

# An Alternative Eco-Friendly Avenue for Castor Oil Biodiesel: Use of Solid Supported Acidic Salt Catalyst

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## 1. Introduction

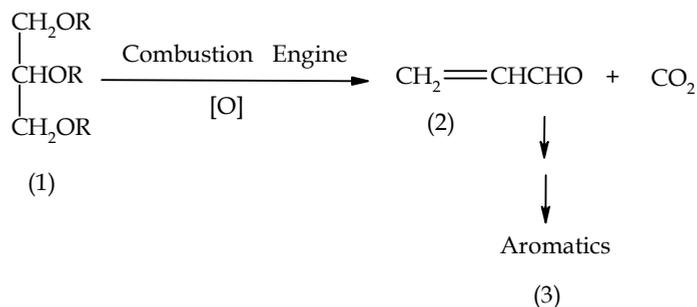
Year back in 1885, when Rudolf Diesel first invented the diesel engine, it was intended to run it on oil from vegetative sources and in the course of time with gradual depletion of the fossil fuel has now become a mandate of the day. Because it will play an important part in sustainable fuel and energy production solution for the future. Vegetable oil which remains in the form of triglyceride(1) of long chain fatty acid with carbon chain  $C_{16}$ - $C_{18}$  is not fit to use directly but needs certain transformation such as pyrolysis, microemulsion formation, transesterification etc. to suit it to use as diesel fuel



R= Long Chain Fatty acid moiety  
Triglyceride

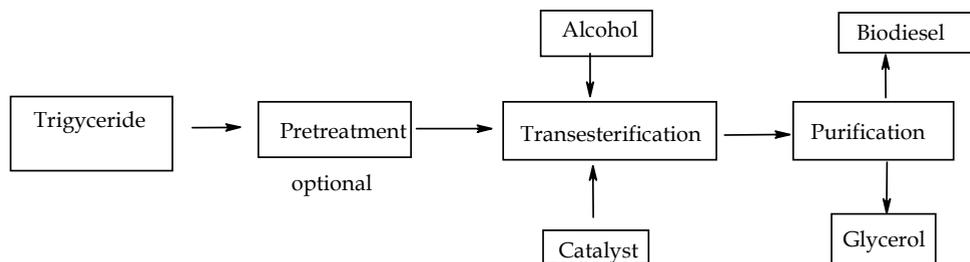
The transformed oil is termed as biodiesel due to its original biological source. Finite fossil fuel reserve, political, economic, biodegradability, low toxicity, health and environmental issues have led it to consider as the alternative and more importantly renewable and eco-friendly fuel. It has been found to show its ability to meet the world energy demand in transportation along with agricultural and other industrial sectors (Akoh et al. 2007). Since the source is plant, it is green as it does not have ash content, sulphur, aromatic ring compounds, renewable and so it has come out as superlative alternative and can be used in compression ignition engine with minor or no modification of the engine (Xu and Wu, 2005). A breakthrough in the process of converting vegetable oil into useful form promises a cheaper way to go green as it contributes mitigating global warming also. However the slow pace of progress in this direction in alternative fuel technologies has prevented the vision

from materializing. On the other hand vegetable oil as such is expensive and direct use of it in diesel engine is not possible. Because, firstly the vegetable oils are very viscous. High viscosity in fuel causes transportation problems, carbon deposits in engine, suffering of engine liner, injection nozzle failure, and gum formation, lubricating oil thickening and high cloud and pour point. Secondly, the glyceride moiety in the triglyceride form of the vegetable oil during combustion could lead to formation of acrolein (2) and this in turn lead to formation of different aromatics (3) as polluting by-products. This is one of the reasons why fatty esters of vegetable oils are preferred over triglycerides.



Scheme 1.

In 1970 it was discovered that reduction of viscosity of vegetable oils could be made by simple chemical process called transesterification by which the vegetable oil is treated with a low alkyl alcohol such as methanol or ethanol in presence of a suitable catalyst to form low alkyl esters whereby it could perform as petro diesel in modern engine. Glycerol that is produced during transesterification as by-product can be utilised in other industries. Thus by definition, biodiesel is low alkyl esters of long hydrocarbon chain fatty acids prepared from vegetable oils and animal fats through chemical or by biochemical process of transesterification.



Scheme 2.

## 2. Feedstock of biodiesel

Different feedstocks have been explored for extraction of vegetable oils in order to transform it to biodiesel. The feedstocks are animal fats, renewable plant resources basically from Euphorbiace family viz. *Jatropha caracas*, Soya, Sunflower, Castor seeds etc. besides waste

cooking oils from different restaurants and food processing industries. Considering several aspects castor oil from castor seeds seem to be an alternative promising feedstock for commercial production of biodiesel particularly for cold climatic regions.

## 2.1 Why castor oil

Although from the economic point of view waste cooking oils from different sources is a better choice for biodiesel preparation compared to all other sources and vegetable oils, considering the multifarious advantages oil from castor seeds from *Ricinus Communis* (Palma christi)- a species from Euphorbeace family is believed to be a better option. Because castor oil is possibly the plant oil which is industry's most unappreciated asset that contains about 90% ricinolic acid as the major constituent. The plant originates in Africa but now is available in all the tropical and subtropical countries. The plant can stand long periods of drought. The oil has versatile utility such as cosmetics, lubricants, brake fluids, softener in tanning, solar cell, textile company, small components of PC, mobile phones, boots and shoe manufacturing etc. Presently India is the largest producer of castor oil in the world with China and Brazil being the next two. India exports about 15000 tonnes castor seeds per year and 1,00,000 tonnes of castor oil annually to European Union and the domain has been increasing rapidly. In the seed, the oil content is about 50% of the total weight. It is the only unique oil which has an unusual chemical composition of triglyceride of fatty acid. It is the only source of an 18-carbon hydroxylated fatty acid viz ricinoleic acid with one double bond. It is reported that fuels having fatty acids with 18 or more carbon atoms and one double bond have viscosity low, higher cetane number and lower cloud and pour point properties are better. From that point of view alkyl ester from castor oil satisfies most of the criteria with the exception of viscosity and cetane number to stand as promising biodiesel candidate. The chemical composition of castor oil triglyceride (castoroil.in - the Home of castor oil in Internet) is

1. Ricinolic acid- 89.5%
2. Linoleic acid- 4.2%
3. Oleic acid- 3%
4. Stearic acid- 1%
5. Palmitic acid- 1%
6. Dihydroxy stearic acid- 0.7%
7. Eicosanoic acid- 0.3%
8. Free fatty acid in refined castor oil- 8.45%

Although considerable researches have been done on palm oil, soya oil, sunflower oil, coconut oil, rapeseed oil, tung oil, jatropha oil etc not much informations are available on castor oil as biodiesel even though it is currently undergoing a phase of active research in several institutions.

