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An Easy Method for Biodiesel Production via Reactive-Extraction of Jatropha Curcus Oilseed

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Abstract

The alkyl ester of vegetable oil represents as an alternative fuel for diesel engines which is to used the easy method of biodiesel by increasing the efficiency of biodiesel production by single step reaction i.e. production of biodiesel by combing extraction of oil from seed and reaction of extract with alcohol. This process is called Reactive-extraction. It consists of the investigation of the optimum conditions (seed size, seed/solvent ratio, and catalyst concentration).

Keywords: Jatropha Seed, Methanol, Biodiesel, Reactive-Extraction, Homogeneous Base Catalyst.

Introduction

India is one of the largest petroleum consuming and importing countries. India imports about 72% of its petroleum demands. The current yearly consumption of diesel oil in India is approximately 40 million tones consuming of the total petro-product consumption. So, India is looking at alternative fuel sources to reduce its dependence on imported oil (*1*). Vegetable oils have been considered as alternative fuels for compression ignition engines. Vegetable oils are renewable, non-toxic, biodegradable fuel and have low emission profiles. However, there are some drawbacks related to the use of straight vegetable oils in diesel engines. Primarily due to their high viscosity, lower volatility and lower heat content (*2*). High viscosity of pure vegetable oils would reduce the fuel atomization and increase fuel spray penetration, which would be responsible for high engine deposits and thickening of lubricating oil (*3*).The use of chemically altered or transesterified vegetable oil called biodiesel which does not require modification in diesel engine.

Biodiesel', a renewable, low-emissions diesel fuel derived from fats and oils, consisting of the simple alkyl esters of free fatty acids (FFA) are presently making a global transition from a research and demonstration item to an accepted transportation fuel. Among the challenge to widespread adoption of biodiesel is economic no competitiveness, compared with Petroleum diesel fuel. The relative high price of biodiesel arises from the high costs of the refined edible oils that are predominant feed-stocks for fuel production (*4*). Biodiesel derived from vegetable oil and animal fats is being used in USA and Europe to reduce the air pollution, to reduce the dependence on fossil fuel. In USA and Europe, their surplus edible oils like soybean oil, sunflower oil and rapeseed oil are being used as feed stock for the production of biodiesel (*5-7*) to their compression on ignition engines. In other countries, the use of edible oils for engine fuel is not usual; however there are several non-edible oil seed species which could be utilized as a source for all production. The Indian biofuel programme became a reality when the Government of India issued a notification of Sept. 2002, making 5% ethanol blend in petrol mandatory. Also concrete plans are being formulated to utilize large tracts of degraded and waste land to grow non-edible tree borne oil seeds (TBO) plantation such as Jatropha and Pongamia (Karanja). It has been estimated that about 5-7.5 million tons of biodiesel can be produced from cultivating 5 million hectares of this land. In India more concentrated efforts on utilization of Jatropha curcus oil to biodiesel are being promoted due to the food vs. fuel debate globally. Jatropha curcus is a multipurpose species with many attributes and considerable potential. The oil from the seeds is potentially most valuable product, with properties like: low acidity, good oxidation stability as compared to soyabean oil, low viscosity as compare to castor oil and better cold properties as compared to palm oil. In addition

viscosity, free fatty acids contents, density of the oil and biodiesel are stable within the period of storage(*8*).

Biodiesel is usually prepared in the presence of homogenous base or acid catalysts. The acid catalyzed process often uses sulphonic acid and hydrochloric acid as catalyst; however, the reaction time is very long even at reflux of methanol, and a high molar ratio of methanol to oil is needed (*9*). Potassium hydroxide, sodium hydroxide and their carbonates, as well as potassium and sodium alkoxides are mainly used as base catalysts for transesterification reaction (*10*-*11*). Biodiesel fuels are currently synthesized using alkaline catalysts because the transesterification reaction is much slower with acid catalyst than alkaline catalyst.

