density at 15°C of crude *P. pinnata* oil were found to be 39 mm²/s and 0.936 g/cm³, respectively. Acid value was found to be 12 and 22 mg KOH/g. Refractive index of oil at 29°C was 1.476 and calorific value was 38.8 MJ/kg. The major fatty acid methyl ester composition of *P. pinnata* oil was estimated as palmitic acid (14.1%), stearic acid (7.37%), oleic acid (58.64%) and linoleic acid (18.70%).

Microwave assisted single step alkali catalyzed transesterification

Microwave assisted single step-alkali catalyzed transesterification of crude *P. pinnata* oil was carried out in presence of potassium hydroxide catalyst (1.0% w/w) at 62°C reaction temperature and 5 min reaction time. Stoichiometry for reaction was 6 : 1 alcohol to oil (Kumar et al. 2011). Results show a significant decrease in biodiesel yield with increase in acid value of oil (Fig. 1). Satisfactory transesterification, with 99% biodiesel yield was obtained in oil having low (< 4.0 mg KOH/g) acid value. Complete gel formation and no methyl ester separation was observed in oil having high (> 6.0 mg KOH/g) acid value (Fig. 1). Naik et al. (2008) have made similar observation of reduction in yield of biodiesel (97% to 6%) with increase in acid value of *P. pinnata* oil (0.6 to 10.6 mg KOH/g) under conventional heating.

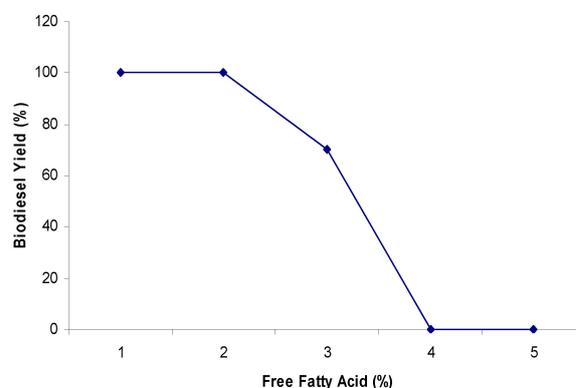


Fig. 1. Effect of FFA content on biodiesel yield during microwave assisted alkali catalyzed transesterification.

Microwave assisted esterification

The results of microwave assisted esterification of crude *P. pinnata* oil with methanol are presented in Table 1 and Table 2. A rapid reduction in acid value of oil was observed in the initial phase of reaction. Slow reaction rate in latter stages may be due to negative effect of water produced during esterification of free fatty acids (Ghadge and Raheman 2005). From Table 1 and Table 2, it can be seen that the rate of reaction was influenced by H₂SO₄ concentration and quantity of methanol. Optimum catalyst (H₂SO₄) concentration was found to be 1.5%, at which acid value of oil was reduced from 12 and 22 mg KOH/g to 2.95 and 3.91 mg KOH/g, respectively in 3 min microwave irradiation time (Table 1). Rate of reduction in acid value was found to be comparatively less while using 0.5 and 1.0% H₂SO₄ (Table 1). From Table 2, it can be seen that by using 9 : 1 and 12 : 1 methanol to oil ratio, acid value was reduced from 12 mg KOH/g to <4.0 mg KOH/g in 3 min reaction time. However, a higher methanol amount (12 : 1) and increased microwave irradiation time (15 min) was required for reducing acid value of oil from 22 mg KOH/g to <4.0 mg KOH/g (Table 2). Rapid esterification reaction under microwave heating can be attributed to enhanced molecular movement of reactants with increased possibility of molecular encounters and product yield (Lidstrom et al. 2001).