Production of castor oil worldwide is 0.5 million tonnes per annum. Consumption of petrodiesel per day is approximately 10 million tonnes. If the entire petrodiesel is to be replaced by castor biodiesel it needs to produce 7000 times the castor oil that is being produced today. However, since it is one of the oldest traded goods mankind has been trading a few thousand years ago, it has a lot of industrial usages and therefore market is already in existences. Further, as the plantation of castor plant has been cultivated commercially, its biology is well understood and high yield hybrid is available. It can also be found in medium climate areas as an annual crop or in tropical area as a small tree. It gives faster oil yield and can be planted as marginal plant in unattended idle areas. The gestation period of harvesting the plant for oil is 4-6 months only.

## 2.2 Properties of biodiesel from castor oil

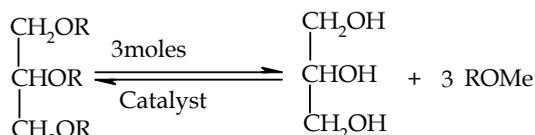
The biodiesel prepared from castor oil has certain properties that are attractive particularly for cold climate. It may be mentioned that it has flash point of 190.7°C which is much higher than petrodiesel and other vegetable oil biodiesel. The oil is stable at low temperature and makes it an ideal combustible for region of extreme seasonal weather. From cost point of view although 100% biodiesel from castor oil (B<sub>100</sub>) seems to be expensive its 10% (B<sub>10</sub>) or 20% (B<sub>20</sub>) blending with petrodiesel show good flow properties and further lowers the cloud and pour point. Further, due to its ability of displaying as a solvent, sedimentation does not occur which could otherwise potentially obstruct pipes and filters. However, the oil is sensitive to contamination by ferrous salts and rusts particles. Its higher cooling capacity is a key factor in the conservation of engine components. Considering the technical features, castor oil biodiesel is advisable taking into accounts its renewable resources. Because of its biodegradability and lower emissions, it presents a favourable impact on the environment. Moreover, it could be used as a crop substitution program turning it into a factor that promotes growth in many regions affected by several economic problems. Awareness is there in recent times for cultivation of castor plants boosting rural economy by government and private agencies by establishment of transesterification plant with million tonnes capacity per day, trial run using biodiesel from castor oil by Indian Railways, roadways, IOCL, HPLC etc. In addition to it a national mission on biodiesel has been proposed by the government of India with six micro missions to cover different aspects.

## 3. Transesterification of vegetable oils

Transesterification of vegetable oils has now come a long way for preparation of biodiesel. There are four basic methods for biodiesel production. These are acid catalysed, base catalysed, enzymatic/microbial transesterification and conversion of the oil to its fatty acids and then esterification to have ester as biodiesel.

### 3.1 Transesterification catalysts

The transesterification reactions require a catalyst in order to obtain a reasonable conversion rate and the nature of the catalyst must conform to the feedstock. Further, the reaction condition and post separation steps are predetermined by the nature of the catalyst. Generally, transesterification of vegetable oil is done with methanol or ethanol in presence of a base catalyst such as NaOH, KOH, K<sub>2</sub>CO<sub>3</sub>, NaOMe, NaOEt, NaOPr, NaOBu etc. A minimum content of water and free fatty acid result in the saponification with consequent formation of soap. Presence of large content of water results in hydrolysis of the product formed. Theoretically 3 moles of methanol are required per mole of triglyceride. As the transesterification reaction of triglyceride is a reversible reaction, the excess of methanol shifts the equilibrium towards the direction of ester formation. Freedman et al (Freedman et al, 1984) suggested that 6:1 molar ratio of alcohol to oil is necessary to get the maximum ester yield thus minimising the concentration of tri, di and mono glycerides.



Scheme 3.

### **3.2 Solid catalysts for transesterification reactions:**

#### **3.2.1 Solid base catalysts**

There are reports of many solid base catalysts to be active in transesterification reactions such as supported CaO catalysts (Yan et al, 2008), supported VO<sub>2</sub> catalysts (Kim et al, 2008) various other metal oxides such as BaO, SrO, MgO etc to have transesterified camaelina sativa oil as biodiesel with upto 80-89% yield (Patil and Deng, 2009). However, these solid base catalysts show much lower activity than traditional homogeneous catalysts. Potassium nitrate supported on alumina as solid base catalyst was reported by Vyas et al (Vyas et al, 2009) for production of biodiesel from jatropha oil and has been successful in getting 84% yield. Certain of these catalysts are very much sensitive to trace amount of free fatty acid present. Reports of lanthanum based (Kurian et al, 1998) strong basic catalysts have appeared for transesterification and esterification reaction.

#### **3.2.2 Enzyme catalysis**

Over the last few decades considerable research have been done on the use of enzyme in transesterification using lipase enzyme from filamentous fungi and recombinant bacteria under various condition. However not considerable attention has been received except in China where 20,000 tonnes of biodiesel per year (Du et al, 2008) is produced. But due to large reaction volume, time, higher conc. of catalyst, cost (\$1000 per kg), loosening of catalyst activity on repeated use the process is not commercially viable although friendly to the environment.

#### **3.2.3 Acid catalysts**

Homogenous acid catalysts such as H<sub>2</sub>SO<sub>4</sub>, HCl, sulfonic acid etc. have the potentials to replace base catalysts since they do not show measurable susceptibility to free fatty acid (FFA) and can catalyse esterification and transesterification simultaneously (Kulkarni et al, 2006). However, separation problem, requirement of high temperature, high molar ratio of oil and alcohol, serious environmental and corrosion related problem make their use non practical for biodiesel production.

