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Biodiesel production from neem oil –an alternate approach

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ABSTRACT
In this study, neem oil which is one of the abundant non-edible oils in India, Nepal, Pakistan, Sri Lanka and bangladesh is used for biodiesel production. The conventional 2-step transesterification production of biodiesel using sulphuric acid and potassium hydroxide as catalysts is carried out. The optimum process parameters like reaction time, temperature, catalyst loading and methanol-oil molar ratio were investigated with respect to maximum yield. A maximum yield of 88% biodiesel is obtained via this method. A novel technique to produce biodiesel via complete hydrolysis followed by acid esterification is developed. Optimum reaction conditions were found to be 100ml 0.5N sulphuric acid loading, reaction temperature of 40ºC and reaction time of 2 hours. This resulted in a maximum FFA of 82%. Then acid esterification was carried out at the following reaction conditions of 0.55:1 v/v methanol-oil-ratio, 0.5% v/v H2SO4 acid catalyst loading, 50˚C and 4 hours reaction time. A maximum biodiesel yield of 92% was obtained by this method. The viscosity of biodiesel produced by this method as well as the other physicochemical properties, were found to be in compliance with international standard.

Keywords–Acid value, esterification, hydrolysis, transesterification, vegetable oil

I. INTRODUCTION

Making biodiesel, producing it on a large scale and using it to replace petrodiesel is one among the most researched and anticipated developments of today. The ever-rising demand on transportation fuels like petrol and diesel leading to its gradual depletion has led to this situation. Fossil fuels are non-renewable sources of energy which generate pollutants and are associated with global warming, climate change and even some incurable diseases. Thus, there are exhaustive works going on to find alternate sources of fuels which are both environment-friendly and easily available.

Biodiesel, by definition, are the methyl esters of long chain fatty acids. When compared to petrodiesel, biodiesel has many advantages such that it is a renewable source of fuel, no engine modifications required for using biodiesel blends, lower CO_2 and other exhaust gas emissions, etc. Most commonly used feedstocks for biodiesel production currently are canola oil, soybean oil [1], rapeseed oil and corn oil oil. Since usage of edible oils for biodiesel production raises issues regarding food security especially in the developing countries, a lot of research is carried out using non-edible oils.

Transesterification is the most widely used method of biodiesel production. A simple method was developed for biodiesel production from non-edible Jatropha oil using a bifunctional acid base catalyst $CaO\text{-}La_2O_3$ with a high biodiesel yield of 98.76% at transesterification conditions of 160°C, 3 h reaction time, 25 methanol/oil molar ratio and 3 wt% catalyst loading by H.V. Lee et al., 2014 [2]. Yuang-Chung Lin et al., (2014) [3] developed a novel method to produce biodiesel with a microwave assisted heating system apart from the conventional heating system using a solid base catalyst $NaNH_2$ from Jatropha oil. Also, it was concluded that the total energy consumption for microwave assisted heating was 10 times less than that required for conventional heating system. Amonrat et al. (2014) conducted a Comparison study of biodiesel production from crude Jatropha oil and Krating oil by supercritical methanol transesterification. Using non-catalytic supercritical methanol transesterification, high methyl ester yield (85-90%) can be obtained in a very short time (5-10 min) [4].

H. Muthu et al. (2010) conducted stufy on neem oil. Neem Methyl Ester (Biodiesel) was prepared by a two-stepprocess of esterification and transesterification from Neem oil with methanol in the presence of catalyst. Acid catalyst was used for the esterification and alkali catalyst (KOH) for the transesterification reaction. Optimal Free Fatty Acid (FFA) conversion was achieved using 1 wt% SZ as an acid catalyst with a methanol-to-oil molar ratio of 9:1, temperature of 65°C and reaction time of 2 h. The acid value was reduced to 94% of the raw oil (24.76 mg KOH/g), which confirmed the conversion. Consequently, this pretreatment reduces the overall complexity of the process and a conversion efficiency of 95% is achieved when pretreated oil reacts with methanol in the presence of KOH.

