

Prospective Feedstock for the Production of Biodiesel in India

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Biodiesel (fatty acid methyl ester) which is derived from triglycerides by transesterification with methanol has attracted considerable attention during the past decade as a renewable, biodegradable and non-toxic fuel. Several processes for biodiesel fuel production have been developed, among which transesterification using alkali as catalyst gives high level 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 the present studies, the properties of edible oils like soybean, sunflower, mustard, palm, cotton seeds and non-edible oils like karanja and jatropha have been determined by suitable standard methods. Refined edible oils, whose acid values were less than 3 were transesterified with methanol in the presence of sodium methoxide as catalyst. But the non-edible and raw karanja and jatropha oils having acid values more than 3.0 were esterified followed transesterified. The methyl esters produced by these methods were analyzed to ascertain their suitability as diesel fuels.

Key Words: Vegetable oils, Esterification, 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 mainly in western countries 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 deemed necessity. Now serious efforts are being made on the production and utilization of biodiesel in India. According to Indian scenario, the demand for petroleum diesel is increasing day by day hence there is a need to find out an appropriate solution. Under Indian condition only such plants can be considered for bio diesel, which produce non edible oil in appreciable quantity and can be grown in large scale on non cropped marginal lands and waste lands. India has more than 300 different species of trees, which produce oil-bearing seeds¹. Around 75 plant species, which have 30 % or more fixed oil in their seeds or kernel, have been identified². Traditionally the collection and selling of tree-based

oilseeds was generally carried out by poor people for use as fuel for lighting. Presently there is an extended use of these oils in soaps, varnishes, lubricants, candles, cosmetics, *etc.* However, the current utilization of non-edible oilseeds is very low. Bio-diesel has become more attractive recently because of its environmental benefits and the fact that it is made from renewable resources³. Although short term tests using neat vegetable oil showed promising results, longer tests led to injector coking, more engine deposits, ring sticking and thickening of the engine lubricant⁴. These experiences led to the use of modified vegetable oil as a fuel. Although there are many ways and procedures to convert vegetable oil into a diesel like fuel, the transesterification process was found to be the most viable process⁵. Transesterification is the process of using an alcohol (*e.g.*, methanol, ethanol or propanol), in the presence of a catalyst, such as sodium hydroxide or potassium hydroxide, to break the molecule of the raw renewable oil chemically into methyl or ethyl esters of the renewable oil, with glycerol as a by product. Biodiesel, defined as the mono-alkyl esters of fatty acids derived from vegetable oil or animal fat, in application as an extender for combustion in diesel engine, has demonstrated a number of promising characteristics, including reduction of exhaust emissions⁶. Transesterified oils have proven to be a viable alternative diesel engine fuel with characteristics similar to those of diesel fuel. Its physical and chemical properties required for operation of diesel engine are similar

to petroleum based diesel fuel⁷. Transesterification is a chemical reaction that aims at substituting the glycerol of the glycerides with three molecules of monoalcohols such as methanol thus leading to three molecules of methyl ester of vegetable oil⁸. The molecular weight of ester molecule is 1/3rd of oil and low viscosity. However, higher ratio of alcohol to oil is generally employed to obtain biodiesel of low viscosity and high conversion⁹. Methyl esters are clean burning fuel with no sulfur emission. Although its heat of combustion is slightly lower than that of petrodiesel, there is no engine adjustment is necessary and there is no loss in efficiency⁷. Methyl esters are non-corrosive and are produced at lower operating pressure and temperature conditions. Concentrated (*ca.* 80 %) glycerin is obtained as byproduct during transesterification process. Leyes¹⁰ has shown the effect of alcohol to oil ratio on the yield of ester at equilibrium when the reaction is carried out homogeneously. Bradshaw¹¹ stated that 4:8:1 molar ratio of methanol to vegetable oil leads to 98 % conversion. They noted that the ratio greater than 5.25:1 interfered with gravity separation of the glycerol and added useless expense to the separation. Freedman *et al.*¹² studied the effect of molar ratio of methanol to oil and effect of changes in concentration of tri-, di- and monoglycerides on ester yield. They used four different oils namely soybean, sunflower, peanut and cotton seed oils varying the molar ratio of methanol to oil from 3:1 to 6:1 and concluded that 98 % conversion was obtained at a molar ratio of 6:1. Hass and Schott¹³ described the combined chemical enzymatic process for the conversion of soap stock into methyl esters into two steps. In the first step the glycerides present in the soap stock were transesterified with alcohol and potassium hydroxide and in the second step the free fatty acids were esterified using a lipase. It has been reported that an alkali catalyzes both esterification and transesterification at a pressure of 90 bar.

