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Research Article

Optimization of Jatropha Methyl Ester and Study of its Physico-Chemical Properties using GC-MS and FT-IR Analysis

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Abstract

Biodiesel is becoming prominent among the alternatives to conventional petro-diesel due to economic, environmental and social factors. The quality of biodiesel is influenced by the nature of feedstock and the production processes employed. The process of transesterification is affected by the molar ratio of alcohol to oil, amount and nature of catalysts (NaOH and KOH), reaction time, and temperature. Jatropha methyl ester was analyzed for qualitative and quantitative characterization by using GC-MS and FT-IR techniques. C H N O S was analyzed using elemental analysis. Its fuel properties like cetane number (ignition quality indicator), iodine value (unsaturation levels), molecular weight, density, kinematic viscosity, heating value, flash point etc., is also calculated it is concluded that the biodiesel from these species can be feasible, cost effective and environment friendly.

Keywords: Transesterification; Catalyst; GC-MS; FT-IR; Elemental analysis

Introduction

The growth of industries, transport, agriculture and other human needs depends largely on petroleum fuels. In recent years, the fossil fuel resources are depleting rapidly with consequent environment degradation [1] which causes global warming and green house effects. This environmental issues have set the starting point for research in new and less harmful technologies [2]. Biodiesel (methyl ester) as an alternative has attracted considerable attention during the past decade as a renewable, biodegradable, and non-toxic fuel [3]. The monoalkyl esters of long chain fatty acids derived from a renewable lipid feed stocks such as vegetable oil or animal fat [4-5]. Methyl esters are generally produced from edible and non-edible feed stocks. Edible oils like coconut oil, peanut oil, sunflower oil, palm oil and soyabeen oil are used for methyl ester production. However, fortunately non-edible feed stocks such as Karanja (pongamia pinnata), Neem (azadirachta indica), callopyllum inopyllum and Jatropha Curcas provide an alternative feedstock without competing with food usage [6]. Hence the use of non-edible vegetable oils compared to edible oil is significant for methyl ester feedstock because of the tremendous demand for edible oils as food [7]. So, non-edible feedstock is considered for methyl ester production among those Jatropha curcas seeds are taken because it has high oil content 30-50% and abundant availability.

Many researchers have demonstrated several ways for production of methylester from selected feedstock, but base catalyzed transesterification is still widely used method in methyl ester production. Among the most commonly used alkaline catalysts potassium hydroxide (KOH) and sodium hydroxide (NaOH) flakes which are inexpensive, easy to handle in transportation and storage [8]. The activity of catalyst depends upon the amount of methoxide radicals available for the reaction [9]. In transesterification of vegetable oils and animal fats, each mole of triglycerides reacts stoichiometrically with 3 moles of a primary alcohol and yields 3 moles of alkyl esters (methyl ester) and I mole of glycerol (by-product) [10]. The actual mechanism consists of sets of equilibrium reactions in series and all of the reactions are reversible [11]. The reaction depends upon types of feedstock, catalyst concentration, reaction temperature and methanol to oil ratio [12].

The paper reports the study on processing optimization and characterization using different alkali catalyst like NaOH and KOH by examining their effects on methyl ester yield at different catalyst concentrations, molar ratios, reaction temperature and reaction time. The optimized conditions for higher yield with their characteristics are analyzed.

Materials and Methods

Chemicals and reagents

Jatropha Curcas seeds are purchased from Tamilnadu traders, Coimbatore. Chemicals like H_2SO_4, KOH, NaOH of Indian drugs and pharmaceutical Ltd., methanol (99.5%), H_3PO_4 of E Merck India Ltd., were used in the experimental work.

Extraction process

Oil can be extracted from the seeds by heat, solvents or by pressure. Extraction by heat is not used commercially for vegetable oils. The oil from Jatropha seeds can be extracted by three different methods. These are mechanical extraction using screw press, solvent extraction and an intermittent extraction technique viz. soxhlet extraction. Mechanical extraction process is used for the extraction of oil as shown in Figure 1.

