RESEARCH ARTICLE

Chemical Transformation of Triglycerides of Fatty Acid of Pongamia pinnata Seed to Fatty Acid Methyl Esters by Microwave Irradiation

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Chemical Transformation of Triglycerides of Fatty Acid of *Pongamia pinnata* Seed to Fatty Acid Methyl Esters by Microwave Irradiation

Mehulkumar L Savaliya, Bharatkumar Z Dholakiya*
Department of Applied Chemistry, S.V. National Institute of Technology,
Ichchhanath, Surat 395007, Gujarat, India.

***Correspondence:** bharat281173@gmail.com, msmehulsavaliya@gmail.com

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Abstract
This work was done to study microwave assisted transesterification of *Pongamia pinnata* seed oil carried out for the production of Fatty Acid Methyl Esters (FAME, biodiesel). The experiments were carried out using methyl alcohol and two different alkali catalysts i.e., potassium hydroxide (KOH) and sodium hydroxide (NaOH). The experiments were carried out at 1:6 oil/alcohol molar ratio and 60 ˚C reaction temperature. The effect of catalyst concentration and reaction time on the yield and quality of biodiesel (FAME) was studied. The result of the study suggested that 0.5% sodium hydroxide and 1.0% potassium hydroxide catalyst concentration were optimum for biodiesel production from *P. pinnata* oil under microwave heating. There was a significant reduction in reaction time for microwave assisted transesterification as compared to conventional heating.

Keywords: Fatty Acid Methyl Ester (FAME); vegetable oil (VO); microwave reactor; *P. pinnata* seed oil; transesterification.

1. Introduction

The fast growing population, rapid modernization and industrialization have extensively increased the demand of energy in developing countries like India. The recent demand of energy in developing countries is mostly met from non-renewable sources such as petrochemicals, natural gas and coal [1]. The dependency on these fossil fuels, which are largely being imported, has serious implications on economy and environment. Hence, efforts are being made to explore for alternative sources of energy [2, 3]. The vegetable oils (VOs) obtained from the renewable resources has caught the attention of researchers for the production of biodiesel, which is biodegradable and contributes a minimum amount of net greenhouse gases to the atmosphere. Although the calorific value of VOs is as good as diesel fuel, the low volatility and high viscosity of VOs prohibits its direct application as fuel for diesel engines. However, this technical problem of higher viscosity of VOs has been overcome by transesterification [4]. Transesterification is the process of reacting triglyceride (vegetable oil) with alcohol in presence of catalyst. During this process, triglycerides are first converted to diglycerides, which in turn are converted to monoglycerides, and then to glycerol. Each step produces a molecule of an ester of a fatty acid [5]. The trees of *P. pinnata* are naturally distributed throughout India. *P. pinnata* is a multipurpose tree which is planted by state forest departments and by the farmers for various end uses. Depending upon the age of a tree, single tree can give seed kernels between 8 and 24 kg [6]. The seeds contain 30–40% of oil which is reported to be non-edible and inappropriate for human consumption [1]. *P. pinnata* has been recognized as one of the major biofuel species in India [7]. The oil obtained from *P. pinnata* has been studied for production of biodiesel and different reaction parameters i.e., reaction temperature, reaction time, and catalyst amount and alcohol–oil ratio are optimized [8, 9]. The latest study reported the optimum reaction conditions for alkali catalyzed transesterification of *P. pinnata* oil as 1% KOH as catalyst; 1:6 oil/methanol molar ratio and 65 ˚C reaction temperature. In the above experiment, a 97% methyl ester yield was reported at 6:1 methanol/oil molar ratio after 3 h. It was also concluded that a similar yield (97%) can be obtained in 30 min, when the reactions are carried out at 1:24 oil/methanol molar ratio [10]. The yield and reaction time are reported to vary greatly when the conventional heating systems are replaced by microwaves. Microwave assisted transesterification is a current research topic and there are few studies which deal with it [11-13]. Some person had reported a significant reduction in the reaction time and an increase in product yield under microwave irradiated transesterification [14]. The microwaves are basically electromagnetic radiations, having electric field component and a magnetic field component. The former component is responsible for the dielectric heating. Many molecules (such as those of water, alcohol, fats, etc.) are electric dipole and therefore they rotate as they try to align themselves with the alternating electric field of the microwaves. This results in molecular friction and collisions, giving rise to intense localized heating and thereby accelerating the chemical reaction and giving high product yields in a short time [15]. Compared with conventional heating, microwave

irradiation requires very less energy input for heating, when solvents with higher dielectric loss factors are used [16]. The mixing of solvents is an important variable in the transesterification reaction. The immiscibility of catalyst–alcohol solution with the VOs hinders the progress of transesterification reaction. Hence, a vigorous mixing is required for creating fast and sufficient contacts between the two immiscible phases to accelerate the reaction [10, 17]. The use of microwave as alternative source of heating offers a greater advantage of immediate agitation and rapid mixing between catalyst–alcohol solution and VOs because of excellent dielectric property of alcohol [15]. In this article, we have presented preliminary results on the effect of microwave irradiation on production of biodiesel from indigenously available *P. pinnata* seed oil. The experiments were carried out at 1:6 oil/alcohol molar ratio and 60 ˚C reaction temperature. The effect of microwave heating on variables i.e. catalyst concentrations and reaction time were studied with an objective to search out optimum reaction conditions.

