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Transesterification of non edible oil for fatty acid methyl esters production assisted by ultrasonication

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Abstract
Biodiesel is a renewable fuel, consistituting an alternative to petroleum-based diesel fuel. It is non-toxic and biodegradable and has a low emission profile, is better from environmentally sensitive areas. Research study on alternative fuels is essential for increased energy security. Transesterification of Jatropha curcus oil is carried out in the presence of methanol and potassium hydroxide (KOH) as catalyst, keeping the molar ratio of oil to alcohol 1:6, catalyst concentration 0.75 wt% of oil, ultrasonic amplitude 60% and pulse 0.3 cycles, 7 min reaction time under atmospheric condition. Ultrasonic mixing has increased the rate of transesterification reaction as compare to the mechanical mixing.

Keywords: biodiesel, methanolysis, reversed-phase HPLC, ultrasonication, *Jatropha curcas* oil

1. Introduction
Biodiesel refers to a vegetable oil or animal fat-based diesel fuel consisting of long-chain alkyl (methyl, ethyl, or propyl) esters. Biodiesel is typically made by chemically reacting lipids (e.g., vegetable oil, soybean oil, [1] animal fat (tallow) [2, 3] with an alcohol producing fatty acid esters. The environmental problems caused by the indiscriminate use and scarcity of petroleum are prompting researches to search renewable resources of energy such as derivatives of vegetable oil [1-3]. The merits of using biodiesel as an alternative of mineral diesel include the fact that it is a non-toxic, biodegradable, domestically produced, renewable source. In addition, biodiesel possess higher cetane number compared to diesel obtained from petroleum and favorable combustion emissions profile such as reduced levels of particulate matter and carbon monoxide and, under some conditions, nitrogen oxides [4]. Fossil fuels increase greenhouse gas emissions and cause global warming, the use of alternative resources like bio-fuels are more pronounced every day. The majority of the energy sources are supplied through petrochemical, coal and natural gases. Petrochemical energy is very important in the world, especially diesel, because this is the main fuel used for industrial and agricultural transportation. Pumps, heavy trucks, city transport buses, locomotives, electric generators, etc. the huge energy demand in the industrialized world and the population problems caused due to the widespread use of fossil fuels, depletion of the world petroleum reserves and increasing environmental concerns has stimulate the search for renewable fuels and made it increasingly necessary to develop alternative sources of energy to resolve these question [5, 6]. Alternative diesel fuels must be acceptable, economically competitive, environmental friendly and easily available. From this view of point, the use of vegetable oil as alternative fuels for diesel engines is a promise in many countries [7]. In these reaction triglycerides, the main components of vegetable oils, react with alcohol to produce fatty acid mono-alkyl esters and glycerol. Methanol is the most common alcohol because of its low price compare to the other alcohols [8]. In this case, the reaction is referred to as methanolysis [9]. The stoichiometry of methanolysis, reaction required 3 mole of methanol and 1 mol of triglyceride to give 3 mole of fatty acid methyl ester and 1 mole of glycerol. However excess alcohol is used to increase the yield of the alkyl esters and allow phase separation from glycerol formed. Several aspects, including the type of temperature, purity of the reactants (mainly water content) and free fatty acid content, have an influence of the transesterification rates. The conventional catalysts used are acid and alkali catalysts depending upon the nature of the oil used for biodiesel production. Choice of the acid and alkali catalysts depends on the free fatty acids (FFAs) content in the oil. FFA should not exceed 3% in oil for transesterification to occur by alkali catalyst [10, 11]. The alkali catalysts are the most commonly used in the biodiesel industry, it processes faster and the reaction conditions are moderated. These catalysts include sodium hydroxide, potassium hydroxide and sodium methoxide. However, sodium methoxide is more expensive than the hydroxides and also more difficult to manipulate since it is a very hygroscopic. Potassium hydroxide has the advantage that it can be neutralized with phosphoric acid after the reaction, resulting in potassium phosphate, which may be used as fertilizer. The utilization of potassium or sodium hydroxide in vegetable oil methanolysis produces soaps by neutralizing the free fatty acid in the oil or by triglyceride saponification. Owing to their polarity, the soaps dissolve into the glycerol phase during the separation stage after the reaction. In this sense, both soap formations decrease the biodiesel yield obtained after the separation and purification stages. In addition, the dissolved soaps increase the methyl ester solubility in the glycerol, an extra cause of yield loss [12].

