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Research Article

BIODIESEL PRODUCTION FROM *JATROPHA CURCAS* (L.) OIL OF NEPAL BY TRANSESTERIFICATION PROCESS

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ABSTRACT

The highest percentage of the oil i.e. 58.3% was found in the seeds (Kernel) collected from Rolpa district. The physico-chemical parameters like moisture content, oil content, specific gravity, density, viscosity, refractive index, iodine value, saponification value and acid value (% Free Fatty Acid), were determined. Then extracted oil was converted into biodiesel by transesterification process with methanol using different concentration of alkali catalyst viz. 0.5%, 1.0% and 1.5% NaOH. The result showed that 1 % NaOH catalyst was found to be the most effective concentration producing 87% crude fatty acid methyl esters (FAME) and 10% crude glycerol. Composition of FAME present in the biodiesel was identified by GC-MS method.

Keywords: Biofuel, FAME, GC-MS, transesterification, *Jatropha curcus*, Euphorbiaceae.

INTRODUCTION

Jatropha curcas (L.) is a perennial plant belonging to the Euphorbiaceae family. It is locally known as “sajivan”. Recently it has received much attention as a potential source for the biodiesel production which can be used as an alternative to the fossil diesel fuel. In developed countries including Germany, United states and even in India, 10% biodiesel is blended with fossil diesel fuel which is known as B10, can be directly used as vehicular fuel without any modification in the existing diesel engine. High viscosity of vegetable oil creates problem in combustion, clogging and high acid value may create corrosion in engine parts. So it cannot be directly used in existing diesel engine that necessitates its chemical transformation into biodiesel[1].

The depletion of the world's petroleum reserves i.e. fossil fuels and the increasing environmental concerns mainly due to the rapid growth of industries transports, agriculture and other human needs; there is a great demand for alternative sources of petroleum based fuel including diesel and gasoline fuels[2].

Biodiesel (Fatty acid alkyl esters), a clean renewable fuel, has recently been considered as the best candidate for a diesel fuel substitution. Conversion of oils to their alkyl esters reduced the viscosity to near the diesel fuel levels and produced a fuel with properties that were similar to petroleum based diesel fuel because it can be used in any compression ignition engine without the need for modification.[3] Biodiesel is mainly obtained from renewable biological sources such as vegetables oils, animal fats or even from waste cooking oils by chemical, enzymatic catalysis. Currently the industrial biodiesel production bases almost exclusively on the chemical transesterification of triglycerides (TAGs) from vegetable oils employing methanol, although other short chain alcohols like ethanol, propanol could be used as well.[4] Among all the feedstocks Vegetable oils (both edible and non-edible) are most promising feedstocks for the biodiesel production since they are renewable in nature and can be produced in large scale. But the use of edible oil as feedstock may cause some problems such as the competition with the edible oil market,

which increases both the cost of edible oils and biodiesel. So to overcome these disadvantages most of the researches are focused in non edible oils which are not suitable for human consumption because of the presence of some toxic components in oils. *Jatropha curcas* (Linn.) , a multipurpose plant , contains high amount of oil in its seeds compare to the other non-edible oil sources and this plant is probably the most highly promoted oilseed crop at the present world due to its availability ,sustainability and of less expensive feedstock.[5] Most of the no-edible oil including Jatropha curcas contains high free fatty acids (FFA). For an alkali catalyzed transesterification, the alkali catalyst that is used will reacts with the FFA to form soap. This reaction is undesirable because the soap lowers the yield of biodiesel and inhibits the separation of alkyl esters from glycerol. In addition it also binds catalyst means that more catalyst will be needed and hence biodiesel production cost will be higher. Thus these require multiple chemical steps (esterification of fatty acids, transesterification) to convert oil with high FFA into biodiesel.[6]

MATERIALS AND METHODS

1. Extraction of Oil and Determination of Physico Chemical Properties of extracted oil

The dried dehulled Jatropha curcas seed were purchased from a framer's field in Jaripal Palpa. Seeds were stored in NPRL laboratory in cool and dry place in a plastic container prior to extraction of oil. Seeds with seed coat were grounded with the help of grinder. The powdered seeds were subjected to Soxhlet extraction using n-hexane as solvent.

Different physico-chemical parameters such as moisture content of seed kernel, oil content of kernel, specific gravity, density, refractive index, peroxide value, % FFA(in terms of oleic acid) saponification value, Iodine value, Absolute (dynamic) viscosity and Kinematic viscosity were determined according to standard method of analysis[7-14] and values were tabulated.

