Published in Offshore World, April-May 2006
Archived in Dspace@nitr, http://dspace.nitrkl.ac.in/dspace

Preparation of karanja oil methyl ester.

R. K. Singh*, A. Kiran Kumar and S. Sethi
Department of Chemical Engineering, National Institute of Technology
Rourkela- 769008 (Orissa) India

Abstract

Biodiesel (fatty acid methyl ester) which is derived from triglycerides by transesterification , has attracted considerable attention during the past decade as a renewable, biodegradable and nontoxic fuel. Several processes for biodiesel fuel production have been developed, among which transesterification using alkali as catalyst gives high level of conversion of triglycerides to their corresponding methyl ester in a short duration. This process has therefore been widely utilized for biodiesel fuel production in a number of countries. In India, non-edible oils like karanja oil and jatropha oil are available in abundance, which can be converted to biodiesel. In the present studies, biodiesel has been prepared from karanja oil. As the acid values of this oil was more than 3, so it was converted to biodiesel by esterification followed by transesterification process. The methyl ester produced by these methods was analyzed to acertain their suitability as diesel fuels.

Keywords: Karanja oil, Biodiesel, Esterification and Transesterification

Introduction

Biodiesel which is derived from triglycerides by transesterification and from the fatty acids by esterification has attracted considerable attention during the past decade as a renewable, biodegradable, eco-friendly and non-toxic fuel. Several processes for biodiesel fuel production have been developed. Biodiesel is recently gaining prominence as a substitute for petroleum based diesel due to environmental considerations and depletion of vital resources like petroleum and coal. The possible use of renewable resources as fuels and as a major feedstock for the chemical industry is currently gaining acceptance. Further as petroleum is a fast depleting natural resource, an alternative renewable route to petroleum is a deemed necessity. Now serious efforts are being made on the production and utilization of biodiesel in India. Methyl esters are clean burning fuel with no sulfur emission. Although its heat of combustion is slightly lower than that of the petro-diesel, there is no engine adjustment necessary and there is no loss in efficiency [1]. Methyl esters are non-corrosive and are produced at low pressure and low temperature conditions. Concentrated (about 80 %) glycerin is obtained as a byproduct during transesterification process. For transesterification reaction in general Leyes [2] has shown the effect of alcohol to acid ratio on the yield of ester at equilibrium when the reaction is carried out homogenously. Bradshaw [3] stated that 4.8:1 molar ratio of methanol to vegetable oil leads to 98% conversion. He noted that ratio greater than 5.25:1 interfered with gravity separation of the glycerol and added useless expense to the separation. Freedman, et al. [4] studied the effect of molar ratio of methanol to oil and effect of changes in concentrations of tri-, di- and monoglyceride on ester yield. Freedman et. al. [5] obtained the results for methanolysis of sunflower oil, in which the

molar ratio varied from 6:1 to 1:1 and concluded that 98% conversion to ester was obtained at a molar ratio of 6.1. Biodiesel from karanja oil shows no corrosion on piston metal and piston liner whereas biodiesel from jatropha curcas has slight corrosive effect on piston liner [6].. In the present investigation, biodiesel was prepared from karanja oil and its properties were analized to acertain its suitability as biodiesel.