2. Material and methods

2.1 Reagents and materials

Commercial grade Jatropha curcus oil was procured from local market purchase and characteristics reported in Table 1. Anhydrous methanol (purity 99.8%) and KOH (purity 85.1%) were purchased from M/S Ranbaxy. Ethanol (purity 99.8%) was purchased from Sigma-Aldrich. All reagents were analytical grade and standards of fatty acid methyl esters from Flucka.

Table 1: Characterization of *Jatropha curcas* oil

Density at 15^0C	**0.918 gm/cm^3**
Refractive index (η_D 40^0C)	1.484
Molecular weight	888
Kinematic viscosity at 40^0C	34.33 cSt
Saponification value	199 mgKOH/gm oil
Acid value	0.5 mgKOH/gm oil (afterpretreatment of oil)
Cetane Number	23
Flash point	186

2.2 Apparatus

An ultrasonic procedure UP 200S from Hielscher ultrasonic Gmblt was used to perform the transesterification reaction. The ultrasonic processes operate at 200W and 24 kHz frequency. The amplitude and cycle for the reaction were adjustable from 20 to 100% and from 0.1 to 1 cycle per tone, respectively. The titanium sonotrode S_7 with a diameter of 7 mm and length of 100 mm, for samples from 20ml up to 500ml was used to transmit the ultrasound into the liquid. All experiments were performed in an Erlenmeyer type flask, having 50 ml total volume.

2.3 Ester preparation

The production of biodiesel (methyl ester) from Jatropha curcus oil involves the base catalyzed transesterification with methanol to give methyl esters. Glycerin is a byproduct in the transesterification reaction. In the case of methanolysis the reaction mixture remains in two phases due to the low solubility of oil in methanol. KOH was dissolved into methanol and the mixture was transferred to the Erlenmeyer type flask to be subjected to the ultrasound waves. A S_7 type sonotrode was submerged up to 25 mm into the solution. The ultrasonic wave cycle and its amplitude as well as the time of the reaction were adjusted by the controller. Amplitude of 60% was set and cycle of 0.3 was set. Under these parameters reactions were carried out for 5 different time durations of 5, 7, 9 and 11 minutes.

2.4 Mechanism of alkaline catalyzed transesterification reaction

In case of the alkaline transesterification reaction, triglyceride molecule reacted with the lower alcohol, the active catalyst species is alkoxide anion. In case of methanol, CH_3O^- methoxide and in case of ethanol, $C_2H_5O^-$, ethoxide anions are formed. This is preliminary step in alkaline catalyzed transesterification reaction

$OH^- + R'OH \leftrightarrow R'O^- + H_2O$

The alkoxide anions formed in the preliminary step attacks the carbonyl atom of the triglyceride molecule to form tetrahedral intermediate in the first step of the reaction. This is a rate determining step of transesterification reaction. Therefore, the rate of the alkaline catalyzed transesterification reaction is determined by the reactivity of the alkoxide anion. Reactivity of methoxide is more than the ethoxide anion. The reason for this is, as the length of the carbon chain increases, nucleophilicity of the alkoxide anion decreases leading to a decrease in the reactivity of alkoxide anion. This causes the slower reaction rate of ethanol than methanol and ultimately less amount of ethyl esters were formed compared to methyl when mixture of methanol/ethanol was used for transesterification of Jatropha curcus oil [13]. Even through the formation of ethyl esters was slow, the overall rate of reaction was fast.