2. Production of Biodiesel

The crude Jatropha oil has high % FFA so it creates problem in the separation of methyl esters layer from the glycerin fraction by the formation of fatty acid salts i.e. soap therefore the two step process was adopted for processing the Jatropha oil into the biodiesel. Firstly the crude Jatropha oil was subjected to the acid pretreatment process (esterification of oil by using acid as a catalyst) and secondly, pretreated oil was transesterified by using methanol and alkali (NaOH) as a catalyst to convert it to the Fatty acid methyl esters (FAME) or Biodiesel.[15]

a) Acid Pretreatment Process (Acid catalyzed esterification)

In this method FFA in Jatropha oil was reduced by selecting the following experimental conditions: i) Methanol- to- oil ratio 40% w/w Ii) Acid catalyst (H_2SO_4) –to- oil ratio 1% iii) reaction temperature 50^{O}C and v) reaction time of 1 hour.

After the one hour of reaction, the mixture was allowed to settle in separating funnel for 1 hr at room temperature (27^{O}C) and methanol- water fraction on the top layer was removed. After this the % FFA was again determined and was found to 0.8 %.

b) Transesterification of acid pretreated oil

In the second step, the acid pretreated oil was used for the transesterification using NaOH as catalyst. The pretreated oil was preheated at 50^{O}C for 10-15 minute and was mixed with methanolic NaOH solution. The transesterification was carried out using different % of NaOH varying from 0.5%, 1% and 1.5% of oil weight and methanol 20% of oil weight (i.e. 6:1 methanol to oil molar ratio.) The reaction mixture was then heated at 65^{O}C and maximum speed of revolution for 1 hour. Then the reaction mixture was allowed to settle overnight in separating funnel to separate methyl ester upper layer and glycerin lower layer. Then the produced biodiesel (FAME) was washed several times with warm distilled water until the biodiesel washed water become fully clear. It was then treated with anhydrous Na_2SO_4 to absorb any moisture then filtered and heated in air heated in air oven. Then different physical parameters of biodiesel produced were analyzed. TLC of FAME was performed for confirmation of complete transesterification. It was carried out in the solvent system of hexane, ethyl acetate, acetic acid in the ratio of 90:10:1.

c) Analysis by GC-MS

The purified fatty acid methyl esters (FAME) were analyzed by GC-MS method of analysis. Hexane (1ml) was added to 1 ml filtered esterified oil and the product shaken gently for 1 min. Then 1 µl was injected into Shimadzu 2010 PLUS, GC/electron ionization (EI) Mass Spectrometry (30 mx0.25mm i.d. HP-5 column: injector temperature 200^{O}C; Detector temperature 250^{O}C;

temperature program 60°C for 3 min, 10°C min^{-1} to 200°C, finally hold for 1 min).
The data were processed using Shimadzu Lab Solutions software (GCMS Release 2. 53). The EI mass spectra of all the peaks were compared to the NIST/EPA/NIH (NIST 08) to provide total-ion chromatogram (TIC) or extracted ion chromatogram (EIC) as required. The EI mass spectra of unknown were compared to the NIST library before proceeding with the interpretation.

RESULTS AND DISCUSSIONS

The oil yield percentage of *Jatropha* seeds collected from eight different districts of Nepal showed the highest amount of oil, i.e. 58.3% in the seeds collected from Rolpa District and lowest in Dolkha, i.e. 38.0% (Table 1). The moisture content ranged from 1 to 6.4 %**.** Then, the Jatropha seed oil was treated with 1% H_2SO_4 catalyst and three different concentrations of Methanol, i.e. 20, 40 and 60% at 60°C for 1 hour. The higher percentage of methanol (60%) was found to be better than other two for acid esterification of free fatty acids present in the oil (Table 3).
Due to the higher amount of Free Fatty Acid, i.e. 14.4% in the oil, it was acid esterified by using H_2SO_4 and methanol (20,40 and 60%), 60% was found to be the best one that decreased the free fatty acid to 0.8% (Table 2). If this step was not performed , during alkaline estrification , FFA will react with sodium hydroxide and soap will be formed that will decrease the percentage of FAME as end product.
After acid pretreatment the oil was treated with different concentration of the catalyst, NaOH (0.5, 1.0 and 1.5%) and 20% MeOH in this experiment. Wieghtt of oil taken, reaction time, reaction temperature, MeOH were 25gm,1 hr, 60°C respectively. The 0.5 and 1% NaOH was found to be very effective for biodiesel production (Table 3).
It was again conformed by thin layer chromatographic (TLC) method using solvent system of hexane, ethyl acetate and glacial acetic acid in the ratio of 90:10:1(v/v/v) respectively.
From TLC analysis also it was found that 0.5 and 1.0 % were found to be the suitable catalyst concentration for biosiesel production (Fig. 2).
The physical and chemical properties of *Jatropha curcas* oil determined were found to be very similar to the reported values (Table 2). But the iodine value is higher than reported data i.e.120 g of I_2/100g of oil [9]. The viscosity was also decreased from 32.95 to 4.71 centipoise after estrirification of the Jatropha oil (FAME)l, which is very close to the fossil diesel (3.60 Centipoises) (Table 4).
Biodiesel thus produced after tranesterification was analyzed by GC –Ms Instrument. The constituents of mainly eight structurally distinct groups of ethyl esters were recognized and are listed below. The result obtained showed that methyl esters of different fatty acids such as almitic,stearic, arachidic, margaric, oleic, linoleic and palmitoleic acids present in the biodiesel sample along with the size, molecular formula, chromatographic peak intensity and retention time is given in Table 5.
The mass spectrum of all the Fatty acid methyl esters were characterized with prominent molecular ion peak (M^+) peak at m/z = 270 and other significant ion peaks[M-31] at m/z=267 due to the loss of methoxy ($–OCH_3$) group and so on for palmitic acid methyl ester.