Alkali-catalyzed transesterification

Microwave assisted alkali transesterification was carried out using esterified oil having acid value <4.0 mg KOH/g. The results on yield and purity of biodiesel are summarized

Table 1. Effect of H₂SO₄ concentration on acid value of *P. pinnata* seed oil under microwave irradiation at 6 : 1 alcohol oil molar ratio

Reaction time	Acid value (mg KOH/g) of <i>P. pinnata</i> oil					
	12.0 (mg KOH/g)		22.0 (mg KOH/g)			
H ₂ SO ₄ (w/w)	0.5%	1.0%	1.5%	0.5%	1.0%	1.5%
3 min	4.30	3.55	2.95	7.17	5.85	3.91
9 min	3.73	3.20	2.34	5.39	4.07	3.04
15 min	3.61	2.96	2.08	4.88	3.80	2.53
20 min	3.20	2.75	1.99	4.26	3.58	2.47
30 min	3.12	2.51	1.98	4.18	3.20	2.17
60 min	3.02	2.23	1.98	3.80	3.10	2.13

in Table 3. The overall biodiesel yield was found to be 99.0%. No significant change in biodiesel yield was achieved by increasing the reaction time from 3 to 10 min (Table 3). The purity of biodiesel was in accordance to EN 14214 (Table 3).

Fuel properties of *P. pinnata* biodiesel

Results on fuel properties of biodiesel from *P. pinnata* oil are shown in Table 4. Flash point of biodiesel was found to be 191°C, which is higher than that of diesel i.e., 68°C. Viscosity (5.04 mm²/sec) and acid value (0.56 mg KOH/gm) of *P. pinnata* biodiesel were found to be in accordance with standards (Table 4). Calorific value of the biodiesel (39.3 MJ/kg) was slightly lower than that of diesel (42 MJ/kg). The measured values of fuel properties of biodiesel are in the range of prescribed American (ASTM 6751) and Indian biodiesel standards (IS 15607:2005).

Energy consumption during microwave assisted transesterification

The result on specific heat of *P. pinnata* seed oil is given

Table 2. Effect of oil-to-methanol ratio on acid value under microwave irradiation condition at 0.5% H₂SO₄ concentration

Reaction time	Acid value (mg KOH/g) of <i>P. pinnata</i> oil					
	12.0 (mg KOH/g)		22.0 (mg KOH/g)			
Oil methanol molar ratio	1 : 6	1 : 9	1 : 12	1 : 6	1 : 9	1 : 12
3 min	4.43	4.02	3.90	6.88	6.48	5.86
5 min	4.24	3.76	2.96	6.25	6.00	5.23
7 min	3.95	3.44	2.31	5.64	5.48	4.54
10 min	3.80	3.40	2.32	5.23	5.12	4.23
12 min	3.66	3.22	2.18	4.76	4.30	4.00
15 min	3.54	3.15	2.19	4.26	4.13	3.91

Table 3. Results of microwave assisted transesterification using 1.0% KOH (w/w)

Temperature	Reaction time (min)	Biodiesel yield (%)	Biodiesel purity (%)
62 °C	3	99.3	98.8
	5	99.2	99.2
	7	99.0	98.7
	10	98.8	98.2

Table 4. Fuel properties of biodiesel obtained from *P. pinnata* oil at 1.0% (w/w) KOH, 62°C reaction temperature and 6 : 1 methanol oil ratio

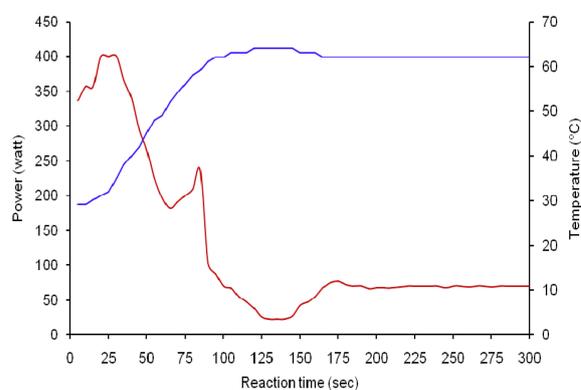
Properties	Crude <i>P. pinnata</i> oil	<i>P. pinnata</i> Biodiesel*	Diesel	Biodiesel standards	
				ASTM	D6571 IS 15607 : 2005
Density at 15°C (kg/m ³)	936	865	850	--	860 ~ 900
Viscosity, 40°C (mm ² /s)	39.0	5.04	2.60	1.9 ~ 6.0	2.5 ~ 6.0
Flash point, °C	-	191	68	> 130	> 130
Acid value, mg KOH/g	22.0	0.56	0.35	0.5 max	0.5 max
Cloud point, °C	-	15	-	- 3 to 12	--
Refractive index, 29°C	1.476	1.4600	-	--	--
Calorific value (MJ/kg)	38.9	39.3	42.0	--	--
Sulfur content (% mass)	-	15 ppm		0.0015 max	---

*Fuel properties analysis of biodiesel prepared at 3 min reaction time.