Experimental procedure

Pre conditioning of Jatropha oil: The Crude Jatropha Curcas oil

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Figure 1: Mechanical press.

is taken and 10% of H_3PO_4 to remove free fatty acid (FFA) (<0.2mg KOH/g) oil, water (<0.1%), phospholipids (<0.04%) and other impurities. This was done to improve the quality of oil before first step.

Esterification of free fatty acids

The presence of FFAs in oils causes significant processing problems in standard biodiesel manufacturing, since the free fatty acid is readily saponified by the homogeneous alkali catalyst used to transesterify triglycerides, leading to a loss of catalyst as well as increased purification costs. The negative influence of high FFA contents on the base-catalyzed transesterification of triglycerides. Free fatty acids react with the basic catalyst added for the reaction and give rise to soap, as a result of which some portion of the catalyst is neutralized and is therefore no longer available for transesterification. These high FFA content oils/fats are processed with an immiscible basic glycerol phase so as to neutralize the free fatty acids and cause them to pass over into the glycerol phase by means of monovalent alcohols. The main approach for improve the processing of free fatty acid oils is to first esterify the free fatty acids to alkyl esters in the presence of an acidic catalyst before transesterification. The pretreated oils, in which the free fatty acid content is lowered to no more than 0.5 wt%, can then be processed under standard transesterification reaction conditions.

Transesterification of triglycerides

Transesterification is, in principle, the action of one alcohol displacing another from an ester, referred to as alcoholysis. In the transesterification of different types of oils, triacylglycerol react with an alcohol, generally methanol or ethanol, to produce esters and glycerin. The main factors affecting transesterification are the amounts of alcohol and catalysts; reaction temperature; pressure and time; the contents of free fatty acids and water in oils. Transesterification is conducted to produce biodiesel with the objective to reduce the viscosity of the parent vegetable oil or animal fat, since it is an order of magnitude greater than that of the corresponding methyl esters (Biodiesel). The kinematic viscosity of Jatropha oil significantly reduces after transesterification. The overall transesterification process is a sequence of three equivalents, consecutive and reversible reactions, in which di and monoglycerides are formed as 13 intermediates. At each reaction step, one molecule

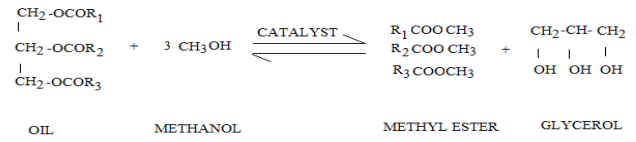

Figure 2: Chemical reaction of transesterification process.

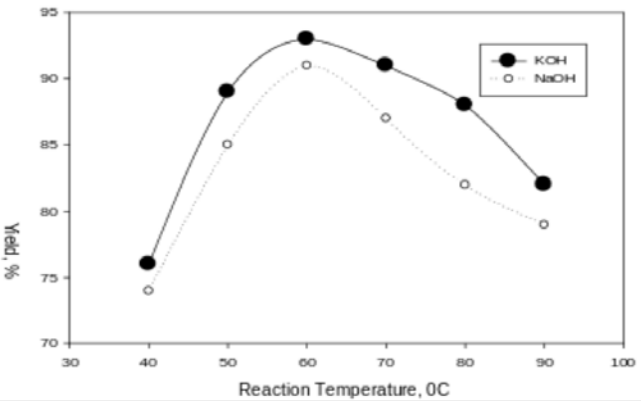

Figure 3: Effect of reaction temperature with yield at 9:1 molar ratio with 1.0 wt % for 90 min for temperatures (40^{0}C to 90^{0}C).

of methyl or ethyl ester is produced for each molecule of methanol or ethanol consumed. The transesterification reaction is represented by the general equation shown in Figure 2.

Results and Discussions

Transesterification reaction mainly influences process parameters like reaction temperature, catalyst concentration and molar ratio. So, in order to find the optimum conditions for better yield, survey was conducted for alkali catalysts say KOH and NaOH using crude Jatropha oil.