The demanding feedstock specification for base catalysed reactions have led researchers to seek catalytic process alternative that can ease this difficulty and lower production cost. To eliminate the corrosion, environment problem and time saving for multiple reaction, solid acid catalysts have recently replaced liquid acids for biodiesel production by simultaneous esterification and transesterification. Methodologies based on acid catalysed reaction have the potential to achieve this since acid catalysts did not show measurable susceptibility to FFAs. Compared to homogenous acid catalysts heterogeneous solid acid catalysts have great potential due to advantage in separation and corrosion related problems and such catalysts having large-pores, moderate to strong acid sites and a hydrophobic surface are idea for biodiesel production.

#### **3.2.4 Solid acid catalysts**

There have appeared in the literature several solid supported acid catalysts such as heteropolyacid, having Keggin structure viz-12-tungsto-phosphoric acid impregnated on various solid supports like hydrous zirconia (Kulkarni et al. 2006), silica, alumina, and activated carbonate using as solid acid catalyst for biodiesel preparation from different feedstock with achievement of more than 77% yield of biodiesel. Zeolites (Lotero E et al, 2005, Wang et al, 2009) with large pore size have been used with success with fatty acid esterification

but at higher temperature. Few other solid supported catalysts for esterification and transesterification of vegetable oils are zeolites with different pore size framework of Si/Al ratio and proton exchange level. These characteristics permit tailoring important catalytic properties such as acid strength. It was observed that zeolite catalysis in transesterification/esterification reaction using large molecules takes place on the external surface of the zeolite catalysts. However, it requires high temperature and the reaction rate is slow. The reactivity on such solid surface catalysts depends upon acid site strength and hydrophobicity of the surface. In fact, pore size, dimensionality of the catalyst channel system related to the diffusion of the reagents and products and aluminium content of zeolite framework strongly affect the zeolite catalytic activity for esterification. Related to zeolites, but with amorphous pore walls, silica molecular sieves such as MCM-41, mesoporous materials are generally not sufficiently acidic to catalyse esterification reaction due to pure silica structure. However introducing aluminium, zirconium, titanium or tin compounds into silica matrix of these solids can significantly improve their acidic properties. However, metal doped materials behave more like weak acids and can only be used for reactions that do not require a strong acid catalyst. It has also been reported that  $\text{SO}_4^{2-}/\text{ZrO}_2$  has been shown to have applicability for several acid catalysed reactions. However the problem is that  $\text{SO}_4^{2-}/\text{ZrO}_2$  deactivates in presence of water due to leaching of  $\text{SO}_4^{2-}$  either in the form of  $\text{H}_2\text{SO}_4$  or  $\text{HSO}_4^-$ . Sulphated tin oxide ( $\text{SO}_4^{2-}/\text{SnO}_2$ ) prepared from *m*-stannic acid has shown activity superior to that of  $\text{SO}_4^{2-}/\text{ZnO}_2$  for esterification of octanoic acid by methanol at 150°C due to superior acid strength (Furuta, S. et al 2004). The use of solid catalyst to produce biodiesel requires a better understanding of the factors that govern their reactivity. Thus, an ideal solid catalyst should show some underlying characteristics such as an interconnected system of large pores, moderate to high concentration of high acid sites and a hydrophobic surface. Large interconnected pores would minimise diffusion problem of molecules having long alkyl chain and strong acid sites are needed for the reaction to proceed at an acceptable rate. It is recently attracted considerable attention for solid acid catalyst such as Bronsted acid zeolites, ion exchange resin, metal oxides viz sulphated zirconia  $\text{WO}_3/\text{ZrO}_2$ ,  $\text{MoO}_3/\text{ZrO}_2$ , sugar based catalyst (Zong et al, 2007). It has been noted that Bronsted acid catalysts are active mainly in esterification while Lewis acid catalysts are active in transesterification reaction. Therefore, preparation of such solid supported catalysts that contain both Bronsted acid and Lewis acid catalyst site having enhanced water tolerance and large pores, hydrophobic surface and low cost is still a challenge. National Chemical Laboratory, Pune India has developed a novel solid double metal composition for transesterification of vegetable oils containing up to 18% FFA to biodiesel (Sree Prasanth et al, 2006). A series of layered aluminosilicates with  $\text{H}_2\text{SO}_4$  impregnation has been reported for transesterification. Activated montmorillonite KSF showed 100% conversion of transesterification within 4 hour at 200°C and 52 bar pressure. However problem encountered is leaching, for which reimpregnation of  $\text{H}_2\text{SO}_4$  on the clay surface is required for reusability. Several other solid acid catalysts were reported but needed higher temperature (>200°C) for conversion. The use of age old polymer matrix Amberlyst-15 has also been reported but need mild condition to avoid degradation (Vicente et al,1998).

#### 4. Materials and methods

In view of the above and having observed certain advantages of castor oil over others it was studied the transesterification of it using a simple, cheap and easily prepared solid supported acidic catalyst considering the positives of this clean catalysts.

$\text{KHSO}_4$ , an acidic salt is ordinarily used as dehydrating agent of alcohol to olefinic compounds at high temperature. It was observed in our earlier study (Goswami et al, 2007) that treatment of it as such with an ester in presence of an alcohol, the ester undergoes partial transesterification very slowly. Dispersing this acidic salt on microporous surface silica gel uniformly triggers transesterification (Goswami et al, 2007) of esters in simple alcohol very satisfactorily giving the product yield more than 95%. The system behaves in a completely different manner on treatment with olefin (Das et al, 2010) leading to dimerization through C-C bond formation or addition product with alcohols depending upon the condition applied. Application of this system to castor oil triglyceride in methanol at its boiling point in 5-6 hours transform it into methyl ester of ricinoleic acid the primary constituent of castor oil along with other fatty acid methyl esters present in it with more than 95% yield.