The current industrial technology for the synthesis of fatty acid methyl esters of vegetable oils involves isolation of oilseed triglycerides by solvent extraction, degumming and refining of the oil, and its alkali catalyzed transesterification. Generally hexane is used as solvent for the extraction of oil (*12*). Ethanol, methanol and acetone have been recommended as solvents for extraction of vegetable oils. Solvent extraction at high temperatures and pressure above its critical point is known as supercritical fluid extraction (SCFE) with carbon dioxide as the extraction solvent has been tried as an alternative deacidification process for high FFA containing oils. But the extract oils contain high FFA, phospholipids and other complex substances; therefore they require a degumming step. Because of this, investigator is to use other solvents than hexane in oilseed extraction and also preserve oil qualities.

A modern and rapid increasing use of lower alkyl esters (methyl and ethyl esters) of vegetable oil is as biodiesel, a diesel fuel replacement and additive. Possibly the largest simple obstruction to wider acceptance of biodiesel is its cost. When produced from refined oil, feedstock cost contributes more than 70% to the cost of the ester product (*13*). Thus, there is interest in reducing feedstock cost in biodiesel production. Simplification of the oil production or esterification processes could lower the cost of this alluring bio fuel.

An integrated process combining the extraction of non-edible vegetable oils such as Jatropha from oilseeds with reaction of alkali MeOH of that oil to form biodiesel in one step is called "Reactive-extraction''. It is also called in-situ method of transesterification of oilseeds. Since India is deficient from edible oils, there is an opportunity for obtaining biodiesel from non-edible oilseed such as Jatropha. The advantages of successful development of such a process are a reduction in capital cost with less environment impact as well as easy method. To show striking difference, transesterification reagents might be able to near approach triglyceride directly, in-situ. Such a way to alkyl esters of vegetable oil could eliminate the outlay associated with solvent extraction and oil cleanup, and simplify the steps in biodiesel production. This could result in a decrease cost of the product (*14*).

The objective of this study is use of Jatropha oilseed for biodiesel production by the in situ method of transesterification reaction.

1. Materials and methods

(i) Reagents and Materials

Jatropha curcus seeds used in Reactive-extraction were procured from Uttarakhand region in India with characteristics reported in *Table 1*. Potassium hydroxide (85%) and methanol employed in the Reactive-extraction purchased from M.S. Merck chemicals. Carbon tetra chloride is used to in the present study from M/s Ranchem.

2. Method

(ii) Cutting of The Seeds

The Jatropha seeds were crushed in cutting mill from Retsh Model SM-100 with feed rate up to 10kg/hr using feed size of 1-3 mm and an output size of 0.25-20 mm is obtained. These crushed seeds were separated by sieves to give the three particle sizes of seeds (<1, >1-2, >2.). Each size of seeds was used in experiments.

Conventional Method for Biodiesel Production

Hexane has been chosen as the method of oil extraction from Jatropha seed oil. Care has to be taken to prevent any emission of hexane from the closed system because it is toxic. Oil extraction will be done in a batch-wise operation for the extraction process. Solvent is evaporated from the oil at reduced pressure. Solvent losses over the whole operation can be as high as 1% (*15*) and dangers associated with the large-scale use of the volatile and highly inflammable solvent have been reported (*16*).

After solvent removal, the oil is available for further processing. Transesterification of the extracted oils was carried out according to following example: The procedure of biodiesel from Jatropha oil involves the base catalyzed transesterification with methanol to give methyl esters. Glycerin is a byproduct in the transesterification reaction.

KOH is being dissolved into MeOH. When the catalyst fully dissolved into the MeOH the mixture was transferred to the glass reactor and agitated for 1-4 hours at 65 ^{o}C. After completion of the reaction, the reaction mixture was transferred into a rotarvapour flask to recover some unreacted MeOH and then transferred into a separating funnel for phase separation. The ester mixture formed the upper layer and the glycerol form in the lower layer. The traces of catalyst in ester layer were washed with hot water and the biodiesel dried over the anhydrous sodium sulphate or under vacuum.