Experimental

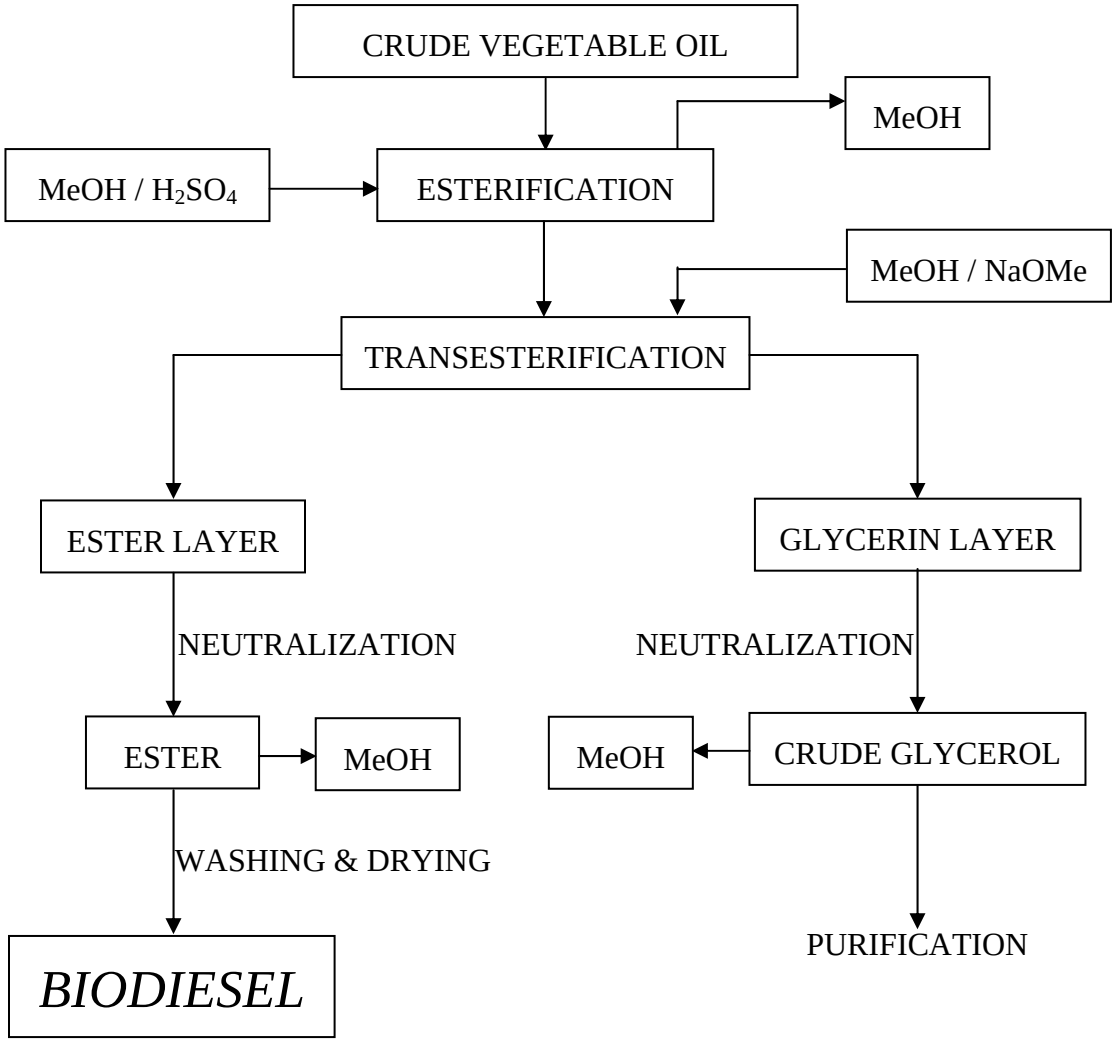
The experimental setup is shown in figure 1. A 2000 ml three-necked round-bottomed flask was used as a reactor. The flask was placed in a water bath, whose temperature could be controlled within $\pm$ 2 ^{o}C. One of the two side necks was equipped with a condenser and the other was used as a thermowell. A thermometer was placed in the thermowell containing little glycerol for temperature measurement inside the reactor. A blade stirrer was passed through the central neck, which was connected to a motor alongwith speed regulator for adjusting and controlling the stirrer speed.

