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Sustainable agriculture products *Jatropha* plant oil an alternative biodiesel fuels

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Abstract

As we are familiar with the increasing demand of energy fuel for commercial and domestic purposes', a great challenge has been faced by all countries on earth. Since the sources for fossil fuels like petroleum are limited and increasing refining Expenditures has raised the fuel cost. According to oils market price is highly increasing compared with the last decade, one of the major influences is the highly demand in energy consumption from all over the economic countries, India has imported huge amount of oil each, mainly for industries and transportation sectors. This causes the selling price of diesel has been increasing vertically. This problem effected directly and suddenly to all sectors who depend on the fuel. In order to remove this crisis, the government tried to promote the development of bio diesel which has the same function as diesel but cheaper. Western countries form many kind of bio diesel from Soya bean oil, Sun flower oil, and other edible oil. But India unable to use the edible oil for making bio diesel for this purpose.

Our paper presents *Jatropha* oil as biodiesel fuel. *Jatropha curcas* Linn. Is a native tropical plant of Asia it is often found near rice field. It is expected as high potential of oil plant in India. Several workers are known to obtain biodiesel by using NaOH or KOH as a catalyst with methanol but less attention or no attention has been paid for the manufacturing of bio diesel from *Jatropha* oil using methanol and solid catalyst. The main advantages of solid catalyst are the recovery of catalyst, improving the characteristic of biodiesel. Decreasing the capital cost of biodiesel formation, increasing the rate of formation etc.

Keywords: *Jatropha curcas* oil, trans esterification, methanol, biodiesel, solid catalyst, India

Introduction

Homogeneous acid catalysts are very toxin on equipment and at elevated temperatures. Severely affect any metallic components. Although acid catalyzed reaction are slower than basic ones, they potential if they can be immobilized. Problems with homogenous catalyst are well known.

Heterogeneous catalysts are the key to new developments in the production of biodiesel, combined with their application in a continuous process and easy separation they will substantially decrease the cost of production.

The concept of bio fuels dates back to 1885 when Dr. Rudolf Diesel built the first diesel engine with the fuel intention of running it on vegetative source. In 1912, he observed, "The use of vegetable oil for engine fuels may seem insignificant today, but such oils may in the course of time become as important as petroleum and the coal tar products of present time".

In 1970, scientists discovered that the viscosity of vegetable oils could be reduced by a simple chemical process and that it could as diesel fuel in modern engine. Since then the technical developments have come a long way and the plant oil to days has been highly established as bio fuel, equivalent to diesel.

Efficient heterogeneous catalyst offer economic benefits in producing bio fuels since unlike Homogenous catalyst, they are easily separated after Trans esterification and so can be readily recycled lowering production cost.

Bio diesel is methyl or ethyl ester of fatty acids made from virgin or used vegetable oil (both edible and non-edible oil) and animal's fat. The main commodity sources for bio diesel in India can be non-edible oil obtained from plant species such as *Jatropha curcas* (Ratanjyot). Biodiesel contain no petroleum but it can be blended at any level with petroleum diesel to create a bio diesel blend or can be used in its pure form.

Just like petroleum diesel, Biodiesel operates in compression ignition (diesel) engine which essentially require very little or no engine modification because bio diesel has properties similar to petroleum diesel fuel. It can be stored just like the petroleum diesel fuel and hence does not require separate infrastructure. The use of Biodiesel in conventional diesel engine result in substantial reduction of unburned hydrocarbon, carbon monoxide and particulate matters. Biodiesel is considered clean fuel since it has almost no sulphur, no aromatic and has about 10% built in oxygen, which helps it to burn fully. Its higher cetane no. improves the ignition quality over when blended in the petroleum diesel. Biodiesel has been accepted as clean alternative fuel by us and its production presently is about 100 million gallons. Each state has passed specific bills to promote the use of bio diesel by reduction of takes.

