

Methanolysis of jatropha curcas oil by each sodium hydroxide and calcium oxide as a catalyst

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ABSTRACT

Jatropha curcas is a new crop in Egypt and grows well under low fertility and moisture conditions, the purpose of this search study the characterization of Egyptian *Jatropha* oil to be used as feedstock for bio diesel production by Sodium hydroxide and Calcium oxide catalysts, sodium hydroxide catalyst is the most common catalyst in bio diesel production but it need waste water treatment after removing the dissolved catalyst however solid catalyst dissolved this problem due to easy separation of the catalyst from FAME chemical constituents of oil were determined by GC showed that oil contain Palmitic acid (15 %), Stearic acid (6.6), Oleic acid (42.7) and Linoleic acid (35.2), Also the optimum conditions for methanolysis *Jatropha curcas* oil by sodium hydroxide catalyst were a methanol: oil molar ratio of 6:1, a catalyst concentration of 1.0% w/w of oil, a reaction temperature of 60°C and a reaction time of 40 minutes. But calcium oxide catalyst showed good catalytic activity at 120 °C with 5 wt % catalyst and reaction time 2 hr methanol: oil was 12:1.

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KEYWORDS

Jatropha curcas;
Bio diesel;
Methanolysis;
Fatty acid composition.

INTRODUCTION

Currently, fossil fuels are the main resources of energy meeting the world requirements. The fossil-based resources, such as gasoline, petro-diesel and natural gas are limited and insufficient for the future world's energy demands. In this connection there is much concern for search of renewable fuels^[1]. The idea of using vegetable oil for fuel has been started by Rudolph Diesel, the inventor of the engine that bears his name, when tested peanut oil as fuel for his engine for the first time on August 10, 1893^[2]. In the early 20th century, however, diesel engines were adapted to burn petroleum distillate, which was cheap and plentiful. In the late 20th century, however, the cost of petroleum distillate rose, and by the late 1970 s there

was renewed interest in bio-diesel. The major disadvantage of using petroleum based fuels is atmospheric pollution created by the use of petroleum diesel. Petroleum diesel combustion is a major source of greenhouse gas (GHG). Apart from these emissions, petroleum diesel is also major source of other air contaminants including NO_x, SO_x, CO, particulate matter and volatile organic compounds^[3]. Bio- diesel is an alternative fuel for diesel engines. Its primary advantages are that it is one of the most renewable fuels currently available and it is also non-toxic and biodegradable. It can also be used directly in most diesel engines without requiring extensive engine modifications^[4]. Bio-diesel derived from surplus edible oils like soybean, sunflower and rapeseed oils is already being used in USA and Europe to reduce air pollution, to reduce

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dependence on depleting fossil fuel localized in specific regions of the world and increases in crude oil prices^[5]. The global food system faces a crisis of unprecedented scope. This crisis, which threatens to imperil the lives of hundreds of million, and possibly billions of human beings and this, is an indirect consequence of high oil prices-which lead to the increased demand for bio fuel, which is resulting in farmland being turned from food production to fuel production, making food more costly^[6]. So it must be search about source of oil not Affect or displacement of food to produce bio-diesel, as such, the key to the future of bio-diesel is finding inexpensive feed stocks that can be grown by farmers on marginal agricultural land, and *Jatropha* is one of many plants that hold a great deal of promise. *Jatropha* proves to be a promising bio-fuel plantation, and could emerge as a major alternative to diesel, reducing world dependence on oil imports and saving foreign exchange, aside from providing much-needed energy security^[6]. The use of vegetable oil is restricted to diesel engines, since they contain free fatty acids (FFAs), phospholipids, sterols, water, odorants, and other impurities. In addition, vegetable oil's high viscosity, about^[11-14] times higher than diesel fuel,^[7] affects the flow properties of the fuel, such as spray atomization, consequent vaporization, and air-fuel mixing in the combustion chamber, leading to an adverse effect on the combustion process^[8]. To overcome these drawbacks, the oil has to be chemical modified. One way is by Trans esterification, which is the most common process used to reduce the high viscosity of triglyceride^[7] reaction can be represented by Triglyceride + 3 ROH → 3 R₂CO₂R + Glycerol, Trans esterification is a very slow reaction which can be accelerated by the presence of a catalyst, such as a strong acid or base, Base catalysis is much faster and has lower corrosion than acid catalysis and so, is most used commercially^[9]. Suitable alcohols used in this reaction include methanol, ethanol, propanol and butanol. The most common is methanol, due to its low cost and its physical and chemical advantages.^[4,7] alkaline catalysts used for Tran's esterification include sodium and potassium hydroxides, carbonates, and alkoxides^[10]. The usual alkalis are sodium and potassium hydroxides.^[4,7,10] But alkali sodium and potassium hydroxide have some dis-

advantage like a massive amount of the waste water, which is due to the purification to wash the homogeneous catalyst off the crude bio diesel with water. And besides, emulsification of bio- diesel occurs during the purifying operation, which causes not only obstruction of the process operation but also loss of bio-diesel, however solid catalyst dissolved this problem due to easy separation of the catalyst from FAME and to the reusable properties of the catalyst^[11,12].

EXPERIMENTAL

Material

Jatropha seed was obtained from the Ministry of Agriculture, Egypt. *Jatropha* oil used in this study was obtained from solvent extraction from its seeds. Commercial hexane is used as a solvent, calcium oxide was obtained from a local cement factory, but sodium hydroxide and methyl alcohol from al Gomhorya Company, The methyl esters, such as methyl hepta decanoate, methyl esters of palmitic, palmitoleic, stearic, oleic, and linoleic acids, were of GC reference standards.