Reactive Extraction of Jatropha Seeds for Biodiesel Production

Whole seeds or seed fractions were used in Reactive extraction as a starting material. The in-situ transesterification process was carried out in using three necked round bottom flask with condenser, Soxhlet, and thermometer pocket with thermometer. Each size of seeds was used in experiments by taking different seed/solvent ratio (w/w) (1:100, 1:300, 1:500), & KOH concentration (0.5, 1.0, 1.5 %). The solvent was taken in three necked round bottom flask. Catalyst was dissolved in the solvent at room temperature with mechanical stirring. Then seeds (X

gm) were poured and the reaction mixture was refluxed for one hour at 65^{o}C with mechanical stirring. After one hour the solid cake and mother liquor were separated by vacuum filtration. A rotary evaporator was used for separation of solvent. A brownish colored crude product was obtained. Transfer the hot water into the crude product and extracted with CCl_4. The solvent was removed off give the light yellow product which purified and analyzed by HPLC.

Cost Benefit of in Situ Transesterification Process For Biodiesel Production

Manufacturing costs and raw feedstock prices are the main economic criteria to take into account for biodiesel production to compete with diesel fuel. Manufacturing costs include direct costs for oil extraction, reagents, operating supplies, and manpower, as well as indirect costs related to insurance and storage (*17*). The aim of this article is to demonstrate the cost effective new source of energy by single step reaction effect of reaction parameters on in-situ transesterification is studied to obtain optimum yield of biodiesel. In in-situ transesterification seed is extracted with alcohol where alcohol acts as a solvent as well as reactant. This process reduces the cost of final product as this process has less number of unit operations than conventional process.

The processes of conventional and in-situ transesterification are summarized schematically in *Fig. 6.*

HPLC

To analyze the purity, conversion and FAME composition of the biodiesel esters sample the Reverse phase high performance liquid chromatography (RP-HPLC) which separates different component according to their polarity was used (*18*). The chromatographic apparatus consisted of a model waters 600 pump with waters 600 controller, waters 2996 photodiode array detector, a nova-pack®, 3.9 X 150 mm column with guard column of dimension 3.9 X 20 mm, both packed with C18 particle with diameter 4 µm. (all from waters, Milford MA, USA).

HPLC condition: RP-HPLC method with flow rate of 1ml/min, an injection volume of 5µl, a column temperature of 45^{o}C, the UV detection at 215 nm and a 40 min gradient mobile phase 15% H_2O + 85% CH_3OH in 0 min, 100% CH_3OH in 10 min, 60% CH_3OH + 15% hexane + 25% propane-2-ol in 30 min and for the last 10 min system back to initial state 15% H_2O + 85% CH_3OH were used for the separation and determination of the compound produced during the in-situ transesterification of Jatropha curcus seed oil in all the experiments. *Fig. 5.* Shows the HPLC separation of biodiesel (different fatty acid composition of Jatropha curcus oil are given in *Table 2*).

Result and Discussion

Transesterification occur in-situ in the Reactive-extraction. Transesterification process is a forward-backward reaction. Studies of physicochemical characteristics of the seeds are necessary for transesterification process because it gives an idea about what reaction conditions are necessary for forward reaction. The suitable parameter conditions for experiments, preliminary study of Jatropha seeds have been carried out. It showed that Jatropha has a good potential for biodiesel production. The percentage of biodiesel from Jatropha curcus seeds oil was found to be 98%.

3.1.1. Effect of seed size in Reactive-extraction.

Seed size has played a great role in reactive-extraction. The experiments have three different sizes of seeds (<1, >1-<2, >2mm). The results show in *Figs. 1-3* the smaller seed size (<1mm) does not gives satisfactory conversion which showed zero conversion at 0.5% catalyst concentration, 1: 100 seed/solvent (w/w) ratio and 91.02% conversion at 1.5% catalyst concentration, 1:500 seed/solvent (w/w) ratio shown in *Fig. 1* Medium seed size (>1-<2) gives the maximum conversion at 1.5% catalyst concentration, 1:500 seed/solvent (w/w) ratio shown in *Fig. 2***.** Being the smaller size effected more by moisture. It showed 8.02 % as minimum conversion at 0.5% catalyst concentration and 1:100 seed/ solvent (w/w) ratio. In the optimum study, results from >2 mm seed size was observed to be better in comparison to other two seed sizes. It gives 35% conversion at lowest reaction conditions. At 1:500 seed/ solvent (w/w) ratio, these seed size showed a comparable result at 1% and 1.5% catalyst concentration as 95.06% and 98.01% conversion respectively shown in *Fig. 3.*