#### 4.1 Experimental condition

Instruments : The GC was recorded on Chemito 1000 GC using column OVIE+SP2401 (2mX10.635 cm, od) glass column and nitrogen as carrier gas. The textural properties were recorded on Quantachrome Automated Gas Sorption system. The FTIR was recorded on Perkin Elmer System-2000 and FT NMR was recorded on Bruker Avance-DPX-300MHz instrument. Reagents: Castor oil was obtained from local grocery shop (Dabur, 99%). methanol (99.8%) from Fisher Scientific, potassium bisulphate (98%) from Rankem and silica gel (60-100 mesh) were taken from Aldrich Chemicals. Methanol taken was made super dry following standard method:

##### 4.1.1 Catalyst preparation

Potassium bisulphate ( $\text{KHSO}_4$ ) 20 gm (144mmol) was dissolved in 100ml distilled water to have a clear saturated solution. The solution was soaked completely in microporous silica (40gm). The soaked mixture was thoroughly mixed and dried in a hot air oven at 150°C for 24 hours to have a free flowing powdery solid. The dried solid mixture was than kept in vacuum desiccator to use as a stock solid supported catalyst (A) in different reactions.

##### 4.1.2 Experimental procedure

25 ml of refined castor oil containing 8.4% FFA was charged with 1 litre dry methanol in a 1.5 litres round-bottomed flask fitted with a condenser and fused calcium chloride guard tube on a preheated oil bath under vigorous stirring. To it was added 1.25gm (5%) catalyst A and stirred at 600 rpm under heating at 70°C (external) for 5 hours. Occasionally TLC was monitored to check the progress of the reaction. After completion, the reaction mixture was distilled to recover methanol. The product with the catalyst remained after separation of methanol was obtained with glycerol as a separate layer. Methyl ester of castor oil along with glycerol layer was decanted out from the solid catalyst surface. Glycerol separated as the bottom layer was taken out from the methyl ester of castor oil (CastMe) layer. The solid catalyst was washed several times with petroleum ether and dried at 150°C for 24 hours in a hot air oven for subsequent runs. The product isolated was found to have yield 95%. During the period of the reactions, samples were taken out at regular intervals and analysed on GC (Fig. 1) using carrier gas nitrogen at flow rate of 2.5kg/cm<sup>2</sup>. Triglyceride, diglyceride, monoglyceride and methyl ester CastMe as transesterified product were quantified by comparing the peak areas of their corresponding standard.

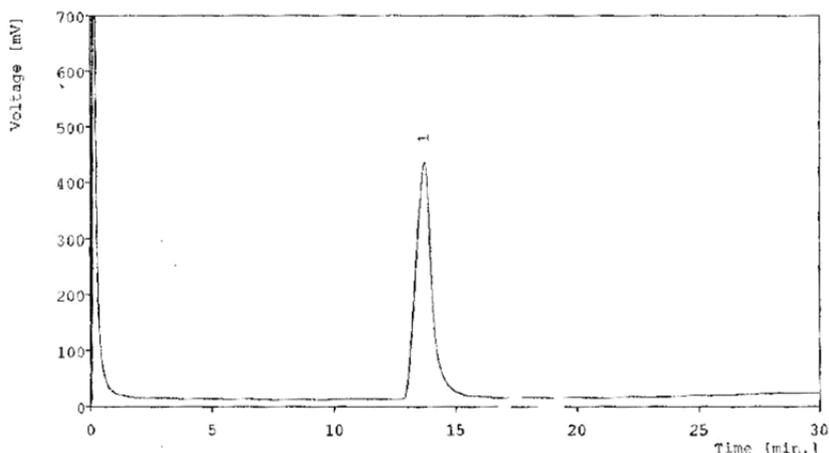


Fig. 1. GC of standard ricinoleic acid methyl ester

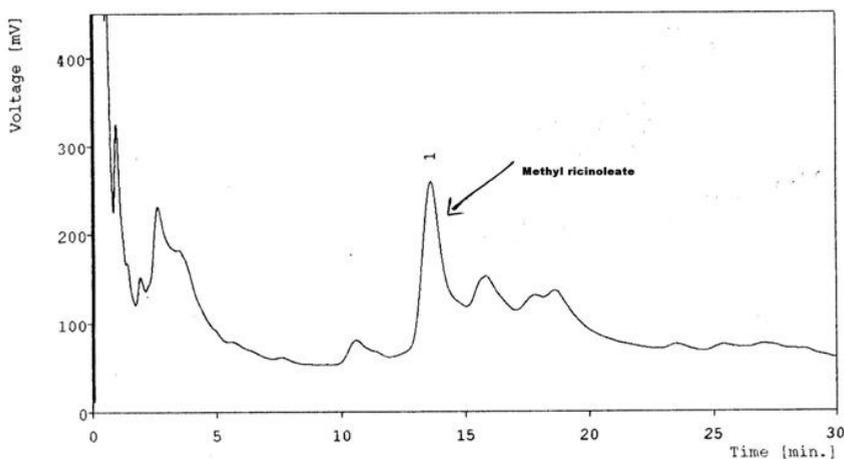


Fig. 2. GC of CastMe

#### 4.1.3 Physical properties of CastMe determined by ASTM D6751 standard

The physical properties of CastMe viz. kinematic viscosity, density, pour point, and cloud point have been determined following standard ASTM D675 method and given in the Table 1 along with reported (Forero, C.L.B., 2004) values of corresponding castor oil, petrodiesel and methyl esters of few other vegetable oils. In Table 2 suggested ASTM standard for pure biodiesel (100%) were given. The properties of CastMe are comparable to those of petrodiesel and acceptable within what is specified for 100 % pure biodiesel as per ASTM standard except that of viscosity and cetane numbers which are the bottlenecks. However, 10% or 20% blended CastMe with petrodiesel that are known as B<sub>10</sub> and B<sub>20</sub> have their kinetic viscosity 4.54 & 4.97 mm<sup>2</sup>/s and are within ASTM standard.

The corresponding significant FT IR frequencies (Fig 3) and superimposable FTIR spectra of CastMe and standard methyl ricinoleate (Fig 4) and 300 MHz NMR spectral data (Fig5) of methyl ester of castor oil (CastMe) have been as given below.

