

Transesterification of Non-Edible Oil Assisted by Ultrasonication

Sanjay Gupta and Vimal Kumar

Abstract—In the present work an ultrasonicator reactor is used to intensify the biodiesel production from vegetable in the presence of an alcohol and catalyst. The ultrasonicator parameters, such as amplitude ratio, recycle ratio and reaction time have been optimized for transesterification reaction. Refined soybean and crude jatropha oils were used as edible and non-edible oils, respectively, and methanol is used as an alcohol. The transesterification reaction was carried out at atmospheric pressure and the temperature was maintained in between 35–40 °C. The reaction was carried out in the presence of a basic catalyst (CH_3ONa) and the amount of catalyst was kept constant for all the experiments. The vegetable to alcohol ratio was maintained as 1:6 on mole basis. Jatropha oil was first esterified due to the presence of high FFA contents. Therefore in case of jatropha oil, a two step reaction was carried out due to high FFA contents present in the crude jatropha oil. In the pretreatment, i.e. the first step, the FFA content was reduced from 7.43 wt.% to 1 wt.%, which is the required permissible limit for FFAs. The optimized parameters for transesterification of *esterified jatropha oil* to obtain 86% yield were: amplitude ratio as 80%, cycle ratio as 0.4 and reactions time as 10 minutes; while for soybean oil to obtain 89% yield are: amplitude ratio as 30%, cycle ratio as 0.4 and reactions time as 10 minutes. The ultrasonication process with two step process for the production of biodiesel from crude jatropha oil is time saving and efficient.

Index Terms—Biodiesel, FAME synthesis, transesterification, ultrasonication.

I. INTRODUCTION

In last few decades, there is an extensive increase in the consumption of hydrocarbon based fossil fuels worldwide due to the increase in industrialization and human population growth. The consumption and demand of fuels derived from crude petroleum oil has resulted into an increase in price of hydrocarbon based diesel fuels. Further, the combustion of fossil fuels has resulted into the emissions of greenhouse gases into the atmosphere, which is one of the reasons for global warming.

Biodiesel, which is also a first generation bio-oil, is the substitution of hydrocarbon based diesel fuel and is a clean, renewable fuel. Biodiesel, or fatty acid methyl esters (FAME), is an environment friendly fuel and used as BD20, i.e. 20% biodiesel is mixed with hydrocarbon derived diesel fuel. Biodiesel has advantages over hydrocarbon based diesel fuel,

such as lower emissions of green house gases, higher combustion efficiency, negligible sulfur content. Further it is derived from a renewable feedstocks, such as edible (soybean, palm, canola, etc.) and non-edible (jatropha, karanja, castor, etc.) oils. Biodiesel can be used either as pure fuel or as blend with hydrocarbon based diesel fuel. It is also referred as fatty acid methyl esters (FAME) and is derived from renewable feedstocks, which fall in the carbon range C12-C22, and have similar properties as diesel. FAME production through transesterification process involves reaction of oil with alcohol in the presence of a catalyst resulting into the formation of a diesel equivalent bio-fuel (see Fig. 1).

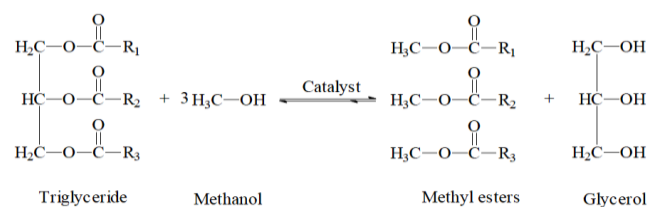


Fig. 1. Transesterification reaction for the production of biodiesel.

Stoichiometrically 1:3 vegetable to methanol on mole basis is required for the transesterification of vegetable oil, however excess amount of methanol is used for the reaction. The transesterification reaction can be carried out using both homogeneous and heterogeneous catalyst. However, due to its high reactivity and less requirement of methanol during the reaction, homogeneous catalyst is preferred over heterogeneous.

Many techniques have been used to intensify the biodiesel production, such as ultrasonic and microwave irradiation, heterogeneous catalysis [1], [2], novel reactors, supercritical conditions [3], etc. Vyas *et al.* [1] carried out FAME synthesis using jatropha oil with high free fatty acids (FFAs) with a solid catalyst ($\text{KNO}_3/\text{Al}_2\text{O}_3$) at 70 °C. They reported 84% biodiesel yield in 6 h. The transesterification of jatropha oil has been carried out under supercritical non-catalytic conditions [4]. They reported 100% biodiesel yield at 320 °C and 8.4 MPa.