Effect of Seed/ Solvent (W/W) Ratio

In the reactive extraction the different seed size of Jatropha curcas is extracted with methanol acts as a solvent as well as reactant. Therefore, a suitable amount of solvent should be able to extract the oil and shift the reaction in forward direction effectively. The investigation has three seed/ solvent (w/w) molar ratios (1:100, 1:300, and 1:500). *Figs. 1-3* indicate that FAME conversion was raised when the seed/solvent (w/w) molar ratio was increased for three different seed size. Therefore the optimum condition for reactive extraction to produce FAME has a 2 mm seed size, 1:500 seed/solvent (w/w) molar ratios with 1.5% catalyst concentration. If increased the seed/ solvent (w/w) molar ratio 1:100 to1:500 the conversion of biodiesel is consequently increased.

3.1.3. Effect of Catalyst Concentration

Potassium hydroxide was used as a catalyst in experimental condition .The amount of base catalyst used in the process was 0.5%, 1%, 1.5% of seed. *Figs. 1-3* Indicates that increase the catalyst concentration conversion also increase as well as. Investigation of 0.50% concentration of catalyst gives the lower conversion. But the 1.5% KOH catalyst concentration was found to be best result as it gave 98 % conversion with >2 mm seed size and 1:500 seed/ solvent (w/w) molar ratio.

Effect of Reaction Time

Fig 4 shows the effect of reaction time on FAME content at different seed size and seed/ solvent (w/w) molar ratio 1:100 to 1:500 with .50 to1.50wt% of KOH catalyst for three molar ratios, the rapid formation of FAME was observed with in the first 30 minutes. After that the conversion rate was slower and finally reached steady state. The highest

conversion 98% was observed after 60 min for optimum conditions.

Conclusion

Biodiesel is an important new alternative transportation fuel. It can be produced from the seeds of Jatropha curcus by Reactive extraction. The maximum conversion of biodiesel was 98% obtained using 1:500 seed/ solvent (w/w) molar ratio, >2 mm seed size and 1.5wt% KOH catalyst concentration. The minimum reaction time required for maximum ester yield was found to be 90 min. This technique is ecologically and economically friendly which will be support the replacement of petro diesel by biodiesel. The catalyst used is KOH which is cheap and easily available. The biodiesel synthesized meets ASTM as well as BIS specification for biodiesel (*Table 3)*. These plants can be useful for the production of Biodiesel which will be suitable for use replacement of diesel without any change in engine.

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Table 1: Characterization of Jatropha Seed

Properties	Quantity	Acid value mg KOH/g sample
Moisture content	4.05%	
Oil content		
1. Direct seeds extraction method	29.85%	
2. Soxhlet extraction Method	33.4%	3.83 mg KOH/gm
3. Ultrasonic extraction method	33.30%	3.4 mg KOH/gm
Free Fatty Acid Content	1.6%	1.9 mg KOH/gm
Fatty Acid Profile	100%	
Phospholipid Content	101 mg/L	3.8 mg KOH/gm
Moisture Content of Jatropha Oil	455.2 ppm	202.53 mg KOH/gm

Table 2: Fatty Acid Methyl Esters (FAMEs) Composition of Jatropha Curcas Oil Based Biodiesel

Fatty acid	Percentage
C16	14.34
C18	10.1
C18:1	44.21
C18:2	31.86
C18:3	0.76

Table 3: Physicochemical Characterization of Biodiesel (Methyl Ester of Jatropha Oil) and Standards Specifications