Effect of reaction temperature

Transesterification reaction was performed for 90 min at 9:1 molar ratio with 1.0 wt % of respective catalyst (say NaOH, KOH) at different temperature ranges with 10^{0}C starting from 40^{0}C to 90^{0}C. From the graph it was observed that as temperature increases, reaction also increases hence the yield also increases up to 60^{0}C and then decreases because higher reaction temperatures causes methanol to vaporize resulting in decreased yield. Thus optimum yield is achieved at 60^{0}C for both alkali catalysts (KOH and NaOH) with 93% and 91% yield as shown in Figure 3.

Effect of catalyst concentration

Catalyst concentration is the key variable which enhances the yield of methyl ester production. In general, as the catalyst concentration increased, the conversion of triglycerides also increased. This is because an insufficient amount of catalyst results in an incomplete conversion of triglycerides into fatty acid esters. That is why transesterification was carried out using alkali catalyst (NaOH and KOH) concentrations of 0.6, 0.8, 1, 1.2 and 1.4 wt% at reaction temperature of 60^{0}C with molar ratio of 9:1 for 90 min reaction time. As the catalyst increases the yield also increases upto 1.0 wt% and then decreases gradually due to because the addition of

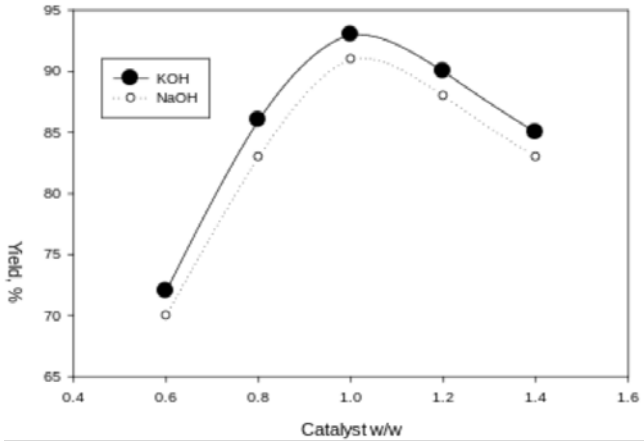

Figure 4: Effect of catalyst concentration with yield at 60°C with 9:1 molar ratio for 90 min reaction time.

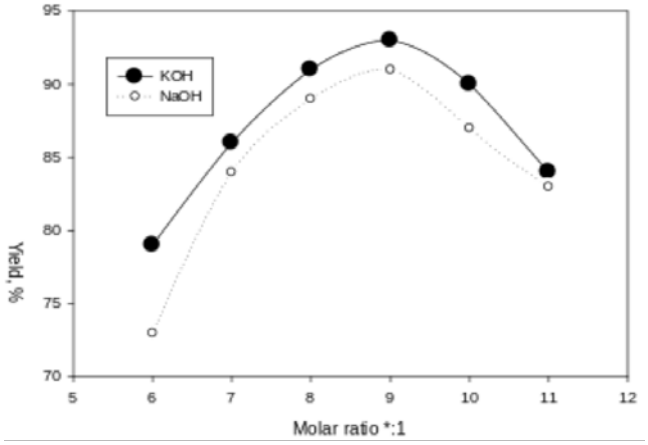

Figure 5: Effect of molar ratio with yield at 60°C with 1.0 wt% alkali catalysts for 90min reaction time.

excess alkaline catalysts caused more triglycerides participation in the saponification reaction, resulting in increased production of soap and reduction of the methyl ester yield. So, any increase in concentration of catalyst beyond the neutralization limit results in decrease in methyl ester conversion. Therefore, the optimum condition for catalyst concentration is 1.0 wt% with 93% yield for KOH and 91% yield for NaOH as shown in Figure 4.