2. Methods

2.1. Reagents

The reference standards of fatty acid methyl ester were procured from Petrosun Co. Methanol, sodium hydroxide and potassium hydroxide were obtained from Aashka Scientific Co. All the chemicals used for experiments were analytical reagent (AR) grade and were used without further purification.

2.2. Extraction of oil from seeds

The seeds of *P. pinnata* were obtained from Gokul Agro Agency, Kalawad, Gujarat, India. A mechanical oil expeller was used for oil extraction. The extracted oil was filtered and left undisturbed for three–four days for settling of any suspended particles. The oil thus obtained was kept in an air tight container for further analysis.

2.3. Transesterification in microwave reactor

The microwave unit Start Synth Model (Milestone Co., Italy) was used for carrying out transesterification. The system is equipped with a reflux condenser, a magnetic stirrer bar and a non-contact infrared continuous feedback temperature control system which allows continuous stirring and constant temperature control. A glass reactor of 500 ml capacity was used for microwave assisted transesterification and a sample size of 160 ml, which is more than 30% of total glass reactor capacity, was taken during each experiment. The transesterification under microwave heating was carried out using two alkali catalysts i.e. NaOH and KOH. The catalysts were used at three different concentrations (0.5%, 1.0% and 1.5% w/w of oil). The stoichiometry (6:1 alcohol/oil) and reaction temperature (60 ˚C) were kept constant for all experiments. A known quantity of catalyst was initially dissolved in desired methanol and the resulting solution was then added to the oil. In order to avoid over shooting of reaction temperature, the microwave unit was programmed to reach 60 ˚C in two steps i.e., 50 ˚C in 1.00 min, using 300W of power and then from 50 ˚C to 60 ˚C in 30 s, using 125 W. Although the maximum power output of microwave unit is 1200W only 10% was used for maintaining 60 ˚C. The reaction was timed as soon as the desired transesterification temperature (60 ˚C) was achieved and it continued for different times i.e., 3, 5, 7 and 10 min. For each reaction condition, the experiment was repeated four times and their average value was obtained. The transesterification reaction is given in Figure 1.

2.4. Separation and purification of FAMEs

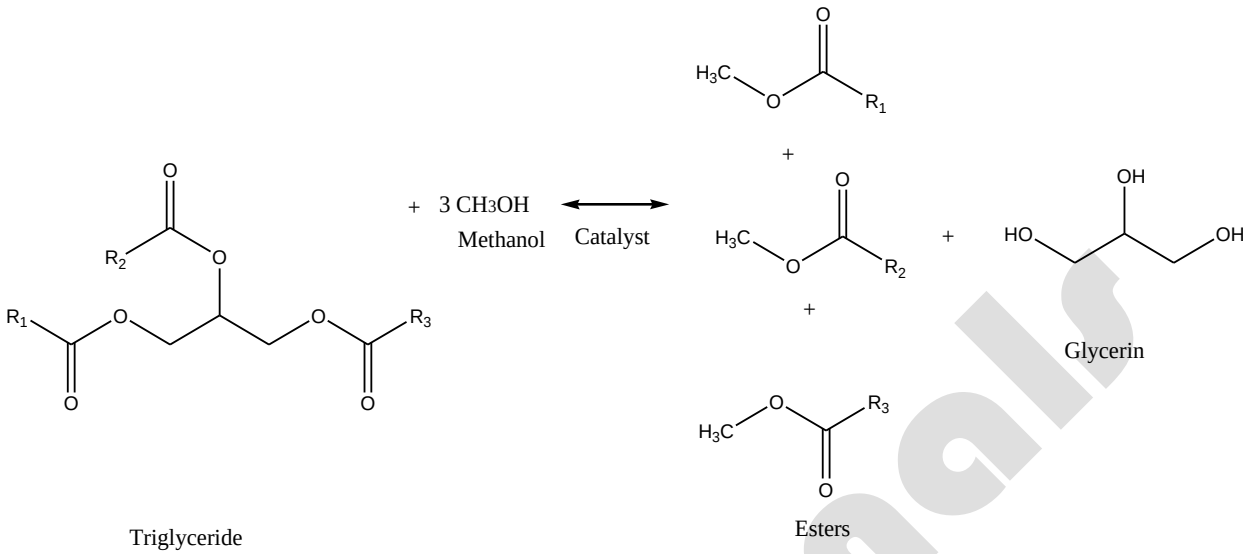
The reaction was captured immediately by immersing the glass reactor in an ice bath. As the reaction was stopped, the product was kept in separating funnel over night for separating biodiesel and glycerol layers. After separating the lower glycerol layer from upper layer of biodiesel, the upper layer was collected for further purification. The biodiesel was first washed with glacial acetic acid mixed in hot water and then washed only with plain hot water for three times. The moisture from the washed biodiesel was removed by using anhydrous sodium sulphate. The biodiesel yield was calculated relative to the initial amount of *P. pinnata* oil by weight and the biodiesel purity was determined according to the relative methyl ester content obtained by gas chromatography (GC) analysis.