Extraction of oil

The crushed seeds (500 g) of each batch of *Jatropha* were extracted using a Soxhlet extractor on a water bath for 8 h with 0.8 L of n-hexane. After oil extraction, the excess solvent was distilled off reduced vacuum using a rotary evaporator.

Equipment

The reactions were carried out in a 250 mL necked flat-bottom flask equipped with a reflux condenser (to reduce the loss of methanol by evaporation), thermometer. The reaction mixture was heated and stirred by a hot plate with a magnetic stirrer.

Experimental conditions

Methanolysis of *Jatropha curcas* oil was carried out by using sodium hydroxide and calcium oxide catalyst at atmospheric pressure. The reaction mixture was well-stirred at a constant stirring speed of 600 rpm The experiments were planned to comparison the optimum conditions and to study the effects of the variables on the reactions, such as methanol-to-oil molar ratio reac-

tion temperature, and reaction time for use each catalyst In the case of use sodium hydroxide catalyst, the reaction was conducted at different methanol-to-oil molar ratios (4:1, 6:1, 8:1, and 10:1), reaction temperatures (room temperature, and 60 °C), and reaction times (5, 10, 20, 30, and 40 minutes).in case of use of calcium oxide catalyst the reaction was conducted at different reaction temperatures (80, 100, and 120°C)^[13,14], and reaction times (40 and 120 minutes), the calcium oxide is heated at 700 °C for activation.

RESULTS AND DISCUSSION

Characterization of crude *Jatropha curcas* oil

Characteristics, determined by standard methods, of the fatty acid composition, density, viscosity, FFA, Saponification value and Iodine value in the oil are shown in TABLE 1:

Sodium hydroxide methanolysis

Effects of methanol-to-oil molar ratio and reaction time

The reaction was carried out by varying the methanol-to-oil molar ratio and the reaction time using a catalyst concentration of 1% w/w of oil and a reaction temperature of 60°C. The methyl ester content increased as the methanol-to-oil molar ratio increased. The methyl ester content for a methanol-to-oil molar ratio of 6:1 was 93.1% w/w after 20 minutes, whereas the same content was obtained with a methanol-to-oil molar ratio of 8:1 and 10:1 after 10 and 5 minutes, respectively, The methyl ester content of 98.6% w/w at methanol-to-oil molar ratio of 6:1 was attained in 40 minutes, Although the methanol-to-oil molar ratios of 8:1 and 10:1 provided the higher methyl ester contents in less

TABLE 1 : Properties of crude *jatropha curcas* oil.

ITEM	VALUE
Acid value	38.5
Saponification value	195.6
Iodine value	102
Viscosity (31°C) "Fatty acid"	40.6
Palmitic acid %	15,5
Stearic acid %	6.6
Oleic acid %	42.7
Linoleic acid %	35.2

time, these two ratios should be avoided for economic reasons; thus, a methanol-to-oil molar ratio of 6:1 was selected as being the optimum.

Effects of reaction temperature and reaction time

The operating conditions were fixed at a methanol: oil molar ratio of 6:1 and a catalyst concentration of 1% w/w of oil. The results indicate that methanolysis could occur at room temperature after 8 hr but the time reduced to 40 minutes at 60 °C.

Calcium oxide methanolysis

The operating conditions were fixed at a methanol: oil molar ratio of 12:1 and a catalyst concentration of 5% w/w of oil The methyl ester content was 75% at 40 minutes and 120 °C, 50% at 100 °C and 30% at 80 °C, The methyl ester content was 98% at 120 minutes and 120 °C, 95% at 100 °C, 92% at 80 °C.^[14]

Properties of *Jatropha curcas* bio-diesel

The quality of bio diesel is very important for the performance and emission characteristics of a diesel engine. Thus, the *Jatropha curcas* bio-diesel produced at the optimum conditions was sent to the Quality Control laboratory of the Suez Petroleum Company for quality testing using standard methods. The results are

TABLE 2 : Properties of *jatropha curcas* bio-diesel

Specification	Standard specification of <i>Jatropha</i> bio-diesel	Standard specification of bio diesel (ASTM D 6751)
Flash point	<130	Minimum 130 °C
Carbon residue	0.06	0.050 maximum wt%
Kinematics Viscosity	4,8	1.9 – 6.0 mm ² /s
Ash content (%)	0.016	0.02 max
Water content (%)	0.025	<0.03
Pour point	2	-
Acid value (mg KOH g-1)	0.40	<0.80

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shown in TABLE 2.

CONCLUSION

Bio-diesel can be produced successfully from crude *Jatropha curcas* oil by sodium hydroxide, calcium oxide methanolysis. The optimum conditions for sodium hydroxide were a methanol-to-oil molar ratio of 6:1, a catalyst concentration of 1% w/w of oil, and a reaction temperature and reaction time of 60°C and 40 minutes, respectively. Produced under these conditions, the methyl ester content of the *Jatropha curcas* bio-diesel achieved 98.6%; the optimum conditions for calcium oxide catalyst were a methanol-to-oil molar ratio of 12:1, a catalyst concentration of 5% w/w of oil, and a reaction temperature and reaction time of 120°C and 120 minutes, respectively. Produced under these conditions, the methyl ester content of the *Jatropha curcas* bio-diesel achieved 98%.

Although a massive water used for washing bio diesel produced by sodium hydroxide catalyst is a big problem for these technical but also calcium oxide need amount of energy more than sodium hydroxide methanolysis.

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