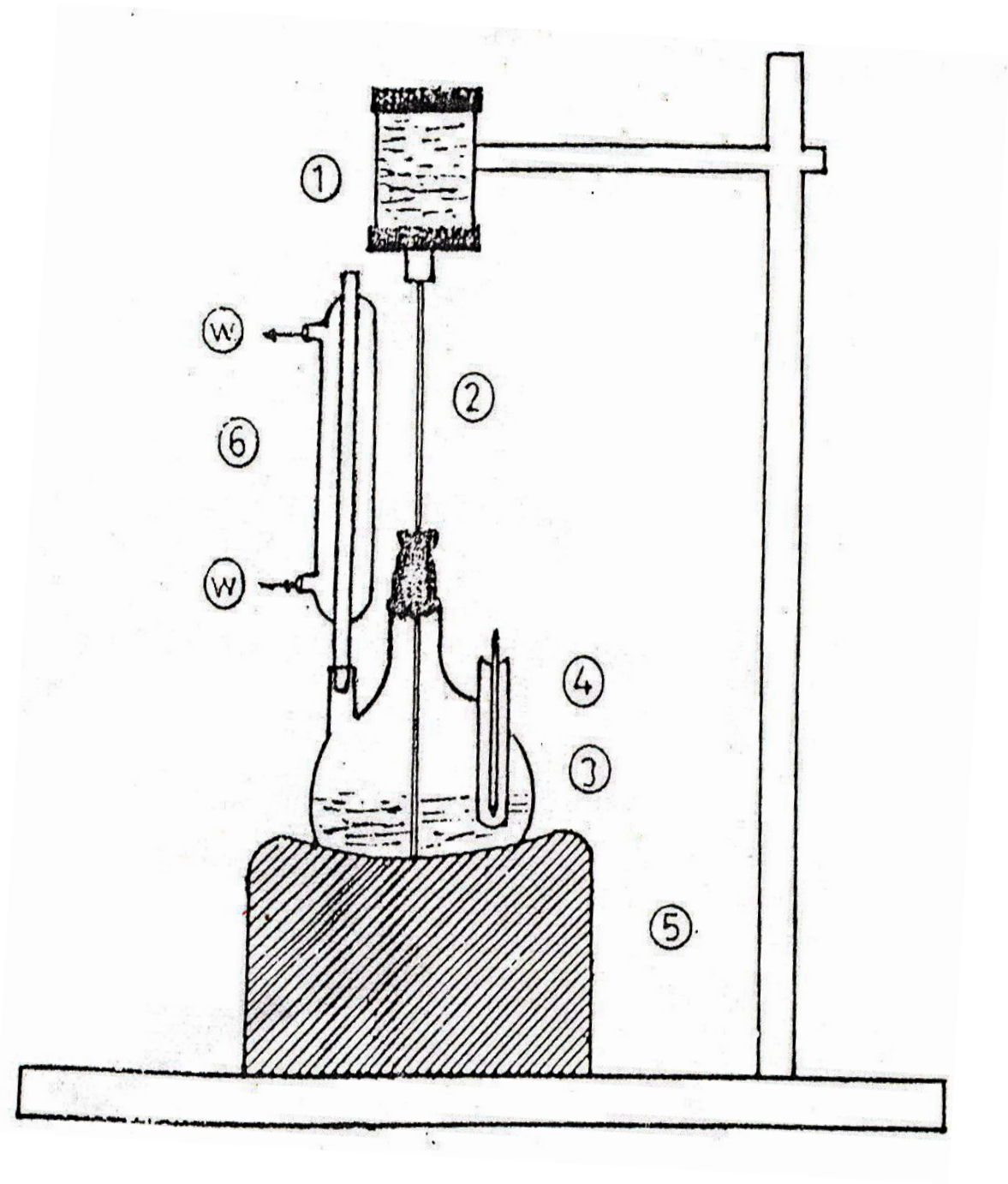
Esterification: A known amount of karanja oil was taken in the above-mentioned setup. Required amount of sulphuric acid and methanol were added to the oil and stirred continuously maintaining a steady temperature of 64^{0}C. Intermittently samples were collected at regular intervals (30min) and acid value was determined. After the confirmation of complete reduction of acid valve to less than 1.0, the heating was stopped and the products were cooled. The unreacted methanol was separated by separating funnel. The remaining product was analyzed for acid value and it was found that the acid value varied from 1.0 to 0.5. This oil sample was for transesterified to obtain methyl esters.

Transesterification: In the same setup, known amount of esterified karanja oil was charged. Required amount of catalyst NaOH was desolved in methanol and the rest amount of methanol alongwith the catalyst solution was added to the oil sample. After proper closing of the flask it was put on the water bath.The system was maintained airtight to prevent the loss of alcohol. The reaction mix was maitained at temperature just above the boiling point of the alcohol i.e. around 70°C to speed up the reaction rate. Excess alcohol was used to ensure total conversion of the oil to its esters. The formation of methyl ester was monitered by using thin layer chromatography(TLC) technique. Coated silicagel glass plates were spotted with karanja oil and the sample of ester. The spotted samples were developed in solvent system in glass chamber using solvent ratio of 80:20 hexane/ether by volume. This confirms the formation of methyl esters. This procedure was followed for all the samples collected at regular interval of time to check the formation of methyl ester. After the confirmation of completion of methyl ester formation, the heating was stopped and the products were cooled and transferred to a separating funnel. Where the ester layer containing mainly methyl ester and methanol and glycerol layer containing mainly glycerol and methanol were separated. The pH level of both layers were measured and neutralised seperately. For neutralisation a known amount of sulfuric acid in methanol was added to both the layers seperately to neutralize the sodium methoxide present in them. The traces of methanol present in ester layer was recovered in a distillation column under control vacuum. Distilled methanol was weighed and stored in sample bottle. Similar procedure was adopted to recover the traces of methanol present in glycerol layer. The methyl ester was washed and dried under vacuum to remove traces of moisture. A sample of esters were analyzed for acid value by using