Sunflower, Rap seed etc. is the raw material used in Europe whereas soya bean is used in USA. Thailand uses palm oil, Ireland uses frying oil and animal fats. Due to its favorable properties bio diesel can be used as fuel for diesel engines [as either B-5 a blend of 5% bio diesel in petroleum diesel fuel B20 or B100].

USA uses B-20 & B-100 Biodiesel. France uses B-5 as mandatory in all diesel fuel. It can also be used as an additive to reduce the overall sulphur content of blend and to compensate for lubricity loss due to sulphur removal from diesel fuel. The viscosity of biodiesel is higher (1.9 to 6.0 cost) and is reported to result into gum formation on injectors' cylinder liner etc. If used neat form. However blend of up to 20% should not give any problem, while any engine can be designed for 100% biodiesel use. The existing engine can use 20% biodiesel blend without any modification and reduction in torque output. In USA 20% biodiesel blend is being used, while in European countries 5-15% blends have been adopted.

Biodiesel as an option for energy security

India ranks sixth in the world in terms of energy demand accounting for 3.5% of world commercial energy demand in 2001. The energy demand is expected to grow at 4.8%. A large part of India's population, mostly in the rural areas, does not have access to it. At 479 Kg. of oil equivalent the per capita, energy consumption is very low. Hence a program for the development of energy from raw material which grows in the rural area will go a long way in providing energy security to the rural people. It has large arable land as well as good climate condition (tropical) with adequate rain fall in large part of the area to account for large biomass production each year. For the reason of edible oil demand being higher than its domestic production. There is no possibility of diverting this oil for production of biodiesel. Fortunately there a large junk of degraded forest land and unutilized public land, field boundaries and follow lands of farmers where no edible oil seeds can be grown. There are many tree species which bear seeds rich in oil, of these some promising tree species have been evaluated and it has been found that there are a no. of them such as *Jatropha curcas* has been found most suitable for the purpose. It will use lands which are largely unproductive for the time being and are located in poverty stricken areas and in degraded forests. *Jatropha curcas* has been found the most suitable tree species.

Economics of *Jatropha* Bio-diesel

In India, it is estimated that cost of bio-diesel produced by Trans esterification of oil obtained from *Jatropha curcas* oil seeds shall be approximately same as that of petro diesel. The cost of biodiesel various between Rs. 16.59-14.98 per lit. Assumptions are that the seed contain 35% oil, oil extraction will be 91-92%, and 1.05 Kg. of oil will be required to produce 1 Kg. of bio-diesel. Recovery from the sale of glycerol will be at the rate of 40-60 per Kg. The price of glycerol is likely to be depressed with processing of such large quantities of oil and consequent production of glycerol raising the cost of bio-diesel. However new application are likely to be found creating additional demand and stabling its price with volatility the price of crude, the use of Bio-diesel is economically feasible and a strategic option.

Literature Survey

The current method [1] of producing biodiesel is the base catalyzed transesterification of *Jatropha curcas* oil is given in equation.

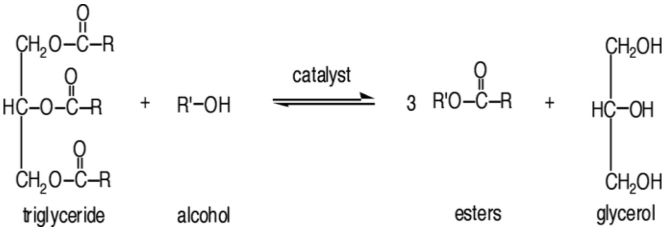

Fig 1: Transesterification of vegetable oil

Here an alcohol, usually methanol or ethanol is added to a triglyceride using a base catalyst such as NaOH, KOH, $NaOCH_3$ or $KOCH_3$ [2].

The process is fast and efficient at relative low temperatures. For example using NaOH and methanol at 50 ^{0}C a > 95% conversion may be obtained in approximately 1 hr [3].

However, cost competitive production of bio-diesel remains an important issued Biodiesel production cost may be reduced by choice of feedstock, production plant location and increased process efficiently.