**FT IR (Cm<sup>-1</sup>, thin film):** 1742 (COOMe str), 2855 & 2928(CH str), 3407(OH str) (Fig 3):

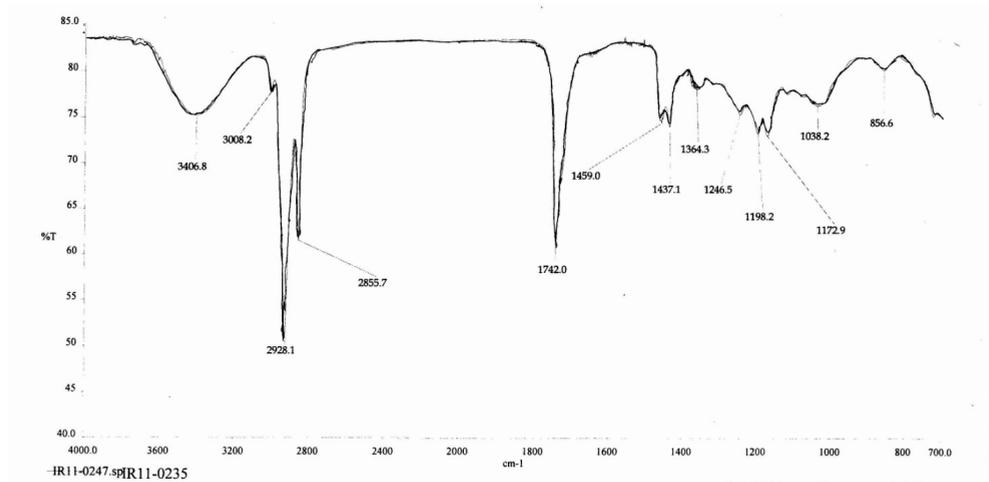


Fig. 3. FTIR of CastMe

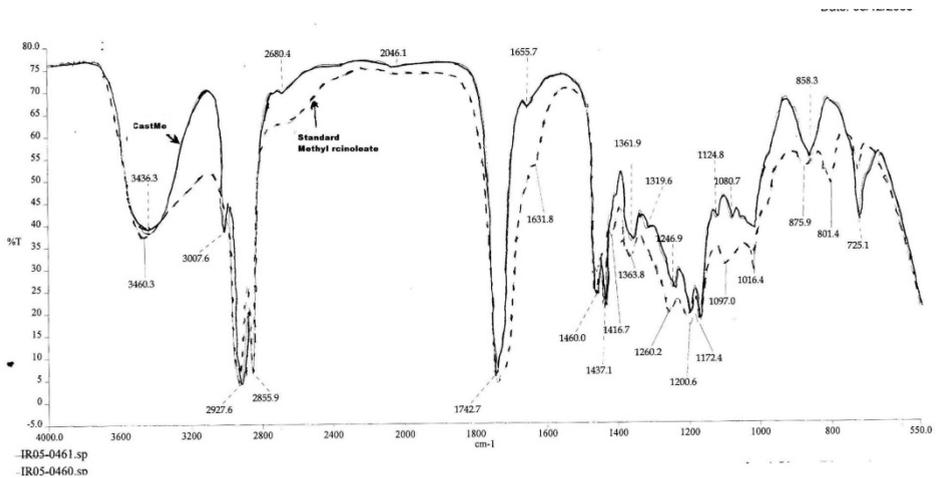


Fig. 4. Superimposable FTIR spectra of CastMe and standard methyl ricinoleate

<sup>1</sup>HNMR( $\delta$  ppm, CDCl<sub>3</sub>) : 1.96(s,1H,OH), 1.23-2.24(m, nH,(CH<sub>2</sub>)<sub>n</sub>Me), 3.55-3.57(m,1H,CH-OH), 3.57(s,3H,COOMe), 5.25-5.47(m, nH, olefinic protons), (n=different numbers of protons of fatty acids), the hydroxyl group present in ricinoleic acid, the major constituent of castor oil imparts unique properties. Because of the branching created by it causes the low cetane number and higher viscosity (Knothe et al, 2008). However the advantage of the present method is that unlike other acidic catalyst, this catalyst system does not facilitate any

methanol olefin etherification (Goodwin et al,2002) even though the constituent of the oil do possess olefinic bonds .

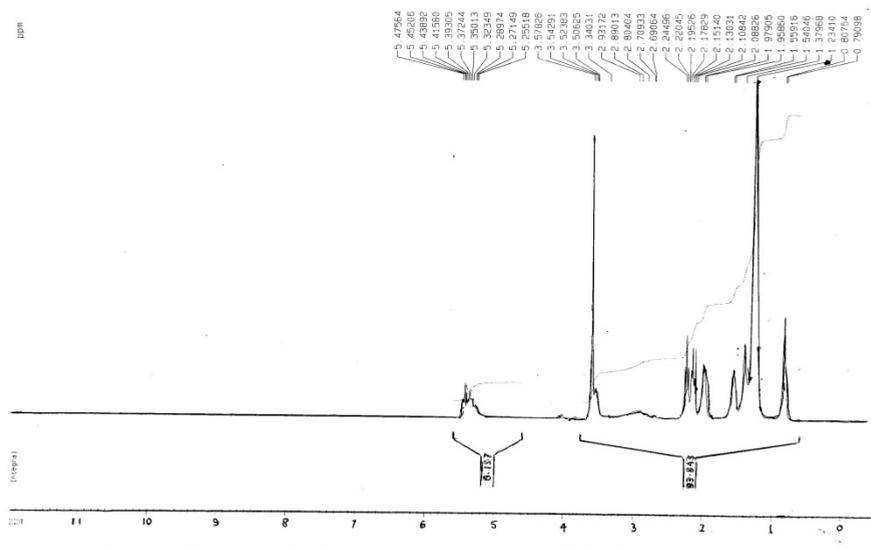


Fig. 5.  $^1\text{H}$ NMR (300MHz) of CastMe

| Item        | Density (g/cc) | Kinematic Viscosity (CST)(38°C) | Pour point (°C) | Cloud point (°C) | Flash point | Cetane no. |
|-------------|----------------|---------------------------------|-----------------|------------------|-------------|------------|
| Castor oil  | 0.963          | 297                             | -32             | -20              | 260         |            |
| CastMe      | 0.34           | 9.4                             | -45             | -23              | 190.7       | 42         |
| Petrodiesel | 0.86-0.95      | 3.81                            | -6              | -15              | 68.3        | 47         |
| Soy ME      | 0.885          | 4.8-4.3                         | -3.8            | -0.5             | 131         | 48         |
| Rape ME     | 0.883          | 4.53                            | -10.8           | -4.0             | 170         | 48         |
| Tallow ME   | 0.876          | 51.15                           | 9               | 13.9             | 117         | 35         |
| Canola ME   | 0.88           |                                 | -9              | 1                | 163         | 48         |