Vegetable oil, catalyst and methanol are immiscible, during the transesterification reaction, because of their chemical structures. This lowers the rate of collisions of the molecules and also the rate of reaction causing longer reaction time and higher product cost [5]. For immiscible liquids mass transfer rate can be enhanced by ultrasonic irradiation. Due to the improvement in yield and reduction in reaction time, ultrasonication technique has been extensively used in a wide range of industrial processes. Intensified reaction causes better product yield, shorter reaction time and lower catalyst requirement. Further, during ultrasonication process the

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reaction conditions are mild, and hence it has better process economy and is simple equipment for transesterification reaction. Wu *et al.* [4] reported that the smaller droplets of the reacting fluids can be obtained using ultrasonication, which resulted in an enhancement in the interfacial area and therefore mass transfer. Therefore, there is a less requirement of energy, due to the reduction in mixing requirement, during the process [6]. In a two step process, i.e. esterification followed by transesterification, using ultrasonication irradiation, Deng *et al.* [7] reported 96% FAME yield in 1.5 h. Kumar *et al.* [8] carried out ethanolysis of coconut oil using ultrasonic irradiation. Jianbing *et al.* [9] carried out transesterification reaction using both ultrasonication as well as hydrodynamic cavitation. A single step transesterification reaction was carried out by Moholkar *et al.* [10] using chlorosulfonic acid catalyst for FAME synthesis with feedstock with high free fatty acid content (jatropha oil) by ultrasonication. They reported 93% FAME yield with 8.5 wt% catalyst, 20:1 alcohol to vegetable oil molar ratio and 333 K temperature. Time taken was more than 4 hours.

In the present work the main objective is to optimize the parameter of ultrasonication for the production of FAME using jatropha oil as feed stock and methanol as another reactant. The recycle ratio and amplitude ratio have been optimized to increase the yield. Further the detailed analysis of biodiesel obtained at optimized conditions has been carried out.

II. MATERIALS AND METHODS

A. Materials

The crude *jatropha curcas* oil was purchased from local market. The chemicals used (Methanol, sulphuric acid and sodium methoxide) in the present work for the esterification and transesterification reactions were of analytical reagent grade. Methyl heptadecanoate (purchased from Sigma Aldrich) in heptane solution was used as an internal standard for the gas chromatography, with concentration 10mg/mL.

The moisture content in the crude jatropha oil was estimated using a KF titrator. The free fatty acid (FFA) content of jatropha oil was determined according to American Oil Chemists' Society (AOCS) method. For crude jatropha oil, the acid value obtained after titration method, was 14.79 mgKOH/g of oil, which corresponds to 7.43% FFA contents (Table I). To carry out the transesterification reaction using base catalyst the FFA contents should be less than the 2% (w/w) and the amount of FFAs in the crude jatropha oil was higher than the permissible limit.

TABLE I: PROPERTIES OF CRUDE JATROPHA OIL

Property	Refined soybean oil	Crude jatropha oil
Acid value	2.03	14.79
% FFA	1.02	7.43
% Moisture content	—	0.1202

B. Reaction Conditions

The molar ratio of alcohol to vegetable oil taken was 9:1 and 6:1 during the esterification and transesterification reactions, respectively, which are the optimized values as

reported in the literature. The esterification reaction was carried out in batch reactor and transesterification was carried out by using ultrasonication. In the batch reactor the reaction was performed at 60 °C, while in case of ultrasonication the reaction temperature was varied from 30 to 40 °C. Both reactions were performed at atmospheric pressure.

C. Apparatus and Methodology

The esterification reactions were performed in a 500 ml three-necked glass flask, which was equipped with a thermometer, a reflux condenser and a sampling port. The temperature was maintained constant during esterification reactions with the help of a silicon oil bath which was controlled by a temperature controller. Agitation was provided by a magnetic beads, and the stirring rate was kept constant, i.e. 700 rpm, during the esterification reactions. The experimental setup used for esterification in the present work is shown in given Fig. 2(a).

An ultrasonicator, UP 400S from Hielscher Ultrasonic GMBT (Fig. 2(b)), was used to perform the transesterification reaction. The maximum operating limit for the ultrasonicator was 400W and 24 kHz frequency. The ultrasonication cycle and amplitude can be adjusted from 0.1 to 1 cycle per ton and 20 to 100%, respectively. The ultrasound waves were transmitted into the liquid using a titanium sonotrode S7 (diameter of 7 mm and length of 100 mm). The transesterification reactions with ultrasonicator were performed using a 50 ml Erlenmeyer type flask.