2.5. Ester content and fuel properties of biodiesel

The purity of biodiesel i.e., relative methyl ester content of biodiesel, was determined using gas chromatography system (AIMIL Nucon 5765) equipped with flame ionization detector (FID). The column used was packed SS DEGS (Diethylene glycol succinate) 2 m in length. The nitrogen was used as a carrier gas at a flow rate of 40 mL/min. The oven temperature was kept 150 ˚C at isothermal condition [14, 18]. The relative

density at 15 ˚C was determined according to ASTM D-4052, using Anton Paar density meter (DMA 4500 M). The fuel properties of *P. pinnata* oil methyl ester were determined using ASTM (D6751) standards.

Figure 1



3. Results and Discussion

3.1. Physical and fuel properties of *P. pinnata* oil

The physical properties of *P. pinnata* oil such as kinematic viscosity at 40 ˚C, density at 15 ˚C and iodine value were found to be 33 mm^2/s, 0.921 g/cm^3 and 79.0, respectively. The acid value of the oil was calculated by titration with KOH as per ASTM 6751 (D-664). The acid value of *P. pinnata* oil was recorded as 2.0 mg KOH/g, which is appropriate for single stage alkali transesterification [18]. The refractive index at 29 ˚C and calorific value of the oil were found to be 1.396 and 37.7 MJ/kg, respectively. The major fatty acid composition of *P. pinnata* oil was estimated as palmitic acid (11.94%), stearic acid (5.37%), oleic acid (57.64%) and linolenic acid (16.70%).

3.2. Alkali-catalyzed transesterification reaction in microwave reactor

Microwave assisted transesterification of *P. pinnata* oil was carried out using NaOH and KOH as catalyst. The catalysts were used at three different concentrations (0.5%, 1.0% and 1.5% w/w of oil) for transesterification at 6:1 alcohol/oil molar ratio and 60 ˚C reaction temperature. In order to determine the optimum catalyst concentration under microwave irradiation, the initial experiments were carried out at 5 min reaction time. The results of the experiments are summarized in Table 1.

Table 1: Yield of microwave assisted transesterification reaction using different concentrations of alkali catalysts.

Catalyst concentration (w/w)	NaOH	KOH
0.5%	95.0	87.5
1%	91.2[A]	96.0
1.5%	[B]	95.0

[A] = Slight gel formation
[B] = Complete gel formations

The optimum NaOH concentration for microwave assisted transesterification was found to be 0.5%. The biodiesel yield was found to be 95% in the presence of 0.5% NaOH after 5 min. The yield of biodiesel was reduced from 95% to 91%, when the NaOH concentration was increased from 0.5% to 1.0%. A slight gel formation was noticed at 1.0% NaOH concentration. However, a complete gel formation was observed when the concentration of NaOH was further increased from 1.0% to 1.5%. In a separate study on microwave assisted transesterification of soybean oil, some researcher has reported a significant decrease in conversion

rate with an increase in catalyst concentration from 3.0 to 5.0 wt%. The use of excessive amount of catalyst causes saponification that in turns leads to a lower conversion rate. The water content present in VOs and methanol also has a determined effect on the yield and purity of biodiesel [19]. The moisture traces in VOs significantly reduces the effectiveness of catalyst and results in soap formation. The resulting soap further causes an increase in viscosity and formation of gels in the biodiesel [20]. The effect of water content in the oil has been reduced by using water resistant heterogeneous catalyst for transesterification [21, 22]. The higher percentage water content in VOs can also be partially compensated by adding more methanol for better yield of biodiesel [23]. In presence of KOH, the biodiesel yield was found to be 87.5%, 96% and 95% at 0.5%, 1.0% and 1.5% concentrations, respectively (Table 1). No significant variation was observed in the yield of the biodiesel when KOH concentration was increased from 1.0% to 1.5%. From the result presented in Table 1, the optimum catalyst concentrations for biodiesel production from *P. pinnata* seed oil were found to be 0.5% and 1.0% for sodium hydroxide and potassium hydroxide, respectively. The transesterification reactions were also carried out at different microwave irradiation times i.e., 3, 5, 7 and 10 min. These reactions were carried out at 6:1 alcohol/oil molar ratio and 60 ˚C temperature using NaOH and KOH at 0.5% and 1.0% w/w of oil, respectively. A marginal increase in biodiesel yield and purity was observed with increase in the reaction time as given in Table 2.