Characteristics	Unit Specifications	Specification (Biodiesel)	Specification (Biodiesel)	Biodiesel
	ASTM	ASTM	BIS India	
Density at 15^0C	Kg/m^3	----	860-900	887.9
Kinematic Viscosity at 40^0C	cSt	1.9-6.0	2.5-6.0	4.25
Acid value	mgKOH/gm	<0.8	<0.5	0.32
Ash content	%wt	<0.02	<0.02	0.005
Cetane Number	^{0}C	>47	>51	54
Flash point	^{0}C	>100	>120	135
CFPP	Ppm	----	----	+5
Total sulphur	ppm	<500	<500	100
Water content		<500	<500	232
Copper corrosion	IP, h	<No. 1	<1	1
Oxidation stability	% mass	3 minimum	----	5
Mono glycerides	% mass	0.8	<0.8	<0.16
Di glycerides	% mass	0.2	<0.2	<0.08
Tri glycerides		0.2	<0.2	<0.06

Fig. 1: A Systematically Flow Diagram for Comparing between Conventional and Our Lab Process

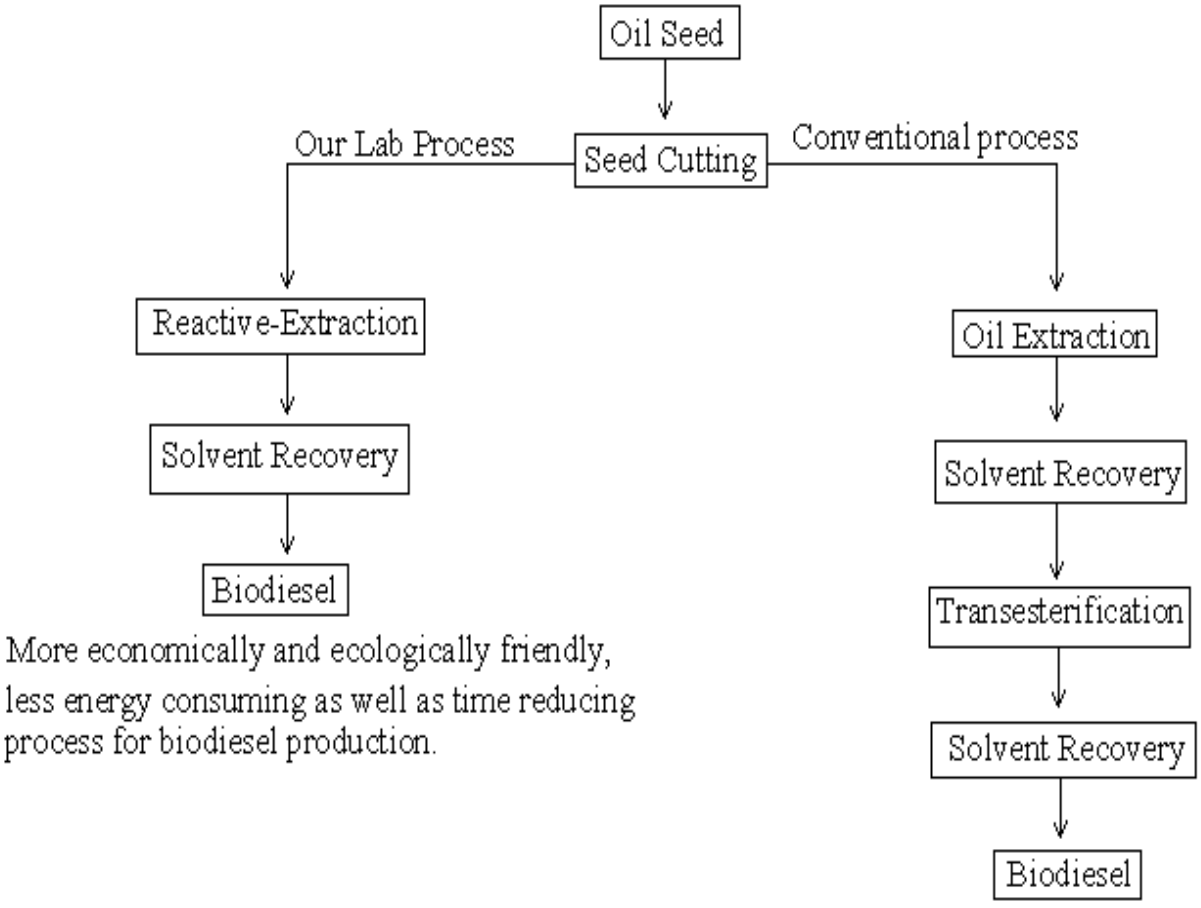

Fig. 2: HPLC Chromatogram of Methyl Esters Showing Presence of Different Fatty Acid Components