Process variables: The most important variables which influence the transesterification reaction are: reaction temperature, ratio of alcohol to vegetable oil, catalyst mixing intensity and purity of reactants.

Reaction temperature: The literature has revealed that the rate of reaction is strongly influenced by the reaction temperature. However the reaction is conducted close to the boiling point of methanol (60-70 °C) at atmospheric pressure for a given time. Such mild reaction conditions require the removal of free fatty acids from the oil by refining or pre-esterification. Therefore degummed and deacidified oil is used as feedstock¹². Pretreatment is not required if the reaction is carried out under high pressure (9000 kPa) and high temperature (240 °C), where simultaneous esterification and transesterification take place with maximum yield obtained at temperatures ranging from 60-80 °C at a molar ratio of 6:1¹²⁻¹⁴.

Ratio of alcohol to oil: Another important variable is molar ratio of alcohol to vegetable oil. As indicated earlier, the transesterification reaction requires 3 mol of alcohol per mole of triglyceride to give 3 mol of fatty esters and 1 mol of glycerol. In order to shift the reaction to the right, it is necessary to either use excess alcohol or remove one of the products from the reaction mixture. The second option is usually preferred for the reaction to proceed to completion. The reaction rate was found to be highest when 100 % excess methanol was

used. A molar ratio of 6:1 is normally used in industrial processes to obtain methyl ester yields higher than 98 % (w/w)¹².

Catalysts: Alkali metal alkoxides are found to be more effective transesterification catalysts compared to acidic catalysts. Sodium alkoxides are the most efficient catalysts, although KOH and NaOH can also be used. Transmethylation occurs in the presence of both alkaline and acidic catalysts¹⁵. As they are less corrosive to industrial equipment, alkaline catalysts are preferred in industrial processes. A concentration in the range of 0.5-1.0 % (w/w) has been found to yield 94-99 % conversion to vegetable oil esters¹³ and further increase in catalyst concentration does not affect the conversion but adds extra cost, as the catalyst needs to be removed from the reaction mixture after completion of the reaction.

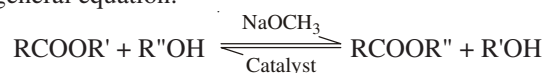
Mixing intensity: It has been observed that during the transesterification reaction, the reactants initially form a two-phase liquid system. The mixing effect has been found to play a significant role in the slow rate of reaction. As phase separation ceases, mixing becomes insignificant. The effect of mixing on kinetics of the transesterification process forms the basis for process scale-up and design.

Purity of the reactants: Impurities in the oil affect the conversion level considerably. It is reported that about 65-84 % conversion into esters using crude vegetable oils has been obtained as compared to 94-97 % yields refined oil under the same reaction conditions¹². The free fatty acids in the crude oils have been found to interfere with the catalyst. This problem can be solved if the reaction is carried out under high temperature and pressure conditions.