Table 1: Major Compounds identified in Neem oil via GC-MS

COMPOUND	FORMULA	MOLECULAR MASS	COMPOSITION
SATURATED FRACTION			
Palmitic acid methyl ester	$C_{17}H_{34}O_{2}$	270.25588	5.031 min
Stearic acid methyl ester	$C_{19}H_{38}O_{2}$	298.28718	8.019 min
UNSATURATED FRACTION **Poly – Unsaturated**			
Linoleic acid methyl ester	$C_{19}H_{34}O_{2}$294.255887.531 min		
Mono – Unsaturated			
Oleic acid methyl ester	$C_{19}H_{36}O_{2}$	296.27153	7.620 min
9-Hexadecenoic acid (Palmitoleic acid/Omega 7)	$C_{16}H_{30}O_{2}$	254.22458	4.809 min

Thus, different methods of biodiesel production are being developed. The conventional method of producing biodiesel via transesterification as have been seen earlier focusses mainly on converting all the triglycerides in the oil sample to the corresponding fatty acid methyl esters (FAME). The pre-treatment process to this step involvessubjecting the oil to acid esterification which converts all the free fatty acids to its corresponding fatty acid methyl esters form. The disadvantage with this method is that when there is insufficient acid value reduction via acid catalysed esterification, there occurs significant soap formation which acts as a hindrance in the efficient separation or removal of the biodiesel.

Thus, an alternative approach to biodiesel production is proposed via the method of acid hydrolysis. In this case, focus is on breaking all the triglyceride esters into their corresponding free fatty acids i.e., acid value is to be increased. It is then followed by acid esterification for the production of fatty acid methyl esters (biodiesel).

II. MATERIALS AND METHODS

The neem oil used in this study was purchased from the local market in Chennai. The chemicals methanol, potassium hydroxide, sulphuric acid were purchased from SISCON chemicals, Chennai. All the chemicals used were analytical reagent grades. Distilled water from local supplier is used for the hydrolysis process.

2.1. Physicochemical analysis of neem oil

The physicochemical properties of the neem oil were studied and carried out in accordance with the procedures mentioned in the Indian Standard : Methods Of Sampling And Test For Oils And Fats [IS : 548 (Part 1) – 1964]. To identify the fatty acid components present in the neem oil, GCMS analysis was done using an Agilent 7890B gas chromatograph equipped with a HP-5 MS capillary column (30 m × 0.25 mm i.d.) connected to an Agilent 5977A MSD mass spectrometer operating in the EI mode (70 eV; m/z 50 – 550; source temperature 230°C and a quadruple temperature 150°C). The column temperature was initially maintained at 200°C for 2 min, increased to 300°C at 4°C/min, and maintained for 20 min at 300°C. The carrier gas was helium at a flow rate of 1.0 mL/min. The inlet temperature was maintained at 300°C with a split ratio of 50:1 [5].

2.2. **Refining of oil**

Neem oil is reported to contain a considerable amount of saturated fraction as high as 37% [6]. The presence of high melting point saturated glyceridesin the Oilleads to problems like gelling especially in cold countries causing unwanted deposits in the engine and creating problems.

Hence, it necessitates the need to winterize the oil. This was done by centrifuging the oil in a Remi C-24 Plus Cooling Centrifuge at 10000 RPM, -2ºC for 10min.

The oil is then water-degummed by addition of 10 v/v% warm water to the oil and stirred for half an hour. The water along with the phosphatides (gum) is separated by centrifuging. The degumming process is repeated twice to ensure maximum removal of gums. Phosphatides are known for theiremulsifying properties and high viscosity. High levels of emulsifiers, when present during transesterification, can cause poorseparation of the methyl-ester and glycerol rich layers which are undesirable [8]

Table 2 : The Physicochemical Properties of neem oil a Muthu et al. (2010); b Awolu et al.(2013)

PropertyValue		**Reference Value**
Acid Value (mg.KOH/gm.oil)	61.2	44^a
Saponification Value (mg.KOH/gm.oil)	295	202^a
Iodine Value (gm.I_2/100gm)	39.67	82^a
Ester Value (mg.KOH/gm.oil)	233.8	
% Glycerin	12.78	
Density (at 30ºC) (Kg/m^3)	875.8	925^a
Viscosity (at 30ºC) (cSt)	22	36.67^b
Cetane Number	54.38	58^b
HHV (mJ/Kg)	36.74	40.27^b
Moisture Content (%)	0.8	

2.3. Two – step acid – base catalyzed transesterification

The neem oil when transesterifieddirectly using 1 w/w% KOH catalyst, , 0.3:1 methanol-oil ratio at a temperature of 60ºCfor 1 hour [7] produced significant amount of soap formation from saponification side reaction. This was due to thehighlevel of free fatty acidsand small quantity of moisture in the crude neem oil. Due to large amount of soap formation, the separation of biodiesel from glycerine was difficult and thus resulted in very low biodiesel yield (28%).