2.5 HPLC analysis

HPLC was used to analyze the purity, conversion and FAME composition of the biodiesel esters sample. The Reverse phase high performance liquid chromatography (RP-HPLC) separates different component according to their polarity. The chromatographic apparatus consisted of a model waters 600 pump with waters 600 controller, waters 2996 photodiode array detector, a nova-pack®, 3.9 X 150 mm column with guard column of dimension 3.9 X 20 mm, both packed with C18 particle with diameter 4 µm. (all from waters, Milford MA, USA).

HPLC condition: RP-HPLC method flow rate of 1ml/min, an injection volume of 5µl, a column temperature of 45ºC, the UV detection at 215 nm and a 40 min gradient mobile phase 15% H_2O + 85% CH_3OH in 10 min, 100% CH_3OH in 0 min, 60% CH_3OH + 15% hexane + 25% propane-2-ol in 30 min and for the last 10 min system back to initial state 15% H_2O + 85% CH_3OH were used for the separation and determination of the compound produced during the methanolysis of Jatropha curcus in all the experiments [14]. Fig. 1 shows the HPLC separation of methyl esters (ME). The fatty acid composition of Jatropha curcus oil is given in table 2.

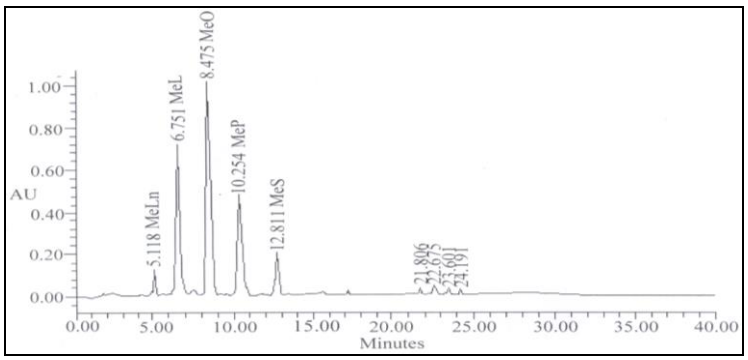

Fig 1: HPLC chromatogram of Biodiesel of Jatropha Curcus oil showing presence of different fatty acid methyl esters.

Table 2: Fatty acid methyl esters (FAME) composition of Jatropha curcus oil based biodiesel.

Fatty acid	Percentage
Palmitic (C16)	15.82
Linolenic (C18:3)	0.73
Linoleic (C18:2)	30.56
Oleic (C18:1)	44.21
Stearic (C18:0)	8.15

3. Results and Discussion

In a conventional batch type reaction methyl ester was synthesized using base homogeneous catalysts. The molar ratio of oil to methanol 1:8 and catalyst concentration 1% of oil was used in the transesterification reaction, reaction temperature 50 to 70 ºC (temperature controlled by circulating water bath) and reaction time 2-4 h. Our investigation is based on using base catalyst (KOH) for biodiesel production by transesterification of Jatropha curcus oil with methanol from ultrasonic procedure. The optimal reaction condition involved using 1:6 oil to alcohol mixtures ratio, catalyst percentage 0.75 wt% of oil, ultrasonic wave amplitude 60%, ultrasonic irradiation pulse is 0.3 s cycle each second, reaction time 9 min. At these optimized condition we got the maximum conversion ≥99% and yield ≥98 of biodiesel.