The present work focused on the testing of non-food based oils like *Jatropha* as alternate feedstock for biodiesel production [5-8].

Another area where process efficiencies may be realized is in the use of heterogeneous rather than homogenous catalysts [9-11].

One way to increase process efficiency is to use heterogeneous catalyst. In principle the catalyst may be recovered and re-used leading to simpler bio-diesel processing.

A no. of recent studies [10-15] highlights the current interest in heterogeneous catalysis of the Trans esterification reaction. Here we report the exploration of alkaline earth metal oxide as heterogeneous base catalyst with *Jatropha curcas* oil for biodiesel production.

Materials Used

Simple of 100% pure *Jatropha* oil collected from Bio tech park, upgrade MgO was taken from Merck, CaO was purchased from qualigens chemicals 99.9% SrO & BaO were purchased from Aldrich. Methanol was purchased from Qualigens.

Experimental set up and process

Jatropha oil samples were analyzed for their fatty acid content on a Clarus 500 GC/MS

(Perkin Elmer, Waltham, MA) by first converting the triglycerides into their respective fatty acid methyl esters (FAME's). For this analysis 200 mL of oil were added to 5 mL of previously prepared 1% NaOCH3 in MeOH (m/v) in a 150 mm x 13 mm screw top vial.

The closed vial was heated for 5 minutes in a 50 °C water bath. The resulting FAME's were extracted into hexane, washed with saturated NaCl water to remove the glycerol byproduct, and dried by passing through a column of MgSO4. Then 1 mL of sample was injected onto an AT-Silar 0.25 mm capillary column (Alltech, Deerfield, IL) using a Tprogrammed run [16]. Fatty acid content was verified using pure components, standard mixes from Alltech, or a 117,000 component NIST spectral library. The pre- and post-sample acidity was determined via titration. First, 250 mg of the feedstock oil or FAME was dissolved in 50 mL of 50:50 ethyl ether: ethanol with 3 drops of phenolphthalein indicator. Then 0.1 M standardized KOH in ethanol was added until the endpoint was reached [17]. SrO catalysts supported on $Al2O3$ or $SiO2$ were made from 3 M $Sr (NO3)2$ solutions and the desired support material according to standard procedures [15]. Briefly the required amount of solution to give the final % loading was determined and stirred with the solid support material with heating at ~ 250 °C until dryness. Then the sample was calcined in air at 800 °C in a tube furnace for 6 hours to decompose the nitrate salt to the oxide. The resulting catalyst was crushed with a mortar and pestle to ~100 µm. Decomposition to SrO was verified using a XE800 powder X-ray diffractometer (Philips Analytical, The Netherlands). Biodiesel synthesis was tested using the base catalyzed scheme shown in Figure 1. Each reaction mixture consisted of 7.5 mL of methanol and 30 mL of oil added to a 125 mL round bottom flask. This corresponded to a 6:1 mol ratio of alcohol: oil which is an actual mol excess of 2:1 since the reaction requires 3 mol of alcohol for every 1 mol of oil. The amount of base catalyst was varied between 0.1 to 1.0 mol %. The reaction flask with vegetable oil was placed in a water bath over a magnetic stirrer whose speed was kept constant at ~1200 rpm. The bath temperature was set at 20, 35, or 50 °C. After approximately 15 minutes thermal equilibrium was reached and the freshly made alcohol plus catalyst mixture was added. Reaction progress was followed using the NMR method of Knothe [3]. Approximately 1 mL of the reaction mixture was sampled at regular intervals, washed with 1 mL of water, and centrifuged. The top layer was transferred to an NMR tube, tetramethylsilane was added as an internal standard, and the NMR spectrum was obtained using a 60 MHz EM360 spectrometer (Varian, Palo Alto, CA) with a digital upgrade (Anasazi, Indianapolis, IN).