Effect of molar ratio

Generally, the stoichiometry of the reaction requires 3 moles of methanol per mole of triglycerides to yield 3 moles of methyl ester and 1 mole of glycerol. The alcohol may be methanol, ethanol, iso butanol and iso propanol. In this survey we considered methanol due its low price and highly reactive nature. Molar ratio of methanol to oil is varied from 6:1 to 11:1 at 60°C reaction temperature of 1.0 wt% catalyst concentrations for 90 min reaction time in transesterification reaction. Starting with 6:1 molar ratio the yield starts increasing for both alkali catalysts because higher alcohol molar ratio interferes with the separation of glycerol because there is an increase of solubility. From the graph it is noticed that yield decreasing from 10:1 and 11:1 due to addition of excess of alcohol was able increase the conversion of

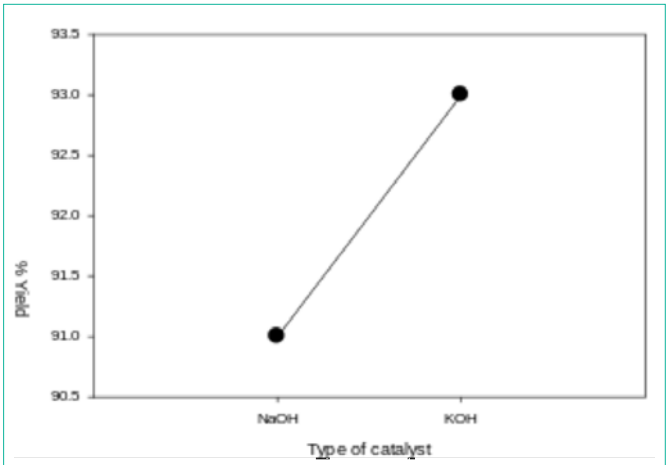

Figure 6: Effect of type of catalyst on % yield.

Table 1: Physical and chemical properties of test fuels in comparison to ASTM **D6751-02** biodiesel standards.

Property	Units	Petro Diesel (HC)	Jatropha (FAME)	ASTM (Biodiesel)
Carbon chain	Cn	C_8-C_{32}	C_{14}-C_{20}	C_{12} – C_{22}
Density @30°C D93	kg/m^3	82	880	870-900
Lower calorific value	kJ/kg	42 500	38 500	-----
Kinematic viscosity @40°C D445	cSt	2.25	3.5	1.9-6.0
Cetane Number D613	----	49	52	47 min.
Iodine Value DIN53241	glodine/100g	38	93	120 max
Flash point, Closed cup D93	°C	70	158	130 min
Fire point	°C	76	162	-----
Molecular wt.	g/mol	225	288	-----
Pour point	°C	-20	-6.5	-15 to 16

dimonoglycerides, but there is possibility of recombination of esters and glycerol to form monoglycerides because their concentration and also increasing during the course of the reaction. Thus the optimum condition obtained for NaOH and KOH at 9:1 methanol to oil ratio is 91% and 93% yield for Jatropha oil as shown in Figure 5.

Effect of type of Catalyst on %Yield the plots reveals that there is no much change in yield of esters with the use of NaOH or KOH as catalyst in the production of esters as shown in Figure 6.

Fuel Properties

Fuel properties like flash point, fire point, viscosity, density and calorific value are calculated for the optimum conditions that are investigated for the highest yield KOH for optimum conditions with 93% yield. All the fuel properties reached ASTM standards which is fit to replace in the place of diesel fuel as shown in (Table 1).

Elemental Analysis

The methyl ester consists of three basic elements namely: carbon, hydrogen, significant amount of oxygen as shown in Table 2. The increase of O_2 in methyl ester is related to the reduction of C and H, causes the lower value of lower calorific value (LCV) of Jatropha

Table 2: Elemental composition of Jatropha methyl ester.