3.1. Effect of molar ratio oil to methanol

The molar ratio of oil to methanol is varied but we have been used pre decided molar ratio of oil to methanol of 1:6, gives the maximum conversion more than 95% and yield 93.57%. The optimum condition for batch ultrasonic procedure to produce methyl ester has reaction time 7 min for high ultrasonic power (60% amplitude, 0.3 s cycle each second) with.75 wt% catalyst (KOH), molar ratio of oil to methanol 1:6. Excess methanol can be recovered after use. In case of methanolysis the reaction mixture remains in two phase due to the low solubility of oil in methanol. Hence, the mass transfer limitations make the rate of the reaction slower. It was reported that the rate of formation of methyl esters from soybean oil is 15 times slower than the butyl esters [15]. Methanol is the most common alcohol because of its low price compared to other alcohols but it is a toxic chemical (Fig. 2).

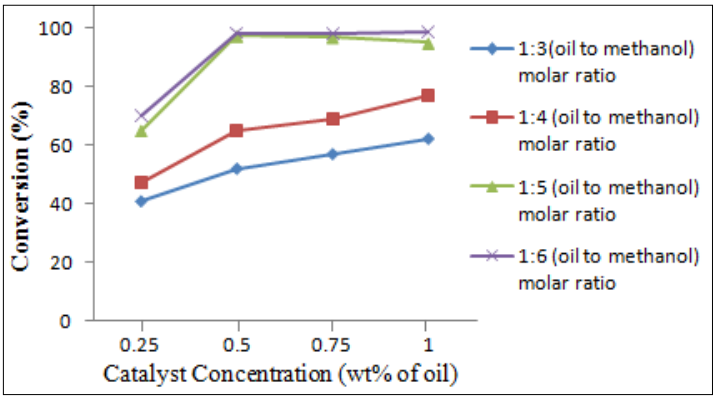

Fig 2: Effect of molar ratio oil to methanol and catalyst concentration on biodiesel conversion (methyl esters contents) at 60% Amplitude, 0.3 cycle and 7.0 minute reaction time.

3.2. Effect of reaction time

Ultrasonication increases the rate of reaction of the transesterification of vegetable oil and reduces the reaction time because ultrasonic cavitational mixing is an effective alternative means to achieve a better mixing in conventional processes. Ultrasonic cavitation provides the necessary activation energy for the reaction. The reaction time is varied from 5-11 min with an interval of 2 min. Fig. 3 shows the effect of reaction time on Jatropha curcus oil methyl ester content molar ratios of oil to methanol 1:6 with 0.75 wt % catalyst for above molar ratio the rapid formation of Jatropha curcus oil methyl ester more than 96% and yield 94.24% was observed with in 7 min after that the conversion rate was slower and finally reached steady state. Ultrasound reduces the processing time from the conventional 2-4 h batch processing to less than 7 min.

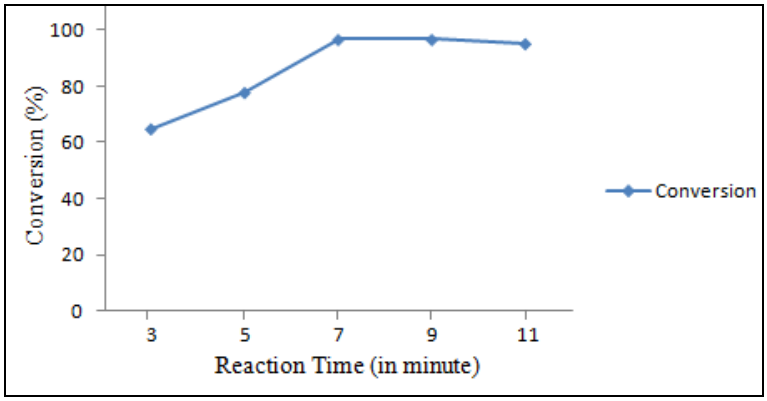

Fig 3: Effect of reaction time on biodiesel conversion at oil to methanol molar ratio 1:5, Ultrasonic amplitude 50%, oil to MeOH molar ratio 1:6 and cycle 0.3 second cycle each second.