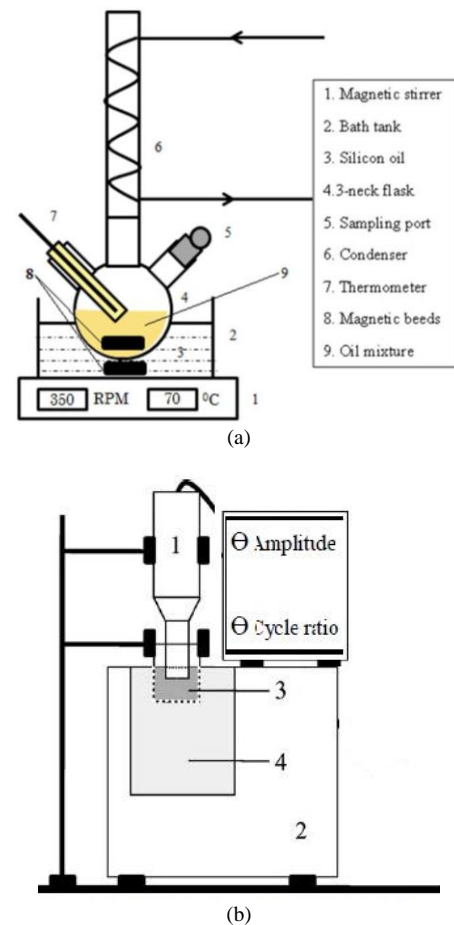


Fig. 2. Schematic diagram of (a) batch reaction used for esterification reaction and (b) ultrasonication system used for transesterification of jatropha oil: (1) ultrasound prob, (2) chamber, (3) reaction mixer, (4) water in cooling bath.

The transesterification reaction was carried out with esterified jatropha oil in the presence of methanol and catalyst (sodium methoxide, CH_3ONa). The reaction mixture was transferred to the Erlenmeyer type flask and the sonotrode was submerged up to 25 mm into the reaction mixture. The amplitude ratio, cycle ratio and reaction time were varied from 30% to 80%, 0.1 to 0.7 and 1 to 10 minutes, respectively. For a particular set of reaction the ultrasonic wave cycle and its amplitude were adjusted by the controller. During the ultrasonication process the temperature was maintained between 35–40 °C using a water bath beaker (Erlenmeyer type flask).

The composition of both soybean and jatropha oils used in the present work was analysed using gas chromatography (GC). The various fatty acid components, with their corresponding retention time, number of carbon atoms and composition of the feedstock used are listed in Table II. The composition of C16:0, C18:0, C18:1, C18:2 and C18:3 esters were determined according to the EN 14103:2003 standard [11]. The composition of various fatty acid components present in the vegetable oil reported in the present work is in good agreement with the composition available in the literature.

TABLE II: THE CHROMATOGRAPH PEAK ORDER AND CONTENT OF METHYLE ESTER

Peak Order	FAME	Molecular formula	Retention time (min)	Content (%)
1	Methyl Palmitate	C 16:0	09.87	11.20
2	Methyl Heptadecanoate(IS)	C 17:0	11.34	18.11
3	Methyl Stearate	C 18:0	12.85	2.87
4	Methyl Oleate	C 18:1	13.40	22.05
5	Methyl Linoleate	C 18:2	14.32	40.94
6	Methyl Linoleanete	C 18:3	15.42	04.07

III. RESULTS AND DISCUSSIONS

The ultrasonication parameters, such as amplitude ratio and recycle ratio were optimized with reaction time and percentage yield using Box–Behnken Design (BBD) method for FAME production from refined *soybean* and esterified *jatropha* oil. The optimization was made considering three value of each variable (amplitude ratio, recycle ratio and reaction time), i.e. maximum, medium and minimum value.

In case of *jatropha* oil, a two step reaction has been carried out for FAME production. In the first step the esterification of crude *jatropha* oil in a batch reactor (three necked round bottom flask) was carried out to reduce the FFA contents from 7.0% to 1.0%. Once the FFA content were reduced to desired limit the transesterification reaction was carried out using ultrasonicator, at different parameters. Tables III and IV lists the experimental conditions, reaction time and yield of soybean and *jatropha* oil methyl esters. The optimized conditions for transesterification of soybean oil were amplitude 30%, cycle ratio 0.4, and reaction time 10 minutes, while for *jatropha* oil were: amplitude 80%, cycle ratio 0.4, and reaction time 10 minutes. At these conditions the yield of biodiesel were 88.93% and 86% from soybean and *jatropha* oils, respectively. All the experiments were repeated twice for transesterification of both refined soybean and esterified

jatropha oils. A similar study was carried out by Maholkar *et al.* (2013) for transesterification of *jatropha* oil using an acid catalyst. In their study the time, molar ratio (vegetable oil to alcohol) and the amount of catalyst used were very high, i.e. 2–3 hours, 20:1 and 8.5 wt.%, respectively, to obtain a yield of 93%. However in the present work a base catalyst was used and the amount of catalyst used was 1.0 wt.% and the time required to have a yield of $\geq 85\%$ was ≈ 10 minutes. Hence the 2 step process used in the present work is efficient for the production of FAME.