Therefore, a two-step process acid catalyzed esterification followed by alkali catalysed transesterification was employed according to the method of Sathya et al. (2013) [7].

2.3.1. Acid pretreatment (acid catalyzed esterification)

100ml centrifuged oil is taken in round bottomed flask attached to a condenser and pre-heated to 50°C. 50ml (50v/v%) methanol is added to the flask and stirred for few minutes, then 0.5ml (0.5 v/v%) H2SO4 is added and heated and stirred for 4 hours. The mixture is then poured into a separating funnel for separation into two layers. After 2 hours, the lower layer which is the pre-treated neem oil is decanted and stored for further processing. The upper layer that consists of the excess acid catalyst, methanol, water and other impurities are discarded. This process reduced the FFA value to less than 2%. Due to the comparatively higher acid value of the neem oil feedstock, there is a slight increase in the methanol consumption and the reaction time parameters from the values reported by Sathya et al. (2013) [7]

2.3.2. Base catalyzed transesterification

After acid pre-treatment, the esterified oil is taken in a round-bottomed flask and heated upto 55˚C. 1 w/w% of KOH is dissolved in 30% methanol. The dissolved solution is poured into flask. The mixture is heated and stirred for 1hr. The mixture is then poured into a separating funnel and kept for a period of 8 hours. The glycerol and impurities are settled in lower layer and is discarded. The impure biodiesel remain on the upper layer. It contains some trace of the catalyst, glycerol and methanol. The washing process is done by addition of hot distilled water to the biodiesel layer and gently mixed. The upper layer is pure biodiesel and lower layer is drawn off. These operating conditions were reported earlier by Sathya et al. (2013) [7]. A maximum biodiesel yield of 86.1% was obtained via this process.

2.4. ALTERNATE METHOD BIODIESEL PRODUCTION

2.4.1. ACID HYDROLYSIS

50 ml of the oil sample is poured into the flask and heated upto 40˚C. A standard mixture of 0.5N sulphuric acid is prepared. 100ml of the 0.5N sulphuric acid solution is added to the oil sample in flask once it reaches 40ºC. Heating and stirring is continued for about 2 hours at atmospheric pressure. After completion of this reaction, the mixture is poured into a separating funnel for separating the water, glycerol and sulphuric acid. The top layer is the acid hydrolysed oil. Thus, it is centrifuged to remove presence of any residual water, sulphuric acid or glycerine. A maximum FFA of 82 % is achieved with this method.

Table 3 : Properties of the biodiesel obtained

Property	**Value**	**EN 14214 [38]**	**IS 15607**
Acid Value (mg.KOH/gm.oil)	0.49	**0.5 max**	**0.5 max**
Saponification Value (mg.KOH/gm.oil)	309	**NS**	**NS**
Iodine Value (gm.I_2/100gm)	34.21	**120 max**	**NS**
HHV (mJ/Kg)	36.25	**NS**	**NS**
Density (at 15°C) (Kg/m^3)	870.43	**860-900**	**860-900**
Kinematic Viscosity (at 40°C) (cSt)	4.6	**3.5-5**	**2.5-6**
Cetane Number	54.77	**51 min**	**51 min**
Moisture Content (mg/kg)	369	**500 max**	**500 max**

2.4.1.1. RESULTS AND DISCUSSION

Effect of sulphuric acid catalyst

The effect of different normalities of sulphuric acid on the hydrolysis extent is shown in Fig 1.

It has been seen that yield is increased upto 0.5N sulphuric acid solution addition. The maximum hydrolysis is achieved at 0.5N. With further increase in normality the acid value decreases. As normality increases, the ratio of water to acid catalyst is changed which in turn promotes the reverse reaction.

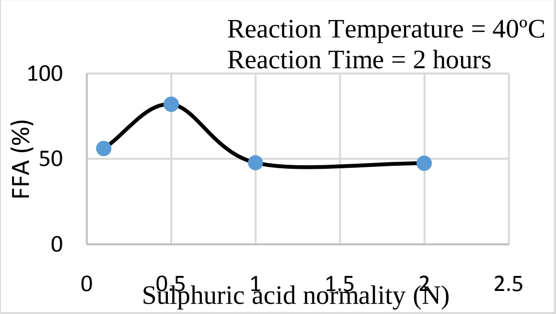

Fig 1: Effect of acid catalyst loading on FFA

Effect of reaction temperature

The hydrolysis reactions are usually carried out at temperatures ranging from 40ºC to 180ºC. The reaction temperature has important role in acid hydrolysis of oils. The effect of temperature variation on hydrolysis extent is shown in Fig 2. Among these, 40˚C gave maximum acid value extent. If greater than 40˚C, acid value is reduced probabaly due to reverse reaction.