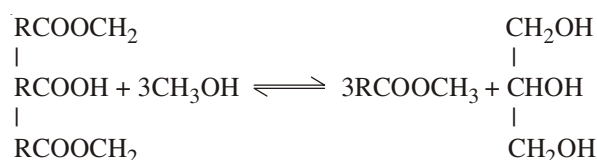
Chemistry of esterification and transesterification: Esterification is the reaction of an acid with an alcohol in the presence of a catalyst to form an ester. The equation is expressed generally as:



Generally, acids catalysts like sulfuric acid are employed. Esterification is a reversible reaction. Thus water must be removed to drive the reaction to the right to obtain a higher ester yield. Transesterification on the other hand is the displacement of the alcohol from an ester by another alcohol in a process similar to hydrolysis, except that an alcohol is used instead of water. This reaction cleavage of an ester by an alcohol is more specifically called alcoholysis and is represented by the general equation:



In this case, a new ester is formed. Generally alkaline catalysts are used with sodium methylate said to be the most effective. Sodium hydroxide and potassium hydroxide can also be used as catalysts. Transesterification is a general term. More specifically, if methanol is used, the reaction is termed methanolysis. Methanol is generally used because it is cheap, but other alcohols can also be used. The reaction with fats and oils using methanol is represented by the general equation:



Although the equation reflects the overall reaction, but the reaction usually consists of a series of consecutive reversible steps. Since the time when the transesterification of oils and fats, a large number of potentially useful catalysts have been investigated as a means to enhance the reaction rate. Without added catalysts some degree of rearrangement can be obtained but only under extreme conditions of temperature and time, leading to undesirable effects such as isomerization, polymerization and decomposition. Apart from the now generally preferred catalysts, *e.g.*, sodium methoxide and alcoholates, the following substances have been claimed to catalyze transesterification are related reactions. This catalyst has the advantages that short reaction time and relative low temperature can be used with only a small amount for catalyst and with little or no darkening of colour of the oil. Transesterification of vegetable oils using methanol and alkaline catalyst is the most commonly used processes for manufacture of methyl esters.

Biodiesel processing: Biodiesel can be produced by a variety of esterification technologies. The oils and fats are filtered and pre-processed to remove water and contaminants. If, free fatty acids are present, they can be removed or transformed into biodiesel using special pre-treatment technologies. The pre-treated oils and fats are then mixed with an alcohol (usually methanol) and a catalyst (usually sodium methoxide). The oil molecules (triglycerides) are broken apart and reformed into esters and glycerol, which are then separated from each other and purified.

EXPERIMENTAL

The experimental setup is shown in Fig. 1. The reactor used for experiments was a 1000 mL four-necked round bottom flask. The flask was placed on a heating mantle of 300 watts capacity, whose temperature could be controlled within ± 2 °C. One of the three side necks was equipped with a condenser and the other two were used for thermo-well and for simple collection respectively. A thermometer was placed in the thermo-well containing little glycerol for temperature measurement inside the reactor. The central neck was adapted to a paddle blade impeller with a glass stirrer. The stirrer rod was passed through the neck using Teflon cap. The motor was connected to a speed regulator for adjusting and controlling the stirrer speed.

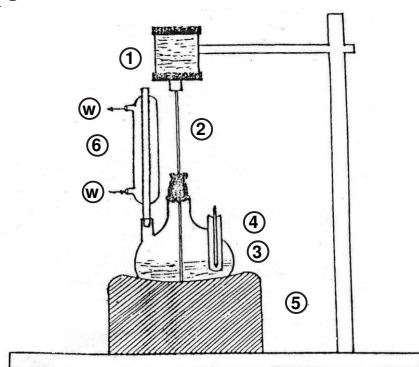


Fig. 1. Experimental setup for preparation of methyl esters from vegetable oil. 1. Electric motor, 2. Glass stirrer, 3. Four-necked round bottom flask, 4. Thermo-well with thermometer, 5. Heating mantle, 6. Condenser

Esterification: A known amount of oil was taken in the above mentioned setup. Heat was supplied to the setup using a heating mantle. A known amount of sulfuric acid in methanol was added to the oil and stirred continuously maintaining a steady temperature of 64 °C. Reaction continued for 2 h. Intermittently samples were collected at regular intervals (0.5 h) and acid values were determined. After the confirmation of completion of the reaction by measuring the acid value of the sample, which should be between 0.1 and 0.5, the heating was stopped and the products were cooled. The un-reacted methanol was separated by distillation. The remaining product was further used for transesterification to obtain methyl esters.