CONCLUSION

The result obtained from the percentage of oil content was high from 40-60%. The highest oil content obtained was 58.3 % in the kernel of Jatropha seed collected from Rolpa district of Nepal, which fall within the range of the percentage oil content reported in different literature, the mode of extraction is important parameter affecting the percentage yield. The chemical method of extraction would results the higher yield while that of mechanical method of extraction would results the lower yield. Due to the higher amount of Free Fatty Acid, acid pretreatment is very crucial before alkali estrification and 1.0 % NaOH was found to be the most suitable concentration to use as catalyst for transestrification producing 87% crude fatty acid methyl esters (FAME) and 10% crude glycerol. GC-MS technique could be used to analyse composition of FAME present in the biodiesel.

Table 1: Oil yield percent of *Jatropha* seeds from eight different districts of Nepal

S. No.	Sample	Altitude (Meter)	Moisture content (%)	Seed coat (%)	Oil content (%)	
					Whole seed	Kernel
1.	Rolpa	600-800	5.2	38.3	36.0	58.3
2.	Palpa	700-750	1.0	36.5	46.6	56.0
3.	Pyuthan	500-700	5.2	43.8	31.2	55.4
4.	Makawanpur	500-700	6.3	40.2	32.5	54.4
5.	Siraha	100-200	6.4	44.5	22.7	40.8
6.	Bishaltar	275-375	5.6	39.7	26.7	44.3
7.	Dhading	300-600	6.3	43.8	24.8	44.0
8.	Dolkha	400-500	5.9	50.4	20.0	38.0

Table 2: The pre acid esterification of Jatropha oil collected from Rolpa

Sample	MeOH % in oil (w/w)	Free Fatty Acid (FFA) %.
Rolpa oil	20	7.8
Rolpa oil	40	1.0
Rolpa oil	60	0.8

Table 3: Yield of Biodiesel after transesterification of pretreated oil

Sample no.	% NaOH (w/w)	MeOH (gm)	% MeOH (w/w)	% crude Biodiesel	% crude glycerin
T1	0.5	5	20	86.76	10.32
T2	1	5	20	82.36	16.24
T3	1.5	5	20	47.24	48.66

Table 4: Physicochemical parameters of seed oil and biodiesel prepared from *Jatropha curcus* collected from Rolpa District

S. No.	Physico-Chemical parameters	OIL	Biodiesel	Fossil Diesel	Unit
1.	Oil content	46.91			%
2.	Oil Content (Kernel)	56.63			%
3.	Free Fatty Acids (FFAs)	14.4			%
4.	Acid Value	28.65			
5.	Saponification Value	230.94			mg KOH/g
6.	Iodine Value	59.64	7.64	3.05	g of I_2/100g of oil
7.	Specific Gravity	0.9161	0.8753	0.841	-
8.	Density	0.9098	0.8722	0.832	g/cc
9.	Refractive Index	1.4703	1.4506	1.4503	-
10.	Dynamic Viscosity (absolute)	31.95	4.71	3.60	Centipoises

Table 5: Chromatographic and mass spectrometric data for the methyl esters of fatty acids in biodiesel