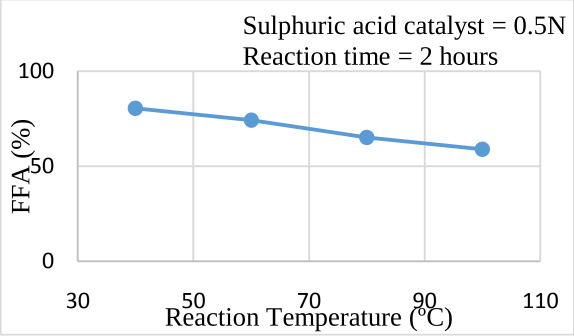

Fig 2: Effect of reaction temperature on FFA

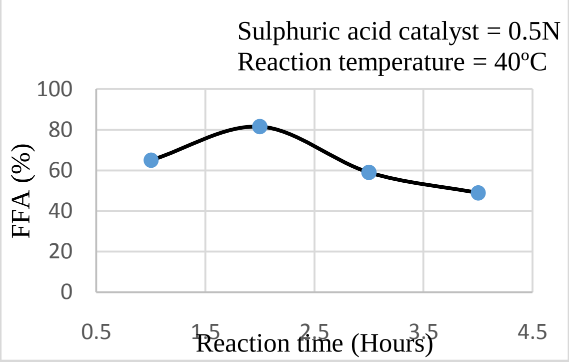

Fig 3 : Effect of reaction time on FFA

Effect of reaction time

The conversion rate is increased with increase in reaction time. The effect of reaction time variation on the conversion efficiency is shown Fig 3. From the figure, acid value was increased up to 2hrs reaction time and after that it is decreased. The maximum efficiency is achieved for 2 hr reaction time, after which the reverse reaction takes place.

Table 4 :Biodiesel production cost by 2 step transesterification

SI. No.	**Component**	**Cost (Rs.)**
1	Neem Oil – 100 ml	93
2	Esterification – 50ml methanol	23
3	- 0.5ml sulphuric acid	0.29
5	Transesterification - 30 ml of Methanol	13.8
6	Catalyst KOH 0.9 gm	0.846
7	Total Cost	130.936/86.75ml

Table 5 :Biodiesel production cost by Hydrolysis-Esterification

SI. No.	**Component**	**Cost (Rs.)**
1	Neem Oil – 50 ml	46.5
2	Hydrolysis – 1.33ml H2SO4	0.77*
3	Esterification – 27.5ml methanol	12.65
	- 0.25ml sulphuric acid	0.145
4	Total Cost	60.065/45.78ml

*Distilled water was obtained from local supplier at very low price

2.4.2. ACID ESTERIFICATION

100 ml of the hydrolysed neem oil is poured into the flask and heated upto 50˚C. The 55% v/v methanol is added with the preheated neem oil and stirred for a few minutes. 0.5% v/v of sulphuric acid is added with the mixture. Heating and stirring is continued for about 4 hours at atmospheric pressure. After completion of this reaction, the mixture is poured into a separating funnel for separating the excess alcohol, water, impurities and sulphuric acid. The excess alcohol, sulphuric acid and impurities moves to the top layer and is discarded. The lower layer which is the biodiesel is separated. Water washing is done with warm distilled water to remove any impurities and purify the biodiesel. A maximum biodiesel yield of 91% is obtained by this method. Biodiesel is then analysed for its physicochemical characteristics and checked for compliance with international biodiesel standards.

2.4.3. PRODUCT ANALYSIS

The characterization of the biodiesel was carried out according to standard methods. The density and the viscosity were measured at room temperature using the specific gravity bottle and the Brookefield viscometer respectively. The parameters are determined with the standard methods. The acid value, iodine value and moisture content were analysed using standard test methods such as EN 14104, EN 14111, EN ISO 12937 respectively. The properties of the biodiesel obtained is checked for its compliance with the European Standard EN 14214. Thus, from the table it can be observed that all properties analysed comply with European Standard EN 14214. The viscosity of biodiesel in this case is within the required range.