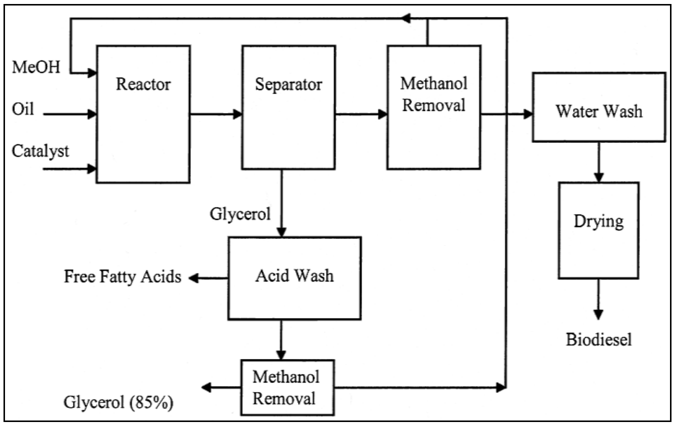

Fig 2: Production of Biodiesel

Results and Discussion

Above figure shows the results of testing the group 2 basic metal oxides as transesterification catalysts for biodiesel formation. MgO and CaO show very little conversion at 1 mol % catalyst and 50 °C Cover a 3 hour time frame. Others have reported significantly higher conversions with CaO catalysts [9, 18, 19]. This difference is due to preparation conditions that affect the surface area and surface states [19]. SrO and BaO show essentially complete conversion in approximately 1 hour under the same reaction conditions. Results for a conventional NaOH catalyst are shown for comparison. Since barium compounds generally have high toxicities BaO was dropped from further studies and additional work focused on SrO. Figure 3 shows a concentration of 0.5 mol % SrO was nearly as effective as 1.0% at 50 °C. If the time is extended to three hours, then 0.2 mol % SrO also quantitatively converted *Jatropha* oil to FAME's. However, 0.1 mol % SrO is limited to approximately 50% conversion. This is likely due to known catalyst "poisoning" effects such as losses from saponification side reactions [20] adsorption of free fatty acids [18] or the formation of carbonates via dissolved $CO2$ from the atmosphere [13]. As expected, decreasing the reaction temperature from 50 to 20 °C led to decreased rates of reaction. Figure 4 shows an Arrhenius plot for SrO and NaOH catalysts over this T range. Both gave good straight line fits and nearly identical activation energies of 19.6 kJ/mol for SrO and 21.4 kJ/mol for NaOH. This is in good agreement with the value of 20 kJ/mol reported by Dossin *et al*. for the mechanism of methoxy formation via methanol adsorption on MgO [18] Additional experiments with SrO catalyst at 1 mol % and 50 °C indicated the catalyst could be generally used with other oils including corn and soybean. Also substituting methanol with ethanol led to high conversions to FAME but at a slower rate. With 1-propanol conversion was negligible even after 3 hours. *Jatropha* oil. Figure 6 shows the results of the transesterification of this sample using SrO catalyst at 1 mol % and methanol. The conversion went essentially to completion but in this case a 1-2 hr induction period was observed. A number of studies have reported mixing to be an important factor in achieving good FAME yields [18, 19, 21, 23]. The stirring rate used in this study was 1200 rpm or two times higher than the 600 rpm rate shown to be the lowest acceptable for maximum yields [21]. Since *Jatropha* Oil is known to have a higher free fatty acid (FFA) content compared to virgin oil, titrations were performed on raw and Trans esterified *Jatropha* Oil. The acidity dropped from 4.01 mg KOH/mg oil to 0.35 mg KOH/mg oil, respectively. Previous work has shown basic catalysts are not effective at transesterifying FFAs where the base catalyst can be neutralized leading to a loss of catalyst as noted above [23, 24]. In Figure 5 the amount of SrO present in the reaction mixture was 0.0022 mol. The amount of acid neutralized calculated from the difference in the KOH titration results corresponded to 0.0019 mol. Thus, it appears the