Table 5. Specific heat (C_p) of *P. pinnata* oils obtained by DSC

Temperature (°C)	C _p (J g ⁻¹ K ⁻¹)
26	2.612
30	2.581
35	2.563
40	2.565
45	2.553
50	2.546
55	2.546
60	2.534
65	2.538

in Table 5. A marginal decrease in specific heat of oil (2.612 to 2.538 J g⁻¹ K⁻¹) with increasing temperature (26°C to 61°C) was observed. Weighted average specific heat of *P. pinnata* oil (2.612 J g⁻¹ K⁻¹) and methanol (2.529 J g⁻¹ K⁻¹) was used for energy calculation. Theoretically, the energy required for raising the temperature of 182 grams of methanol oil mixture from 29 to 62°C (32°C) is 15.7 kJ, whereas, the actual electrical energy consumed was 25.7 kJ. This indicates a microwave energy efficiency of ~61%. In the present experiment, reaction temperature (62°C) was attained in 95 seconds. After reaching 62°C, almost a constant power of ~61 watt was consumed for maintaining the reaction temperature for different reaction time (Fig. 2). The total energy consumption at different reaction time is shown in Table 6. The result indicates an energy consumption of 29.9 and 38.2 kJ after microwave irradiation time of 180 and 300 sec respectively. Considering 180 sec as optimum transesterification time, it was observed that up to 86% of total energy was consumed for raising the temper-

**Fig. 2.** Absorbed microwave power and rise in temperature with time during microwave assisted transesterification.**Table 6.** Energy consumed during microwave assisted alkali catalyzed transesterification

Reaction time (sec)	Temperature (°C)	Energy consumed (joule)
30	35	13085
60	49	19705
90	61	25310
120	64	27125
180	62	29890
240	62	34015
300	62	38180

ature of reaction mixture from 26°C to 62°C. Once the reaction temperature (62°C) was achieved, remaining 14% energy was utilized for maintaining this reaction temperature. When the reaction was continued for 300 sec, a major portion of energy (67.4%) was consumed in the ini-

tial 95 sec for attaining the target temperature. Energy required for microwave assisted transesterification in 180 and 300 sec was found to be 164 kJ/kg (141 kJ/L) and 210 kJ/kg (182 kJ/L), respectively. Results of this study are comparable to the earlier reported results, where microwave assisted esterification was performed using heterogeneous catalyst (Kim et al. 2011). Comparison of energy consumed in transesterification with calorific value of biodiesel (39.3 MJ/kg) suggested a negligible energy inputs ($\sim 0.5\%$) during reaction. It can be concluded that the energy saving under microwave heating is mainly due to rapid heating and significant reduction in reaction time.

Conclusions

The effect of microwave irradiation on production of biodiesel from high acid value *P. pinnata* seed oil was investigated. A two step process i.e., acid esterification followed by alkali catalysed transesterification was adopted for production of biodiesel. Acid value was reduced from its initial values of 12 and 22 mg KOH/g to 2.95 and 3.91 mg KOH/g, respectively, in 3 min microwave irradiation time using 1.5% H₂SO₄ concentration and 1:6 oil methanol molar ratio. Microwave assisted alkali catalyzed transesterification of pretreated *P. pinnata* seed oil resulted in biodiesel yield of 99.3% with 98.8% purity. Reaction was completed in considerable less time under microwave heating. Fuel properties of biodiesel were found to be in line with specified ASTM and Indian biodiesel standards. Electric energy consumed during transesterification reaction was found to be 29.9 kJ. It is revealed that energy saving during microwave heating is mainly due to rapid heating and reduced reaction time.

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