3.3. Effect of catalyst concentration

The ultrasonication affects the catalyst reactivity by enhanced mass- transfer and energy input. Ultrasonic cavitation is a unique way to put energy into chemical reactions. A combination of high speed liquid jets, high pressure (>1000atm) and high temperatures (>4727 ºC), enormous heating and cooling rates (>10^9Ks^{-1}) occur locally concentrated during the implosive compression of cavitational bubbles [16, 17]. The ultrasonication does help to decrease the amount of catalyst due to the increased the chemical activity in the presence of cavitations. When using ultrasonication the amount of excess alcohol required is reduced, too. Another benefit is the resulting increase the purity of glycerol. Pre-optimized catalyst concentration 0.75 wt% of oil was used in each experiment (Fig. 2). If we increased the amount of catalyst there is no increment in conversion of biodiesel but a slightly decreasement is shown in conversion of biodiesel.

3.4. Effect of ultrasonic amplitude and cycle

The variation of biodiesel conversion with amplitude as well as cycle of ultrasonic energy applied. The pre-optimized amplitude (50%) and cycle (0.3) was used to all the experiment. In pre-optimized condition get the more than 96% conversion of biodiesel for methanol, 99% for ethanol and also 99% conversion for mixtures of methanol/ethanol system (Fig. 4).

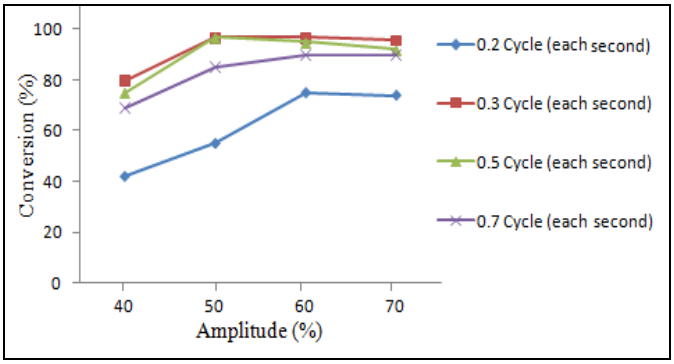

Fig 4: Effect of ultrasonic amplitude and cycle each second of biodiesel conversion at oil to methanol molar ratio 1:6, catalyst 0.5 wt %, and reaction time 7.0 minute.

4. Conclusion

The present study demonstrates base catalyzed transesterification of Jatropha curcus oil using ultrasonic irradiation for biodiesel Synthesis. The optimal reaction condition is the molar ratio oil to methanol 1:6, catalyst concentration 0.75 wt% of oil, reaction time 7 min, ultrasonic amplitude 60% and cycle 0.7 s. The synthesized biodiesel match ASTM and BIS specification (Table 3). The purity and quality of synthesized biodiesel were checked by HPLC technique.

Table 3: Physico chemical characterization of *Jatropha curcas* biodiesel.

Property	ASTM method	ASTM Specification	BIS Specification	Biodiesel
Viscosity 40 ºC (mm^2/s)	D 445	1.9-6.0	2.5-6.0	3.88
Acid number (mgKOH/g)	D 664	0.5	<0.5	0.18
Free glycerin (mass %)	D 6584	0.020	----	0.008
Total glycerin (mass %)	D 6584	0.24	----	0.24
Oxidation stability (IP, h)	EN 14112	3 minimum	----	5.0
Cloud point	D 2500-05	-3 to +12	----	-5
Pour point	D 97-96a	-15 to +10	----	-12
Cetane number	D 613	>47	>51	54
Cold filter plugging point	D 6371	-4 to -9	----	-1
Density at 15 ºC (kg/ml)	D 976	0.575 to 0.900	0.860-0.900	0.8633
Flash point (ºC)	D 93	>100	>120	135
Carbon residue (wt%)	D 4530	<0.02	<0.02	0.005
Copper strip corrosion (3 h at 100 ºC)	D 6751	<No. 1.0	1.0	1.0
Water content (ppm)	D 95	<500	<500	230

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