S. No.	Fatty acid Methyl Ester	Mol. Wt.	Mol. Formula	Retention Time (min)	Peak intensity	Fit value (%)
1	Palmitic acid methyl ester	270	$C_{17}H_{34}O_2$	12.60	High	93
2	Stearic acid methyl ester	298	$C_{19}H_{38}O_2$	16.48	Vey High	92
3	Arachidic acid methyl ester	326	$C_{21}H_{42}O_2$	19.76	Low	90
4	Margaricacid methyl ester	284	$C_{18}H_{36}O_2$	14.30	Low	94
5	Myristic acid methyl ester	242	$C_{15}H_{30}O_2$	8.76	Low	95
6	Oleic acid methyl ester	296	$C_{97}H_{64}O_2$	12.12	High	90
7	Linoleic acid methyl ester	294	$C_{19}H_{34}O_2$	15.72	Very high	92
8	Palmitoleic acid methyl ester	268	$C_{17}H_{32}O_2$	13.91	Low	89

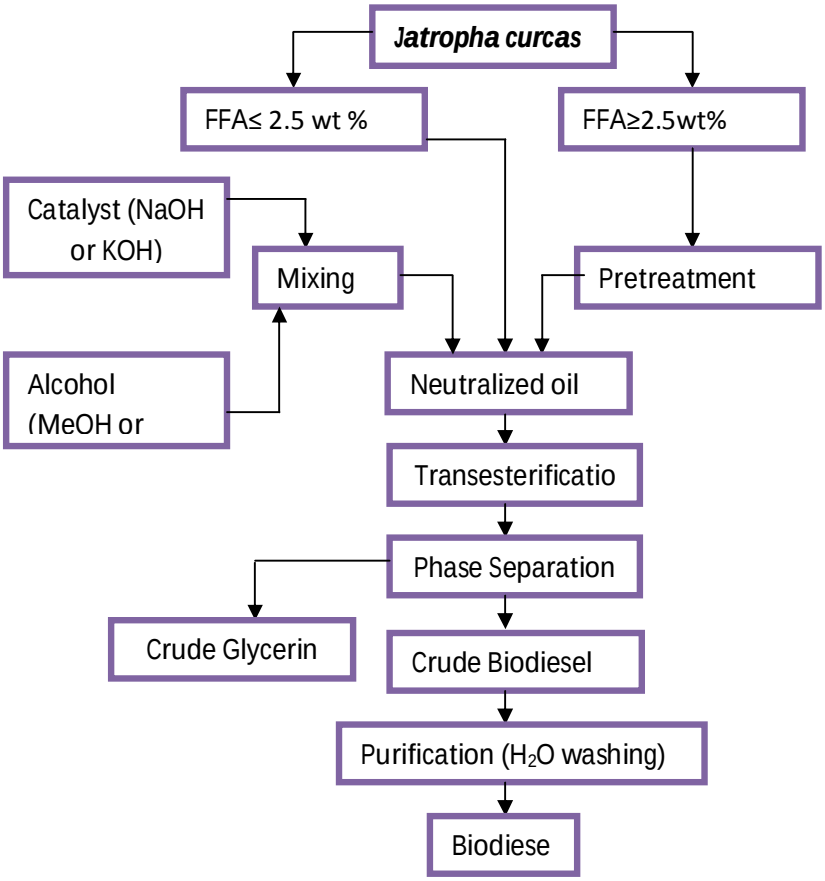

Fig. 1: Flow chart of Simplified alkali-catalyzed biodiesel production from *Jatropha curcas* oil

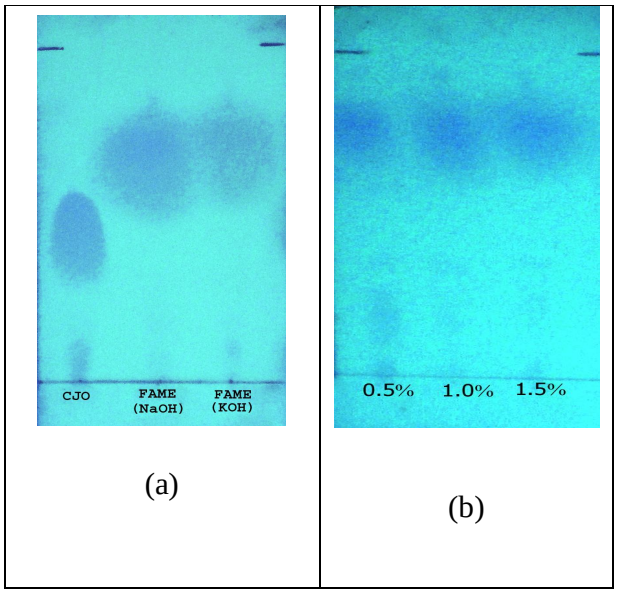

Fig. 2: TLC image using solvent system of hexane, ethyl acetate and glacial acetic acid (90:10:1 v/v ratio)
a) Crude Jatropha oil (CJO) and Biodiesel (FAME) at 1 % NaOH
b) Biodiesel prepared using 0.5%, 1.0% and 1.5% NaOH