standard AOCS procedures for standardization. The sample of glycerol layer was analyzed for glycerol content by using AOCS procedure. The glycerol content was found from 80 to 85 %.

Flow Chart for preparation of biodiesel from karanja oil





1. Electric Motor
2. Stirrer
3. Three-necked Round Bottom Flask
4. Thermo-well with Thermometer
5. Water bath
6. Condenser

Figure – 1: Experimental setup for preparation of methyl esters from karanja oil

RESULTS AND DISCUSSION

Various properties of karanja oil were determined by using standard methods and results are presented in Table 1.Properties of karanja methyl esters were determined experimentally to ascertain their suitability as diesel fuel. The properties of karanja methyl esters has been compared with the properties of biodiesel and petrodiesel in table 2. The fuels properties of karanja methyl esters was within specifications. As the production of biodiesel from edible oils is currently much more expensive than diesel fuels due to relatively high cost of edible oils. There is a need to explore non-edible oils as alternative feed stock for the production of biodiesel. Non-edible oils such as Karanja (Pongamia Pinnata), Jatropha (Jatropha Curcas), Mahua (Madhuca Indica), Undi (Calophyllum Inophyllum), etc. are easily available in many parts of the world including India and are very cheap compared to edible oils. Production of these oil seeds can be stepped up to use them for production of biodiesel

Table 1: Properties of karanja oil:

Properties	**Karanja oil**
Acid value	5.91
Saponification value	191.5
Kinetic viscosity at 38 ^{o} C mm^2/s	41.8
Pour point ^{o} C	6
Flash point ^{o} C	232
Density Kg/l	0.9326
Carbon residue wt. %	1.51
Ash wt %	0.014
Sulfur wt %	0.007

Table 2: Comparison of karanja biodiesel with others.

Test property	**Karanja Methyl Ester**	**Diesel**
Acid Value (mgKOH/g)	0.42	------
Saponification Value(mgKOH/g)	187	------
Iodine Value	91	------
Free Glycerine (wt%)	0.015	------
Total Glycerine (wt%)	0.0797	------
Density (mg/Lt)	0.876	0.876
Conversion, (%)	97.8	
Flashpoint (^{0}C)	183	74
Pour point (^{0}C)	4	- 16
Cloud point (^{0}C)	7	- 12
Viscosity (cSt) @ 40^{o}C	4.657	2.98
Heating Value (MJ/Kg)	37.12	42.9
Cetane Index	55.0	49.2
Ash content (Wt%)	0.005	0.02

FEFERENCES

[1] Srivastava, A and Prasad, R: Triglycerides-based diesel fuel, Renew. Sust. Oil Energy Rev.4,111-133(2000)

[2] Leyes CE; Encyclopedia of Chemical Technology; Edited by Kirk – Othmer, Interscience, Newyork; 1950; Vol. 5, P 776 – 816

[3] Bradshaw GB, Menly WC; US Patent 2360844 (1944)

[4] Freedman B, Pryde EH, Mounts TL; Variables affecting the yield of Fatty Esters from Transesterified Vegetable Oils; J. Am Oil Chem Soc; 1984; 61 (10): 1638 – 43

[5] Freeman B, Butterfield R.O. and Pryde E.H., J. Am. Oilchem. Soc. 63, 1375 (1986)

[6] Haas and Scott J. Am. Oilchem. Soc. 73, 1393 (1999)

[5] Feuge RO., Gros AT; Modification of Vegetable Oils. VII Alkali Catalyzed Inter-esterification of Peanut Oil with Ethanol; J. Am Oil Chem Soc; 1949; 26(3), 97

[6] http//panchayat.nic.in/round/.%5cDrRKGupta,IIP.PPT