Transesterification: In a typical experiment a known amount of oil was charged to a four necked round bottom flask. Solution of known amount of catalyst sodium methoxide was prepared in methanol. The solution and the rest required amount of methanol was added to the oil sample. After proper closing of the flask it was put on heating mantle.

The system was maintained at a temperature just above the boiling point of alcohol, *i.e.*, around 70 °C to speed up the reaction. Recommended reaction time varies from 1-2 h. Excess alcohol was normally used to ensure total conversion of the oil to its esters. The formation of methyl ester was monitored by using thin layer chromatography technique. Coated silica gel glass plates were spotted with vegetable oil and the sample of ester. The spotted samples were developed in a solvent system in glass chamber using solvent ratio of 80:20 of hexane and ether by volume. This confirms the formation of methyl esters. This procedure was followed for all the samples collected at regular interval 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. The product separated by gravity into two layers namely ester layer and glycerol layer. The ester layer contains mainly methyl ester and methanol and the glycerol layer contains mainly glycerol and methanol. The pH level of both the layers were measured and neutralized separately. For neutralization a known amount of sulfuric acid in methanol was added to both the layers separately to neutralize the sodium methoxide present in them.

A trace of methanol present in ester layer was recovered in a distillation column under controlled vacuum. Distilled methanol was weighed and stored in sample bottle. Similar procedure was adopted to recover traces of methanol in glycerol layer. The methyl ester obtained was washed and dried under vacuum to remove traces of moisture. A sample of esters was 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 to vary from 80-85 %.

RESULTS AND DISCUSSION

Various properties of edible and non-edible oils and their esters were determined experimentally according to the methods listed in Table-1. The values of different properties of edible and non-edible oils are given in Tables 2 and 3, respectively. As acid values of karanja and jatropha oils are more than 3, hence esterification followed by transesterification has been

Test property	AOCS method
Acid value (mg KOH/g)	Cd 3d-63
Saponification value (mg KOH/g)	Cd 3-25
Iodine value	Cd 1-25
Free glycerin (wt %)	Ca 14-56
Total glycerin (wt %)	Ca 14-56
Density (mg/L)	Cc 10a-25
Conversion (%)	–
Flash point (°C)	[ASTM] D92
Pour point (°C)	[ASTM] D97
Cloud point (°C)	[ASTM] D2500
Viscosity (c St) at 40 °C	[ASTM] D445
Heating value (MJ/kg)	IS:1350
Cetane index	[ASTM] D976
Ash content (wt %)	[ASTM] D5347-95

Properties	Jatropha oil	Karanja oil
Acid value (mg KOH/g)	5.31	5.91
Saponification value (mg KOH/g)	194.0	191.5
Kinetic viscosity at 38 °C mm ² /s	35.4	41.8
Pour point (°C)	-6	6
Flash point (°C)	186	232
Density (kg/L)	0.9188	0.9326
Carbon residue (wt %)	0.3	1.51
Ash (wt %)	0.7	0.014
Sulphur (wt %)	0.02	0.007
Fatty acid composition (wt %)		
14:0	0.5-1.4	–
16:0	12-17	1.3
18:0	5-9.70	0.5
18:1	37-63	60.9
18:2	19-41	31.2

done to prepare biodiesel from them. The properties of methyl esters of edible oils are given in Table-4 and they have been compared with the properties of diesel fuels. The measured values of properties of jatropha methyl ester and that of karanja methyl esters are given in Tables 5 and 6, respectively and they have been compared with the others work. The properties of vegetable oil methyl esters have been compared with the previous works in Tables 7-11. It is observed that the quality of biodiesel produced here are comparable with that of others and also with diesel fuel. It is also observed that the specific gravities of vegetable methyl esters are slightly higher than that of diesel fuel. As they are slightly heavier than diesel fuel hence their viscosities are also little higher than that of diesel fuel. The heating values of these methyl esters in range of

37-40 MJ/kg, are slightly lower as compared to diesel fuel (42.1 MJ/kg). The vegetable methyl esters are however, have higher cloud and pour points than that of conventional diesel fuel. The fuel properties of vegetable methyl esters were also within biodiesel specifications.