$$\mathrm{SrO + 2\ RCOOH \longrightarrow RCOO{-}Sr{-}OOCR + H2O\ \ E{-}1}$$

Induction period is due to a competition between FAME formation and catalyst neutralization. A test of a *Jatropha* oil sample spiked to 44.7 mg KOH/g oil under the same reaction conditions showed only a 3% conversion to FAME after 63 hours. Recovery of catalyst from the reaction mixture was an important operational parameter. In this study recovery was plagued by loss of catalyst due to secondary reactions as noted above and poor FAME conversion efficiencies for recovered catalysts. For example, recovered SrO under the same reaction conditions in Figure 4 gave a FAME conversion of 38% after 3 hours. To help determine where the Sr was going a flame test was performed on three product components; excess methanol recovered by rotary evaporation, the FAME layer, and the crude glycerol layer. The detection limit of Sr was determined to be approximately 150 ppm by dilution of a stock solution of Sr (NO3)2. Both the recovered MeOH and the glycerol layer tested negative for Sr, while the FAME layer tested positive. This behavior is in contrast to that reported for NaOH catalyst where most of the catalyst ends up in the glycerol layer [22]. Further, the conductivity of each layer was determined to be 0.0 micro Siemens using a Orion 150A + conductivity meter which has a detection limit of approximately 40 ppb NaCl. This is consistent with the loss of SrO according to equation 1 and indicates ion exchange methods of biodiesel clean-up [9] may perform poorly if used with SrO catalysts. Finally, SrO was loaded onto SiO2 or Al2O3 inert support as noted in the experimental section. All of these catalysts gave low FAME conversions similar to MgO and CaO as noted in Figure 3. Work by Granados *et al*. (13) indicates even with heterogeneous FAME catalysts the process is dominated by a homogeneous mechanism. A number of authors have sited the importance of the solubility of the active species [9, 13, 18] even for heterogeneous catalysts for *Jatropha* oil Trans esterification. Our study confirms this view and extends it specifically to SrO. This suggests the alternative heterogeneous acid catalysts [11] for the transesterification of *Jatropha* oils may be a more fruitful approach for future pursuits.

Figures

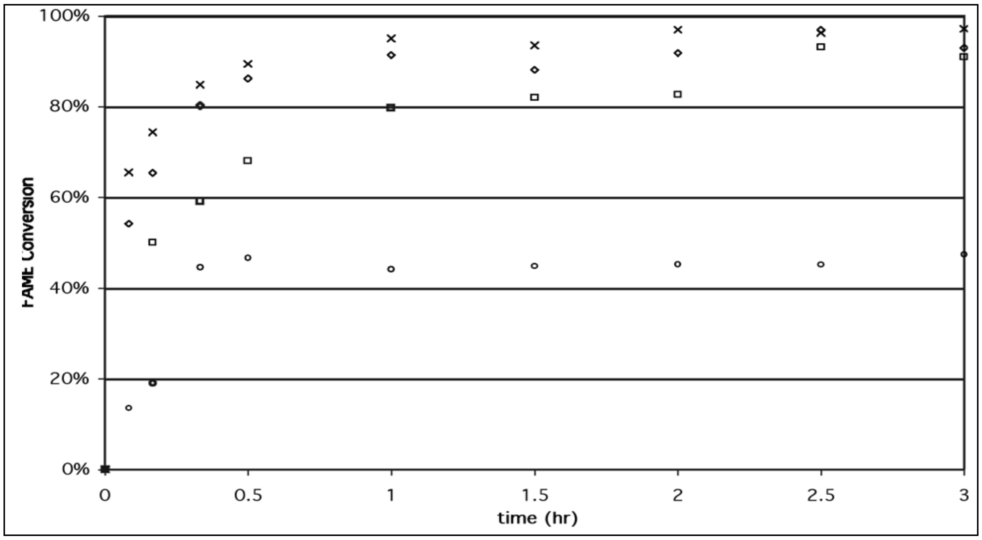

Fig 3: Mole % of SrO. Reaction conditions: 1200 rpm, 50 °C, 6:1 *Jatropha* oil: MeOH, SrO catalyst. X 1.0 mol %, ◊ 0.5 mol %, ❑ 0.2 mol %, O 0.1 mol %