III. COST ESTIMATE OF BIODIESEL PRODUCTION

2.5. Alkaline Transesterification

Biodiesel production from 1 literNeem Oil=0.87 Liter
Cost of Biodiesel per liter = Rs1509.35 per litre biodiesel

3.1. Hydrolysis-Esterification

Biodiesel production from 1 literNeem Oil=0.92 Liter
So Cost of Biodiesel per liter = Rs1312.04 per litre biodiesel

Thus, there is a definite reduction (13.1%) in cost of biodiesel production by the hydrolysis method. Also, the yield of biodiesel is more (5.7%) in the hydrolysis method when compared to the transesterification method. Methanol which is mainly derived from fossil fuels (a non-renewable source of energy) is consumed less in the hydrolysis method which imparts another important advantage. Further reduction in cost be achieved with recycling of methanol and also by the usage of by-products such as soap and glycerin for commercial use.

IV. CONCLUSION

The direct transesterification of neem oil resulted in very low yield (28%) because of the high acid content.

Thus, two-step transesterification process as mentioned in literature [6] is carried out to determine the maximum biodiesel yield.

Acid hydrolysis was carried out at the following optimized process conditions of 100ml (0.5N) sulphuric acid loading, reaction temperature of 40ºC and reactiontime of 2 hours. This resulted in a maximum FFA of 82%. The optimum combination of parameters for acid esterification was found to be

0.55:1 v/v methanol-oil-ratio, 0.5% v/v H2SO4 acid catalyst, 50˚C and 4 hours reaction time. A maximum biodiesel yield of 92% was obtained by this method. The viscosity of biodiesel produced by this method is lower and well within the requirement range. As for the other properties, they were comparable to the biodiesel properties obtained via the two-step transesterification.

The advantage of this new method of biodiesel production is that there is no need to use an alkaline catalyst and thus possibility of soap formation can be eliminated. High feedstock compatibility is another advantage since oils with higher acid value also can be used in this method. Also, the consumption of methanol is greatly reduced as in this method methanol is used only for acid esterification and hydrolysis requires only small amount of sulphuric acid catalyst and excess water. Whereas in the two-step transesterification, methanol is consumed for both esterification and transesterification. Also, in terms of the biodiesel yield and cost of production, the method of hydrolysis-esterification seems more feasible.

REFERENCES

[1]. Omidvarborna et al. "*Characterization of particulate matter emitted from transit buses fueled with B20 in idle modes*". *Journal of Environmental Chemical Engineering 2 (4): 2335–2342.*

[2]. H.V. Lee, J.C. Juan, Y.H. Taufiq-Yap, "*Preparation and application of binary acid base CaO La2O3 catalyst for biodiesel production*", *Renewable Energy 74 (2015) 124 – 132*

[3]. Yuan-Chung Lin, Shang-Cyuan Chen, Chin-En Chen, Po-Ming Yang, Syu-RueiJhang, "*Rapid Jatropha-biodiesel production assisted by a microwave system and a Sodium amide Catalyst*", *Fuel 135 (2014) 435 – 442*

[4]. Amonr at Samniang, Chuenkhuan Tipachan, SomjaiKajorncheappun-ngam. "*Comparison of biodiesel production from crude Jatropha oil and Krating oil by supercritical methanol transesterification*". *Renewable Energy 68 (2014)351-355*

[5]. Narsing Rao, G., *Prabhakara Rao, P. G. and Satyanarayana, A. "*Chemical, fatty acid, volatile oil composition and antioxidant activity of shade dried neemAzadirachtaIndicaflower powder*". *International Food Research Journal 21(2): 807-813 (2014)*

[6]. Martín C, Moure A, Martín G, Carrillo E, Domínguez H, Parajó JC(2010). Fractional characterisation of jatropha, neem, moringa, trisperma, *castor and candlenut seeds as potential feedstocks forbiodiesel production in Cuba*. *Biomass Bioenerg. 34(4): 533-538*

[7]. T.Sathya, A. Manivannan. (2013) "*Biodiesel production from neem oil using two step transesterification*".*ISSN: 2248-9622 www.ijera.com, Vol. 3, Issue 3, pp.488-492*

[8]. http://b100research.com/resources/fat-oil-grease-industry/phosphates

[9]. H. Muthu; V. SathyaSelvabala; T.K. Varathachary; D. KiruphaSelvaraj; J.Nandagopal; S. Subramanian. (2010) "*Synthesis of biodiesel from Neem oil using sulfatedzirconiac viaTranesterification*", *Braz. J. Chem. Eng. vol.27 no.4 São Paulo.*