Element (Wt %)	Diesel	Jatropha Methyl Ester	ASTM (Bio-diesel)
Carbon (C)	86.25	76.02	77
Hydrogen (H)	12.5	12.09	12
Nitrogen (N)	0	-	-----
Sulfur (S)	0.25	-	0.05
Oxygen (O_2)	1	10.86	11
C/H ratio	6.9	6.3	-----

methyl ester as compared to that of fossil diesel. The Jatropha methyl ester contains 76.02% carbon and 12.79% hydrogen. Burning hydrocarbons requires oxygen. The hydrocarbon and oxygen combine, in a process called combustion, to produce water, carbon dioxide, and energy. Hydrocarbons that are contaminated with atoms such as sulfur and nitrogen will also produce nitrogen dioxide and sulfur dioxide. Sulfur dioxide later combines with hydrogen in the atmosphere to produce the weak sulfurous acid as well as the strong sulfuric acid. Both of these contribute to acid rain. In addition to sulfur, nitrogen is also a common contaminant in hydrocarbons. Nitrogen dioxide can react with hydrogen in the atmosphere to produce nitric acid, which also contributes to acid rain. The all the elements reached ASTM Standards which is suitable for environment and can be replace for diesel fuel.

FFA Analysis of Methyl Ester using GC

The GC-MS is composed of two major building blocks: the gas chromatograph and the mass spectrometer. The gas chromatograph utilizes a capillary column which depends on the column's dimensions (length, diameter, film thickness) as well as the phase properties. The molecules are retained by the column and then elute (come off) from the column at different times (called the retention time), and this allows the mass spectrometer downstream to capture, ionize, accelerate, deflect, and detect the ionized molecules separately. The mass spectrometer does this by breaking each molecule into ionized fragments and detecting these fragments using their mass-to-charge ratio. The mass spectrometry process normally requires a very pure sample while gas chromatography using a traditional detector (e.g. Flame ionization detector) cannot differentiate between multiple molecules that happen to take the same amount of time to travel through the column (i.e. have the same retention time), which results in two or more molecules that co-elute. Sometimes two different molecules can also have a similar pattern of ionized fragments in a mass spectrometer (mass spectrum). Combining the two processes reduces the possibility of error, as it is extremely unlikely that two different molecules will behave in the same way in both a gas chromatograph and a mass spectrometer.

The target analytes are extracted and mixed with water and introduced into an airtight chamber. An inert gas such as Nitrogen (N_2) is bubbled through the water; this is known as purging. The volatile compounds move into the headspace above the water and are drawn along a pressure gradient (caused by the introduction of the purge gas) out of the chamber. The volatile compounds are drawn along a heated line onto a 'trap'. The trap is a column of adsorbent material at ambient temperature that holds the compounds by returning them to the liquid phase. The trap is then heated and the

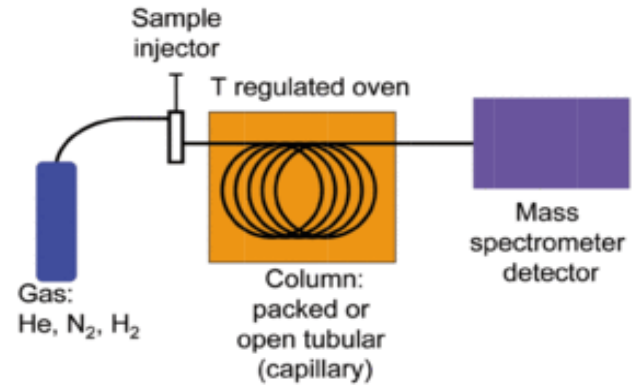

Figure 7: GC-MS schematic.

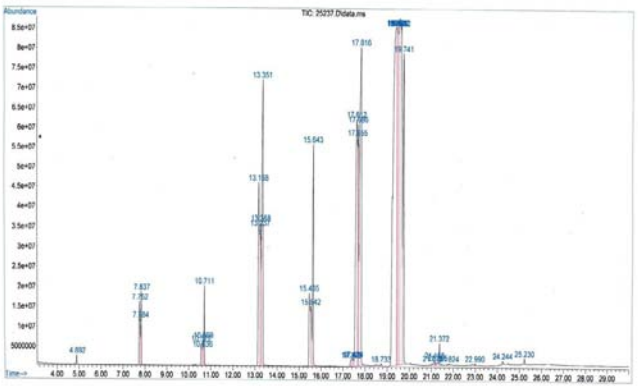

Figure 8: GC- 5973 N MSD Analysis for Methyl Ester of Jatropha oil.

sample compounds are introduced to the GC-MS column via a volatiles interface, which is a split inlet system [14]. P&T GC-MS is particularly suited to volatile organic compounds (VOCs) and BTEX compounds (aromatic compounds associated with petroleum).