TABLE III: EXPERIMENTAL CONDITIONS CONSIDERED FOR TRANSESTERIFICATION OF REFINED SOYBEAN OIL USING ULTRASONICATION

Run	Amplitude (%)	Cycle	Time	% Yield
1	30(-1)	0.4(0)	1(-1)	73.51
2	80(+1)	0.4(0)	10(+1)	78.65
3	55(0)	0.1(-1)	10(+1)	79.22
4	55(0)	0.4(0)	5.5(0)	85.70
5	30(-1)	0.1(-1)	5.5(0)	80.55
6	55(0)	0.7(+1)	10(+1)	79.98
7	80(+1)	0.7(+1)	5.5(0)	83.98
8	30(-1)	0.4(0)	10(+1)	88.93
9	55(0)	0.4(0)	5.5(0)	87.79
10	55(0)	0.4(0)	5.5(0)	84.55
11	55(0)	0.1(-1)	1(-1)	75.41
12	55(0)	0.4(0)	5.5(0)	86.65
13	55(0)	0.4(0)	5.5(0)	85.51
14	80(+1)	0.1(-1)	5.5(0)	78.46
15	80(+1)	0.4(0)	1(-1)	76.94
16	30(-1)	0.7(+1)	5.5(0)	83.22
17	55(0)	0.7(+1)	1(-1)	81.32

TABLE IV: EXPERIMENTAL CONDITIONS CONSIDERED FOR TRANSESTERIFICATION OF ESTERIFIED JATROPHA OIL USING ULTRASONICATION

Run	Amplitude (%)	Cycle	Time	% Yield
1	30(-1)	0.4(0)	1(-1)	75.79
2	80(+1)	0.4(0)	10(+1)	85.70
3	55(0)	0.1(-1)	10(+1)	81.70
4	55(0)	0.4(0)	5.5(0)	80.17
5	30(-1)	0.1(-1)	5.5(0)	77.89
6	55(0)	0.7(+1)	10(+1)	83.98
7	80(+1)	0.7(+1)	5.5(0)	83.41
8	30(-1)	0.4(0)	10(+1)	78.84
9	55(0)	0.4(0)	5.5(0)	80.93
10	55(0)	0.4(0)	5.5(0)	81.89
11	55(0)	0.1(-1)	1(-1)	73.32
12	55(0)	0.4(0)	5.5(0)	79.79
13	55(0)	0.4(0)	5.5(0)	81.51
14	80(+1)	0.1(-1)	5.5(0)	78.27
15	80(+1)	0.4(0)	1(-1)	76.75
16	30(-1)	0.7(+1)	5.5(0)	78.46
17	55(0)	0.7(+1)	1(-1)	75.41

The various properties of biodiesel produced from *jatropha* oil, such as Kinematic viscosity, specific gravity, density, carbon content, fire and flash points, cloud and pour points, have been studied and compared with the standard biodiesel. Properties of biodiesel obtained from esterified *jatropha* oil, at optimized conditions, are shown in Table V. It was observed that the various properties studied for the biodiesel obtained in the present work were within the range of standard biodiesel.

TABLE V: COMPARISON OF PHYSICAL AND CHEMICAL PROPERTIES OF BIODIESEL

Fuel property	Standard Biodiesel*	Biodiesel from esterified <i>jatropha</i> oil (present work)
Kinematic viscosity@40°C, mm ² /s	4.0-6.0	4.8
Specific gravity, @15.5°C	0.88	0.85
Density@15.5°C, kg/m ³	880	860
Carbon, wt%	77	76
Flash Point °C	100-170	165
Fire Point °C	110-205	180
Cloud Point °C	-3 to 15	0
Pour point °C	-5 to 10	-2

*Biodiesel Handling and Use Guide

IV. CONCLUSIONS

In the present work the fatty acid methyl esters was synthesized from edible (refined soybean oil) and non-edible feedstock (esterified *jatropha* oil) of indian origin by ultrasonication method. The FAME was produced from *jatropha* oil in two-step process. In the first step, the esterification reaction was carried out using an acid catalyst and then the transesterification reaction was carried out with a base catalyst. The esterification of crude *jatropha* oil was carried out using a batch reactor and the transesterification of estrified *jatropha* oil was carried out using an ultrasonicator. The conversion of oil to biodiesel was quantitatively analyzed using gas chromatography (GC) and it was found $\approx 90\%$. The optimized conditions for transesterification reactions were determined by performing several number experiments by varying the ultrasonication parameters, i.e. amplitude ratio, cycle ratio and time. The optimized parameters for transesterification of *jatropha* oil were: amplitude ratio – 80%, cycle ratio 0.4 and time 10 minutes, which resulted into $\approx 86\%$ yield. The various properties of biodiesel obtained in the present work were compared with the standard biodiesel and were found in within the permissible limits.

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Electrical Energy