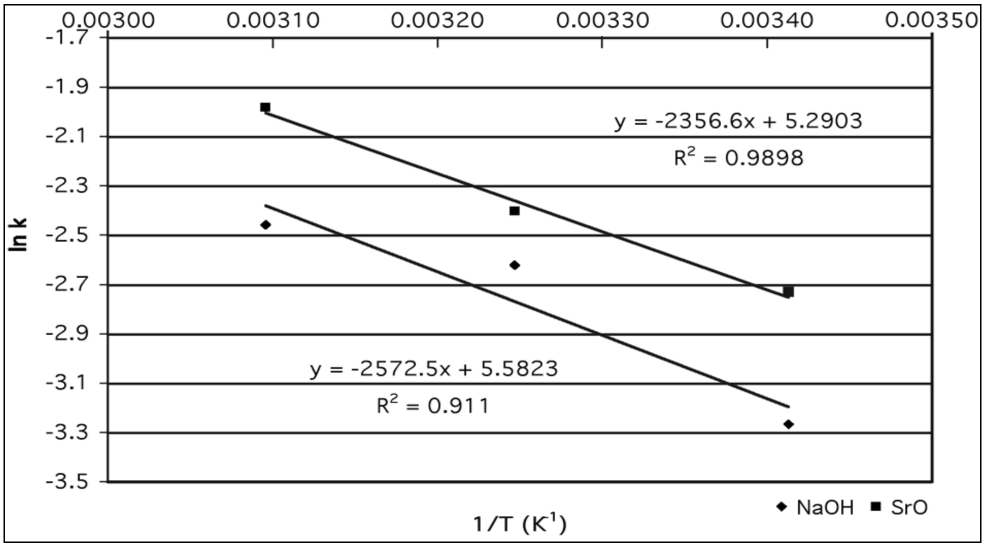

Fig 4: Arrhenius Plots for NaOH and SrO Base Catalysts. Reaction conditions: 1200 rpm, 6:1 *Jatropha* oil:MeOH, catalyst at 1 mol %. _ SrO, _ NaOH

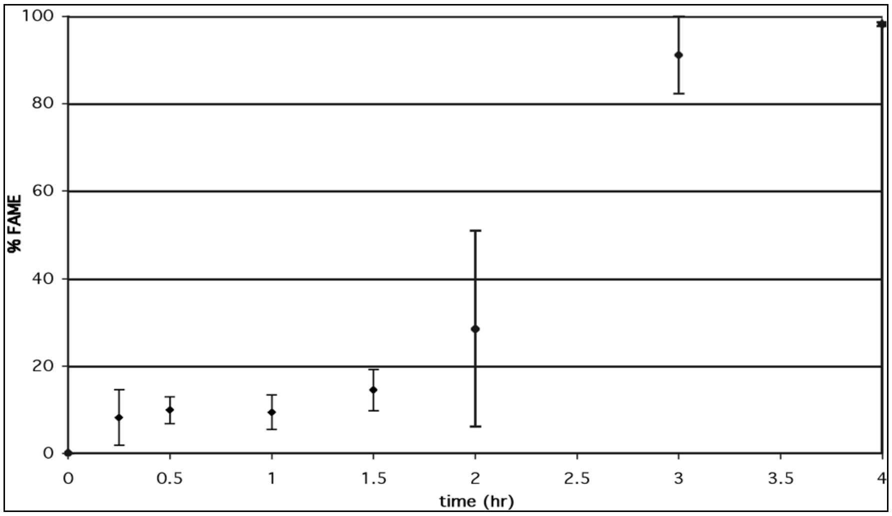

Fig 5: FAME Conversion Using SrO with *Jatropha* Oil. Reaction conditions: 1200 rpm, 50 °C, 6:1 *Jatropha* oil: MeOH, SrO 1.0 mol %. Each point is the average of three trials. Error bars are 1σ.

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