Conclusion

In the present study, it is observed that the quality of biodiesel produced here are comparable with that of others and also with diesel fuel. It is also observed that the specific gravities of vegetable methyl esters are slightly higher than that of diesel fuel. As they are slightly heavier than diesel fuel hence their viscosities are also little higher than that of diesel

Properties	Sunflower oil (refined)	Soybean oil (refined)	Palm oil (refined)	Mustard oil (refined)	Cotton seed oil (refined)
Acid Value (mgKOH/g)	0.04	0.1205	0.1054	0.261	0.111
Saponification value (mgKOH/g)	191.86	193.03	197.35	178.30	191.00
Iodine value	133.27	136.67	52.41	100.99	110.65
Phosphorous content (ppm)	13.50	NIL	NIL	NIL	NIL
Peroxide value (milli eq/kg)	0.50	0.45	1.01	0.89	0.55
Density (g/mL)	0.916	0.919	0.899	0.910	0.917

Properties	Sunflower oil methyl ester	Soybean oil methyl ester	Palm oil methyl ester	Mustard oil methyl ester	Cotton seed oil methyl ester	Diesel
Free fatty acid	0.0675	0.07	0.096	0.230	0.0113	–
Acid value (mg KOH/g)	0.135	0.1405	0.1921	0.461	0.227	–
Saponification value (mg KOH/g)	193.36	191.50	196.22	175.75	188.38	–
Iodine value	135.66	134.90	54.55	101.3	108.4	–
Free glycerin (wt %)	0.011	0.015	0.014	0.009	0.012	–
Total glycerin (wt %)	0.0381	0.0575	0.064	0.0292	0.0612	–
Conversion (%)	98.0	97.1	97.52	98.65	97.35	–
Flash point (°C)	183	180	164	170	162	74
Pour point (°C)	-4	-6	8	-9	-8	-16
Cloud point (°C)	1	0	13	-2	-1	-12
Density (mg/L)	0.860	0.880	0.875	0.850	0.857	0.85
Viscosity (c St) at 40 °C	4.22	4.0	4.42	4.71	4.32	2.98
Heating value (MJ/kg)	36.5	37.1	37.0	39.62	38.72	42.9
Cetane index	44.0	44.5	61.84	54.56	50.88	49.2
Ash content (wt %)	0.005	0.008	0.012	0.01	0.004	0.02

TABLE-5
COMPARISON OF PROPERTIES OF
JATROPHA METHYL ESTERS

Test property	Jatropha methyl ester	Foid <i>et al.</i> ¹⁶
Free fatty acid	0.22	0.24
Acid value (mg KOH/g)	190.0	–
Saponification value (mg KOH/g)	104.0	–
Iodine Value	0.01	0.015
Free glycerin (wt %)	0.0797	0.088
Total glycerin (wt %)	0.8815	0.879
Conversion (%)	98.4	–
Flash point (°C)	160	191
Pour point (°C)	-6	–
Cloud point (°C)	-3	–
Viscosity (c St) at 40 °C	4.2657	4.84
Heating value (MJ/kg)	38.7	–
Cetane index	51.6	51
Ash content (wt %)	0.005	–

TABLE-6
COMPARISON OF PROPERTIES OF
KARANJA METHYL ESTERS

Test property	Karanja methyl ester	Raheman <i>et al.</i> ¹⁷
Acid value (mg KOH/g)	0.42	–
Saponification value (mg KOH/g)	187	–
Iodine value	91	–
Free glycerin (wt %)	0.015	–
Total glycerin (wt %)	0.0797	–
Density (mg/L)	0.876	0.876
Conversion (%)	97.8	–
Flash point (°C)	183	187
Pour point (°C)	4	–
Cloud point (°C)	7	–
Viscosity (c St) at 40 °C	4.657	9.6
Heating value (MJ/kg)	37.12	36.12
Cetane index	55.0	–
Ash content (wt %)	0.005	–