Table 1. Physical values of castor oil methyl ester (CastMe) determined along with values of other vegetable oil methyl esters

| Property            | ASTM standard | limit       | units              |
|---------------------|---------------|-------------|--------------------|
| Flash point         | 93            | 100         | °C                 |
| Carbon residue      | 4530          | 0.050       | wt%                |
| Sulphated ash       | 874           | 0.020       | wt%                |
| Kinematic viscosity | 445           | 1.9-6.0     | mm <sup>2</sup> /s |
| Sulphur             | 2622          | 0.05        | wt%                |
| cetane              | 613           | 40          | °C                 |
| Cloud point         | 2500          | By customer | °C                 |
| Free glycerol       | GC            | 0           | wt%                |

Table 2. Suggested standard for pure (100%) biodiesel as per ASTM.

## 5. Results and discussion

Potassium bisulphate (PBS) impregnated microporous silica has been evaluated as solid acid catalyst for biodiesel production from refined castor oil containing 8.4% FFA compared to other support viz. alumina with 95% yield. The determination of surface area, pore volume and pore diameter and also FTIR spectra of  $\text{KHSO}_4$  supported on microporous silica revealed that  $\text{KHSO}_4$  is well dispersed very evenly generating Bronsted acid site that is responsible for its higher activity. The FT IR spectrum of pure  $\text{KHSO}_4$ , pure silica gel and  $\text{KHSO}_4$  supported silica gel (Fig-6) have been depicted below.

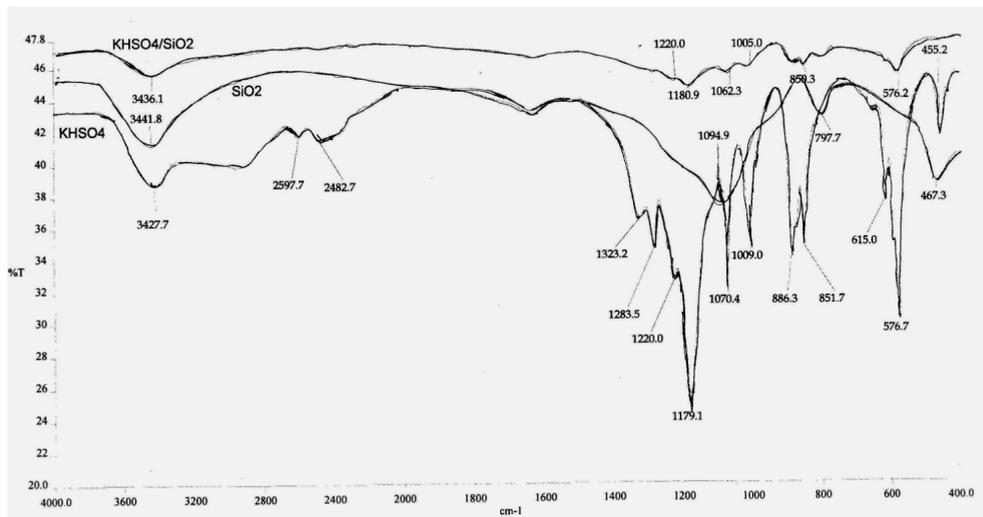


Fig. 6. FT IR spectra of pure  $\text{KHSO}_4$ , Pure  $\text{SiO}_2$  and  $\text{KHSO}_4$  supported on  $\text{SiO}_2$

The pure silica FTIR spectra of  $\text{KHSO}_4$  exhibited typically six major bands located at 577, 852, 886, 1009, 1070 and 1179  $\text{cm}^{-1}$  which are stretching modes of oxygen bonded to sulphur and hydrogen. In supported  $\text{KHSO}_4$  catalyst no clear bands were observed. These results indicated that  $\text{KHSO}_4$  is highly dispersed on the surface of support  $\text{SiO}_2$ . A 40:1 alcohol to oil ratio at 70°C (external) temperature and 5 wt% catalysts loading gave a maximum yield of CastMe up to 95%.

The textural properties (Kulkarni et al, 2006) of the catalyst were summarized in Table 3. The surface area of microporous silica of 60-100 mesh particle size has 300  $\text{m}^2/\text{g}$  and pore volume 1.15  $\text{cm}^3/\text{g}$  and its average pore diameter is 150  $\text{Å}$ . After loading 50 wt% of  $\text{KHSO}_4$  the accessible surface area of silica gel left was only 55.45  $\text{m}^2/\text{g}$  and pore volume and average pore diameter were reduced to 0.13  $\text{cm}^3/\text{g}$  and 98.9  $\text{Å}$ . The reason is attributed to uniform dispersing of  $\text{KHSO}_4$  on the surface leaving only 55.45  $\text{m}^2/\text{g}$  surface and pore plugging of the support. The same reaction when carried out in a similar fashion supporting  $\text{KHSO}_4$  on alumina surface, the reaction gives very poor or no yield at all. It may be due to too narrow micropores of alumina which cannot accommodate  $\text{KHSO}_4$  molecule to disperse uniformly to enhance catalytic activity (Kulkarni et al, 2006) although its surface area is higher (260  $\text{m}^2/\text{g}$ ). Even though alumina is an interesting support it is assumed that the surface basicity could bring about decomposition of  $\text{KHSO}_4$ . It means that particles of