The prepared biodiesel i.e., Jatropha methyl ester were analyzed by GC- 5973 N MSD to determine the composition of fatty acids demonstrated in Figure 7 and as shown in Figure 8.

The higher level of unsaturated fatty acid reduces fuel quality, because of its easy oxidation. As a rule saturated fatty acid such as 16:0 or 18:0 are stable than unsaturated ones like 18:1, 18:2 and 18:3 which decreases the fuel quality. The result also shows that methyl esters

Table 3: Measured values of Fatty acids in the Methyl Ester of Jatropha oil.

Type	Fatty acids			percentage(%)
UNSATURATED	1	Oleic	18:01	49.5
	2	Linoleic	18:02	12
SATURATED	3	Palmitic	16:00	22
	4	Stearic	18:00	5.5
	5	Arachidic	20:00	0.5
	6	Caprylic	8:00	1
	7	Arachidic	20:00	0.5
	8	Myristic	14:00	5
	9	Others		4

Table 4: FTIR Studies of Jatropha Methyl Ester.

SNo	Peaks (cm^{-1})	Bond	Compound type	Mode	Transmi-ttance (%)	Concen-tration
1	3609.47	O-H	Alcohols, phenols	Stretch	95	Strong, sharp
2	3006.49	C-H	Alkanes	Stretch	86	Medium
3	2921.77	C-H	Alkanes	Stretch	9	Medium
4	2852.85	C-H	Alkanes	Stretch	32	Medium
5	1742.61	C=O	Esters, saturated, aliphatic, aldehydes	Stretch	3	Strong
6	1460.9	C-H	Alkanes	Bend	62	Medium
7	1374.79	C-H	Alkanes	Rock	83	Medium
8	1235.71	C-H/C-N	Alkyl halide, Aliphatic amines	Wag, Stretch	67	Medium
9	1160.14	C-H/C-N	Alkyl halide, Aliphatic amines	Wag, Stretch	31	Medium
10	1114.92	C-H/C-N	Alkyl halide, Aliphatic amines	Wag, Stretch	60	Medium
11	721.55	C-H	Alkanes	Rock	68	Medium
12	592.7	C-Br	Alkyl halides	Stretrch	98	Medium

of biodiesel obtained from transesterification has more percentage of saturated fatty acids with less percentage of unsaturated fatty acids. The presence of saturated fatty acid in the obtained biodiesel leads to high viscosity, high cetane number and better biodiesel stability. The measured values of fatty acids present in the methyl ester of biodiesel are given in (Table 3).

Fourier Transform Infrared Spectroscopy (FTIR) Analysis

Procedure

1. To launch the FTIR program, double click the OMNIC icon. 2. From the Collect pull down menu, select Setup, and select the following: No. of scans = 8 Resolution = 2 cm^{-1} Apodization = Happ-Genzel Zero filling = None Final format = Absorbance 3. From the Edit pull down menu, select Options. Click on the Collect tab at the top. Click the "Collect to New Window" box to deselect it. Click OK to close window. 4. From the Collect pull down menu, select Background (Repeat background collection every 30 min^{-1} hr if the humidity is high) 5. From the Collect pull down menu, select Collect Sample Place the sample in the holder in the IR, then select Yes Add to window = Yes 6. From the Process pull down menu, select-Automatic Baseline Correct old spectrum shown in red and new spectrum shown in blue Click on the red one.