TABLE-7
COMPARISON OF PROPERTIES OF
SUNFLOWER METHYL ESTERS

Test property	Sunflower methyl ester	Antolin <i>et al.</i> ¹⁸	Fukuda <i>et al.</i> ¹⁹
Free fatty acid	0.00675	0.015	–
Acid value (mg KOH/g)	0.135	0.3	–
Saponification value (mg KOH/g)	193.36	–	–
Iodine value	135.66	–	–
Free glycerin (wt %)	0.011	–	–
Total glycerin (wt %)	0.0381	–	–
Conversion (%)	98.0	–	–
Flash point (°C)	180	–	183
Pour point (°C)	-4	–	–
Cloud point (°C)	1.0	1.0	1.0
Density (mg/L)	0.860	0.886	–
Viscosity (c St) at 40 °C	4.22	–	4.6
Heating value (MJ/kg)	37.5	40.0	33.5
Cetane index	44.0	46.9	49
Ash content (wt %)	0.005	0.004	–

fuel. The heating values of these methyl esters are slightly lower as compared to diesel fuel. The vegetable methyl esters are however, have higher cloud and pour points than that of

TABLE-8
COMPARISON OF PROPERTIES OF
SOYBEAN METHYL ESTERS

Test property	Soybean methyl ester	Clark <i>et al.</i> ²⁰	Fukuda <i>et al.</i> ¹⁹
Free fatty acid	0.007	–	–
Acid value (mg KOH/g)	0.1405	–	–
Saponification value (mg KOH/g)	191.5	–	–
Iodine value	134.9	–	–
Free glycerin (wt %)	0.015	–	–
Total glycerin (wt %)	0.0575	–	–
Conversion (%)	97.1	–	–
Flash point (°C)	180	141	178
Pour point (°C)	-6	-1	–
Cloud point (°C)	0	2	1
Density (mg/L)	0.88	0.884	0.885
Viscosity (c St) at 40 °C	4.0	4.08	4.5
Heating value (MJ/kg)	37.1	39.8	33.5
Cetane index	44.5	46.2	45.0
Ash content (wt %)	0.008	0.01	–

TABLE-9
COMPARISON OF PROPERTIES OF PALM METHYL ESTERS

Test property	Palm methyl ester	Mohamad <i>et al.</i> ²¹	Fukuda <i>et al.</i> ¹⁹
Free fatty acid	0.096	–	–
Acid value (mg KOH/g)	0.1921	–	–
Saponification value (mg KOH/g)	196.22	–	–
Iodine value	54.55	–	–
Free glycerin (wt %)	0.014	–	–
Total glycerin (wt %)	0.064	–	–
Conversion (%)	97.52	–	–
Flash Point (°C)	164	109	160
Pour point (°C)	8	0	–
Cloud point (°C)	13	0	13
Density (mg/L)	0.875	0.8737	0.879
Viscosity (c St) at 40 °C	4.42	14.94	5.7
Heating value (MJ/kg)	37.0	39.3	–
Cetane index	61.84	–	62
Ash content (wt %)	0.012	–	–

TABLE-10
COMPARISON OF PROPERTIES OF
MUSTARD METHYL ESTERS

Test property	Mustard oil methyl ester	Srivastava <i>et al.</i> ²²
Free fatty acid	0.23	0.24
Acid value (mg KOH/g)	0.461	0.456
Saponification value (mg KOH/g)	175.75	193
Iodine value	101.3	90
Free glycerin (wt %)	0.009	–
Total glycerin (wt %)	0.0292	–
Conversion (%)	98.65	–
Flash point (°C)	170	107
Pour point (°C)	-9	-6
Cloud point (°C)	-2	–
Density (mg/L)	0.85	0.85
Viscosity (c St) at 40 °C	4.71	5.7
Heating value (MJ/kg)	39.62	39.82
Cetane index	54.56	47
Ash content (wt %)	0.01	–

conventional diesel fuel. The fuel properties of vegetable methyl esters were also within biodiesel specifications.

This study suggests that the vegetable oils can be used as a source of triglycerides in manufacture of biodiesel by esterification and/or transesterification. The biodiesel from refined vegetable oils meets the Indian requirements of high speed diesel oil. But 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.

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