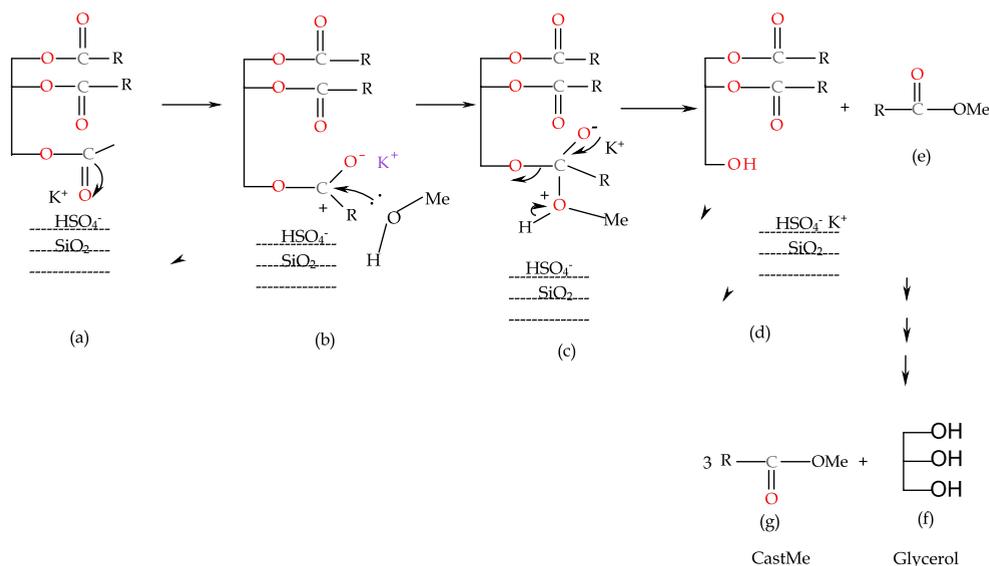
$\text{KHSO}_4$  conform to silica gel particles in order to disperse on its surface. Large pores can easily accommodate a bulky triglyceride molecule giving  $\text{KHSO}_4/\text{SiO}_2$  large active site and surface area resulting in highest activity (Igarashi et al, 1979; Furuta, 2004 and Lecleroq et al, 2001).

| Solid support                | Surface area ( $\text{m}^2/\text{g}$ ) | Pore volume ( $\text{cm}^3/\text{g}$ ) | Pore diameter ( $\text{\AA}$ ) |
|------------------------------|--|--|--------------------------------|
| $\text{SiO}_2$               | 300                                    | 1.15                                   | 150                            |
| $\text{KHSO}_4/\text{SiO}_2$ | 55.45                                  | 0.13                                   | 98.9                           |

Table 3. The textural properties determined for  $\text{SiO}_2$  and  $\text{KHSO}_4/\text{SiO}_2$

## 6. Mechanism

The mechanism of the reaction has been shown in Scheme 4. The interaction of the carbonyl oxygen of the ester with the conjugate acid potassium ion from the silica surface of the catalyst forms carbocation by enolizing it. The carbocation is stabilized by the bisulphate ion and facilitates nucleophilic attack methanol on the carbocation producing a tetrahedral intermediate (c).



Scheme 4.

In the reaction sequence the triglyceride was converted stepwise to di and mono glyceride and finally to glycerol. The tetrahedral intermediate (c) formed during the reaction eliminate di, monoglyceride and glycerol when tri, di and monoglyceride came in contact with the acidic site respectively to give one mole of ester in each step. It has been reported (Freedman, B, 1986) in fact that the rate limiting step varied over time and in three stages in accordance with the observed reaction rate could categorize the overall reaction progress. In the first stage the reaction was characterized by a mass transfer controlled phase in which the low miscibility of the catalyst and the reagent or the non-polar oil was separated from

the polar alcohol phase. The second phase is product formation stage whereby the product formed acts as an emulsifier. It is a kinetically controlled stage and is characterised by abrupt range of product formation. Finally the equilibrium is reached at the completion stage. It was found in castor oil transesterification with 40:1 alcohol to oil ratio acceptable reaction rate was achieved. Thus from this observation it can be stated that the forward reaction is pseudo first order kinetics while the backward or the reverse reaction is second order kinetics.

## 7. Influence of reaction parameters

The transesterification of castor oil in presence of  $\text{KHSO}_4$  supported on silica gel in methanol is influenced by certain reaction parameters which have been studied thoroughly varying the conditions at different stages and the results have been appended below..

### 7.1 Reaction temperature

Initially the transesterification reaction was attempted at room temperature under stirring at 600 rpm for more than 48 hours. However the reaction rate at room temperature was found to be very slow and only 30-35% conversion was observed. It means that the rate of reaction is influenced by the reaction temperature. Gradually when the reaction temperature was raised by  $10^\circ\text{C}$  the reaction rate is increased with increase of product formation and at  $70^\circ\text{C}$  (external) temperature the formation of the product was found to be maximum of 95%. Beyond this temperature there was found to be no further increase of yield (Fig. 7).

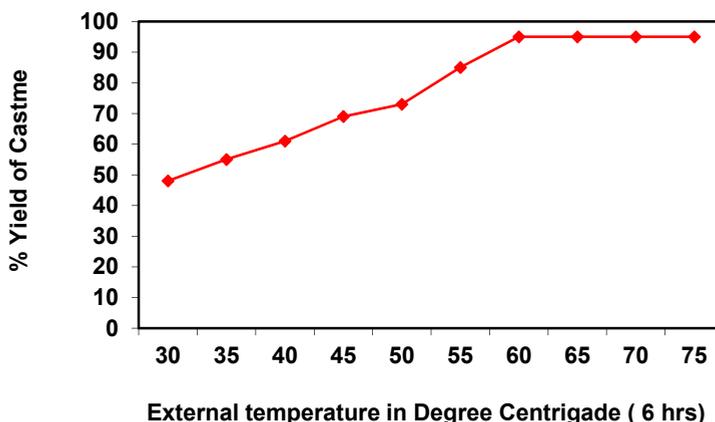


Fig. 7. Effect of external temperature on the reaction course

### 7.2 Effect of time

The effect of reaction time was studied and result was shown in Fig. 8. It was found that increasing the reaction time upto 5 hours enhanced the castor oil methyl ester yield and

beyond it there found to be no further improvement. It means 5 hours time is optimum period required.