Table 2: Results of microwave assisted transesterification in presence of 0.5% (w/w) NaOH and 1.0% (w/w) KOH at 60 ˚C reaction temperature.

Reaction time (min)	KOH		NaOH	
	Biodiesel Yield (%)	Biodiesel Purity (%)	Biodiesel Yield (%)	Biodiesel Purity (%)
3	88.6	91.3	93.2	91.3
5	96.0	92.6	96.4	91.2
7	96.0	94.9	95.1	92.9
10	97.5	94.9	ND	ND

ND = Not determined

In a similar study on microwave assisted transesterification, it is found that the biodiesel purity increases by increase in reaction temperature [14]. The experimental results showed a maximum biodiesel purity of 94.9% and 92.9% in presence KOH and NaOH, respectively. The purity of biodiesel achieved during the experiments were found to be slightly lower than the desired purity i.e., at least 95.7% according to EN 14214. It is therefore desirable to carry out detailed study on temperature variations. The experiments at slightly higher temperature (65 ˚C) may help in obtaining desired purity in lesser time under microwave heating [24].

3.3. Fuel properties of *P. pinnata* biodiesel

The fuel properties including relative density at 15 ˚C, kinematic viscosity at 40 ˚C, flash point, cloud point, acid value, sulfur content and calorific value of *P. pinnata* biodiesel were determined as per the ASTM (D6751). The results of fuel properties of *P. pinnata* biodiesel are summarized in Table 3.

Table 3: Fuel properties of biodiesel obtained from 0.5% (w/w) NaOH and 1.0% (w/w) KOH.

Properties	NaOH				KOH			Biodiesel standards	
	3 Min.	5 Min.	7 Min.	10 Min.	3 Min.	5 Min.	7 Min.	ASTM D6571	IS 15607:2005
Density at 15˚C, kg/m^3	0.901	0.900	0.900	0.900	0.901	0.900	0.900	-	860-900
Viscosity, 40˚C (mm^2/s)	5.22	5.19	5.15	5.10	6.10	5.55	5.49	1.9-6.0	2.5-6.0
Flash point, ˚C	183	195	194	197	191	192	198	>130	>130
Acid value, mg KOH/gm	0.266	0.276	0.340	0.136	0.365	0.423	0.298	0.80	0.50
Cloud point, ˚C	ND	ND	15	06	ND	ND	15	-	-
Refractive index, 29 ˚C	1.4605	1.4600	1.4600	1.4600	1.4610	1.4600	1.4600	-	-
Calorific value (MJ/kg)	40.16	40.24	40.35	40.39	39.28	40.28	40.36	-	-
Sulfur content	15 ppm	15 ppm	15 ppm	15 ppm	15 ppm	15 ppm	15 ppm	0.05% by mass, max	50 mg/kg

ND = Not determined

It is clearly shown from the Table 3 that the viscosity of the biodiesel prepared at different microwave irradiation times were found within the limits of biodiesel standards. The viscosity of the biodiesel prepared in 3 min of microwave irradiation using NaOH was found to be slightly higher (6.10 mm^2/s) than specified limits of biodiesel standards. It can also be seen from Table 3 that there is a marginal decrease in the viscosity of biodiesel with an increase in microwave irradiation time. The flash point (^0C) of the biodiesel was found in the range of 183–198, which is higher than the flash point of diesel i.e., 68 ˚C. The acid value of the biodiesel was also found within the limits of ASTM specifications. The calorific value of the biodiesel was found to be lower (40.4 MJ/kg) than that of diesel (42 MJ/kg). This may be due to higher oxygen content present in biodiesel. It can be seen that the measured values of fuel properties of biodiesel are in the range of prescribed American and Indian biodiesel standards.

4. Conclusion

The biodiesel from *P. pinnata* seed oil was successfully prepared by transesterification reaction in microwave reactor. The experimental results show that the transesterification of *P. pinnata* seed oil can be completed in 5–10 min, as compared to conventional heating where approximately 2-3 hrs is required for the completion of the reaction. The use of microwave will help in lots of time and cost saving.

Competing Interests

None declared.

Authors' Contributions

Both authors contributed equally to this work.

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