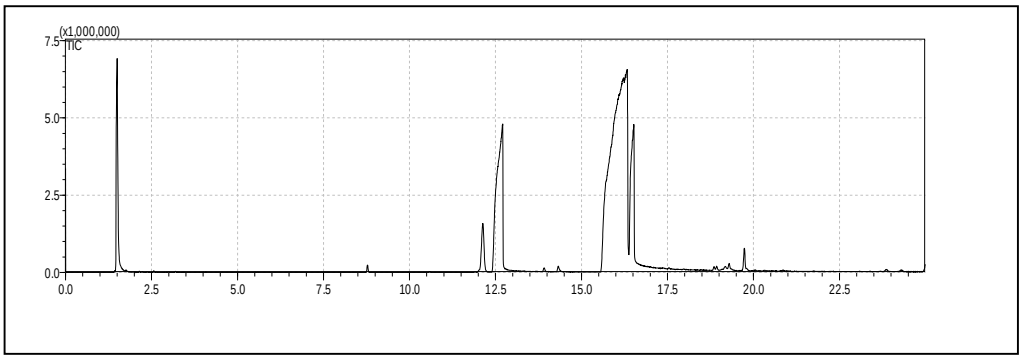

Fig. 3: Total ion chromatogram of biodiesel prepared from Jatropha oil

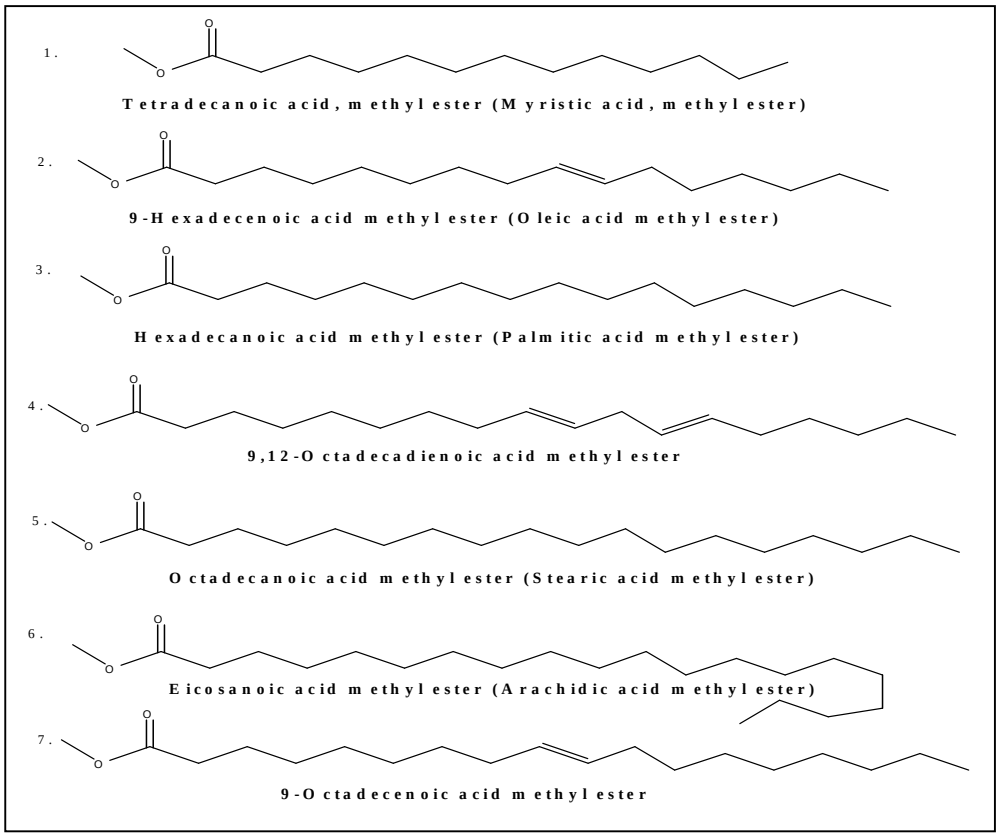

Fig. 4: Major Fatty Acids Methyl Esters (FAME) of biodiesel from *Jatropha curcas* oil detected by GC-MS and compared with the NIST 08 library

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