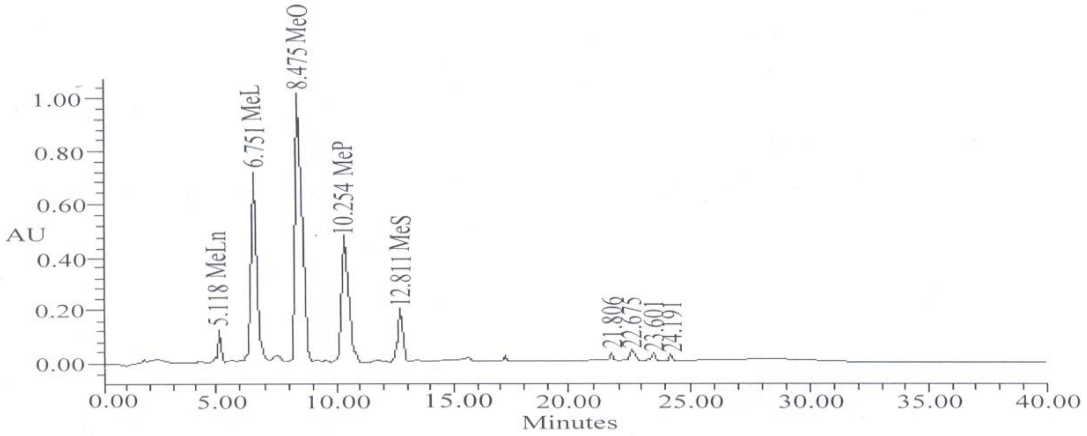

Fig 3: The effect of catalyst concentration (wt %) and seed / solvent ratio of biodiesel conversion on seed size <1 mm

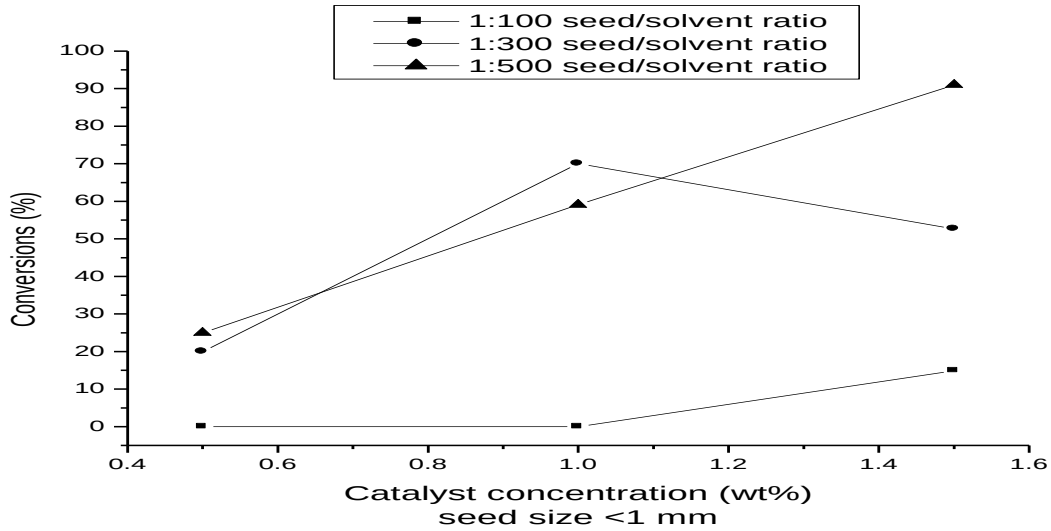

Fig 4: The effect of Catalyst Concentration (Wt %) and Seed / Solvent Ratio of Biodiesel Conversion on Seed Size >1-<2 mm.