FT-IR is used to determine the different functional group such as alcohol, alkane, alkynes, alkenes and other such groups present in the substance which here is Jatropha methyl ester as shown in Figure 9. Interpreting infrared (IR) spectra is of immense help to structure determination. Not only will it tell you what functional groups and structural elements are there, it will also clarify which ones are not there, and also concentration of bands by using values of transmittance as shown in Table 4.

The special contributions are characterized as C-H stretching and bending vibrations which are unique for each sample. Is the main absorption below 3000 cm^{-1}. If so, the compound is probably aliphatic. If the main absorptions are approximately 2935 and 2860 cm-1 and there are also absorptions at 1470 and 720 cm^{-1}, then the compound probably contains a long linear aliphatic chain [15]. Stretching absorptions of a vibrating chemical bond occur at higher

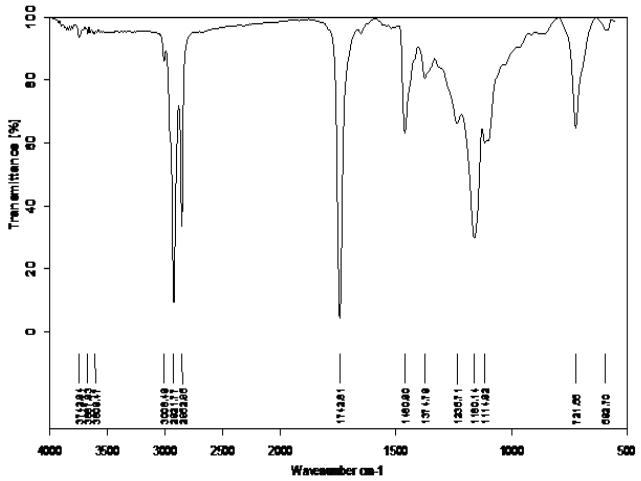

Figure 9: Infrared Spectra of Jatropha Methyl Ester.

frequencies (wave number) than the corresponding bending or bond deformation vibrations, with the understanding, of course that energy and frequency are proportionally related. A good example is the C=H set of vibrations, observed in the hydrocarbon spectra and in virtually all organic compounds. Here, the sample C=H stretching vibrations for saturated aliphatic species occur between 3000 and 2800 cm-1 and the corresponding simple bending vibrations nominally occur between 1500 and 1300 cm-1 [15].

It could be concluded that the most abundant type of bond on Jatropha methyl ester are C-H, C-O, O-H and C-N. The modes of the bonds are stretch, bending and rocking.

Conclusion

Transesterification of Jatropha oil from seeds are successfully carried out and survey was conducted for two different alkali catalysts (NaOH and KOH) to achieve higher yield using different operating parameters like molar ratio, operating temperature, reaction time and catalyst concentration. According to Tiwari et al., 2007 the best optimum conditions are 2wt% KOH catalyst with 5:1 molar ratio at 60^0C gave 99% yield where as for different operations

conditions we found the yield to be 93% with molar ratio 9:1 at 600C with 1wt% catalyst concentration for 90 min of KOH catalyst and similar the reference Singh and saroj padhi 2009 gave 97% yield for 0.7 wt% NaOH at 65^0C 6:1 molar ratio, here we got 91% Yield for optimum conditions with molar ratio 9:1 at 60^0C with 1wt% catalyst concentration for 90 min. From the above information we have come to know that influence of parameters plays a prominent role in Yield of methyl ester produced. Tiwari had took the catlalyst of 2 wt% so yield increases for particular conditions. Results are very close to the references so we have gone through the physical and chemical properties as discussed.

Physical properties like flash point, kinematic viscosity, calorific value, iodine number, cetane number and density are characterized which are within ASTM standards. Chemical characteristics such as elemental analysis (C, H, N, O, S) which are also in permissible limit and reaches ASTM standards and GC-MS is analyzed and saturated and unsaturated fatty acids were studied for KOH catalyst. With the help of FTIR analysis we can find the strength of the bonds present. The bonds such as C-H, C-O, O-H and C-N are abundant in Jatropha Methyl Ester. The modes of the bonds are stretch, bending and rocking.

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