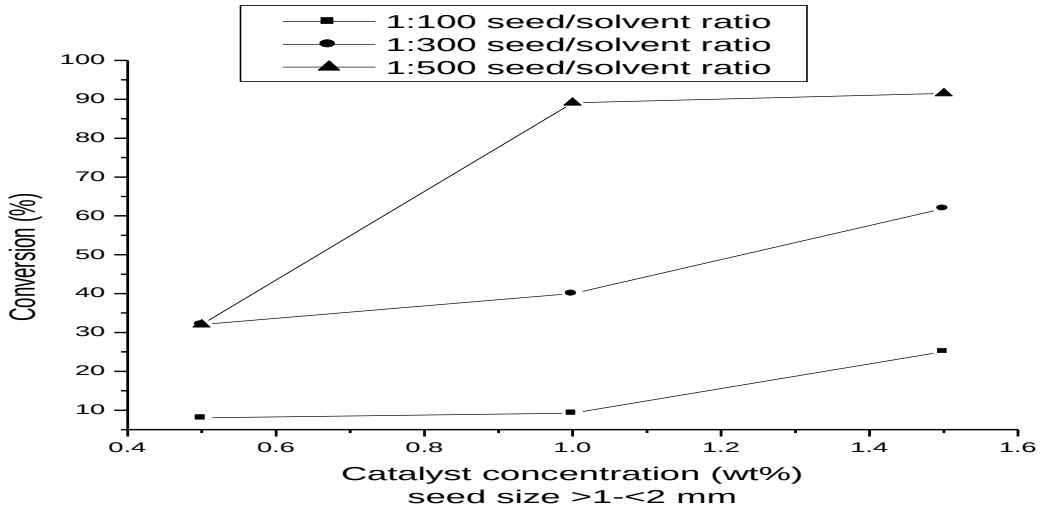

Fig 5: The effect of Catalyst Concentration (wt %) and Seed / Solvent Ratio of Biodiesel Conversion on Seed Size >2 mm

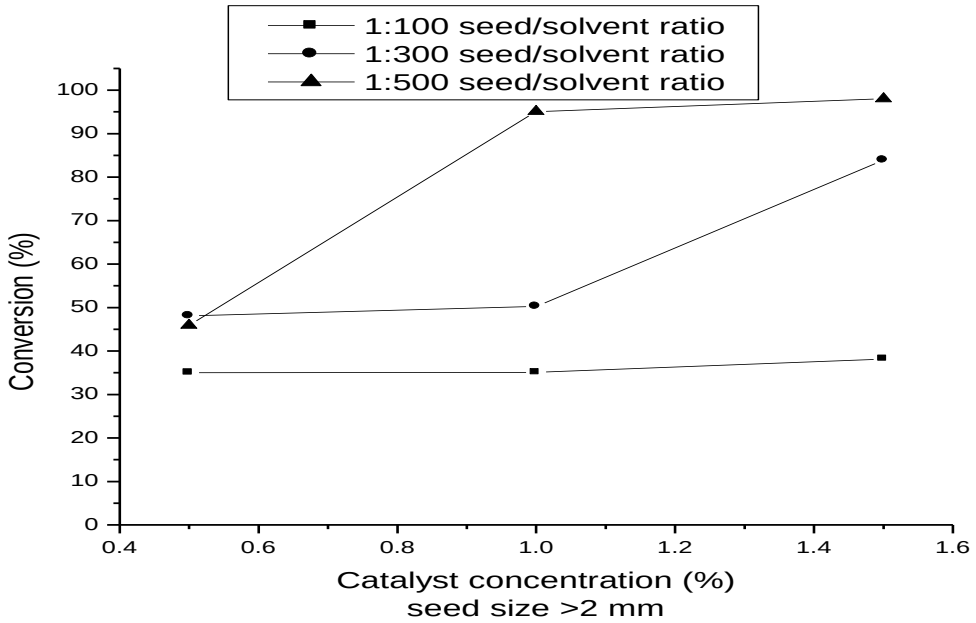

Fig 6: The Effect of Reaction Time of Biodiesel Conversion