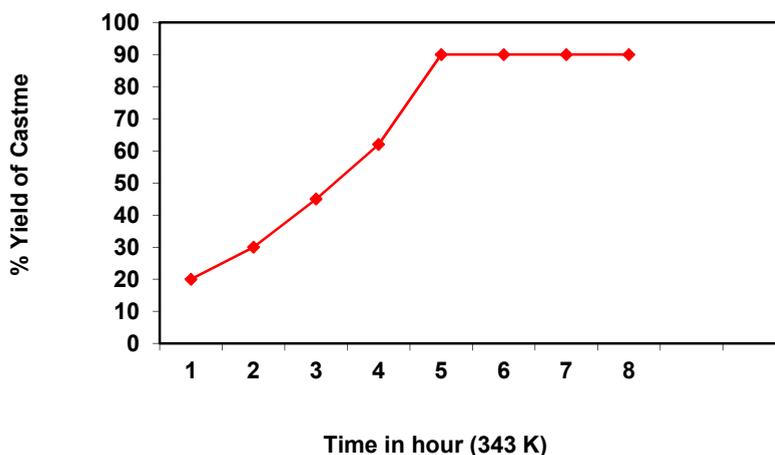


Fig. 8. Effect of time duration on the reaction course

### 7.3 Effect of alcohol to castor oil ratio

Methanol to castor oil weight ratio is one of the important parameters that affect the yield of methyl ester of castor oil. Theoretically the transesterification reaction requires 3 moles of methanol per mole of triglyceride (Lotero et al, 2005). Since the reaction is a reversible one, the excess methanol shifts the equilibrium towards the direction of ester formation (Cannkei et al, 1999). Generally heterogeneous acid catalytic of transesterification reaction is well known for slow reaction rate. In order to improve the rate of this reaction, use of excess alcohol is an option. It was reported (Xie et al, 2005) that increase of the ratio up to 275:1 of alcohol to oil improves the rate of transesterification reaction. In the present work with preoptimized reaction parameters the methanol to castor oil ratio was varied in the range 5:1 to 40:1 and its influence on the yield of CastMe was investigated at the end of 5 hours. It was clearly observed that at 70°C (external) temperature with increase in ratio of alcohol to oil from 5:1 to 40:1 increased the yield of CastMe from 75% to 95%. Presence of 8.4% FFA in the refined castor oil did not affect the activity of the catalyst. Further increase of methanol did not show any significant improvement (Fig 9). The excess methanol can be recovered for reuse and low cost of methanol makes it the first choice for transesterification.

### 7.4 Effect of catalyst amount

The catalyst amount is also an important parameter that needs to be optimized for increasing the yield of castor oil methyl ester (CastMe). The effect of  $\text{KHSO}_4/\text{SiO}_2$  wt/wt of castor oil on the reaction was studied. At low catalyst amount (< 5 wt %) there were not enough active site for reaction. The optimum amount of catalyst employed was found to be 5 wt% of castor oil to isolate a yield of 95% of the product (Fig. 10).

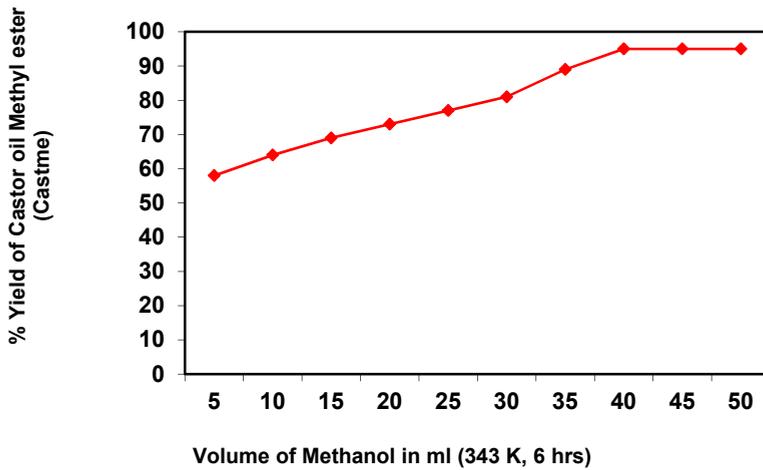


Fig. 9. Effect of volume of alcohol on the reaction course

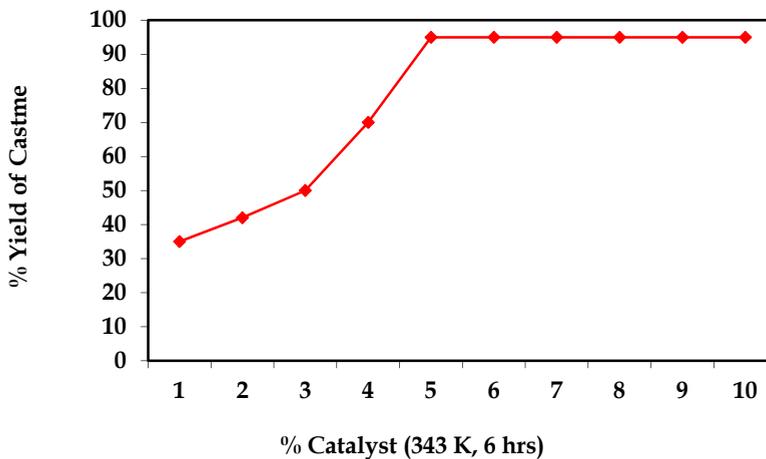


Fig. 10. Effect of catalyst amount

### 7.5 Catalyst recycling

The cost of a process depends upon the recyclability of a catalyst. It has been found that the dispersed catalyst  $\text{KHSO}_4$  on silica gel surface after the transesterification reaction of castor oil in methanol, a certain amount gets leached out with methanol either in the form of  $\text{H}_2\text{SO}_4$  or in  $\text{HSO}_4^-$ . However, after the completion of the reaction, methanol is distilled out completely and methyl ester of castor oil (CastMe) was extracted in dichloromethane

whereby  $\text{KHSO}_4$  is retained on the surface of silica. The catalyst was washed several times with petroleum ether and then dried completely at  $150^\circ\text{C}$  for 8-10 hours. On use of this catalyst for 5 runs with same amount of castor oil and methanol the yield of CastMe decreased was subtle even at fifth reuse (Fig. 11).

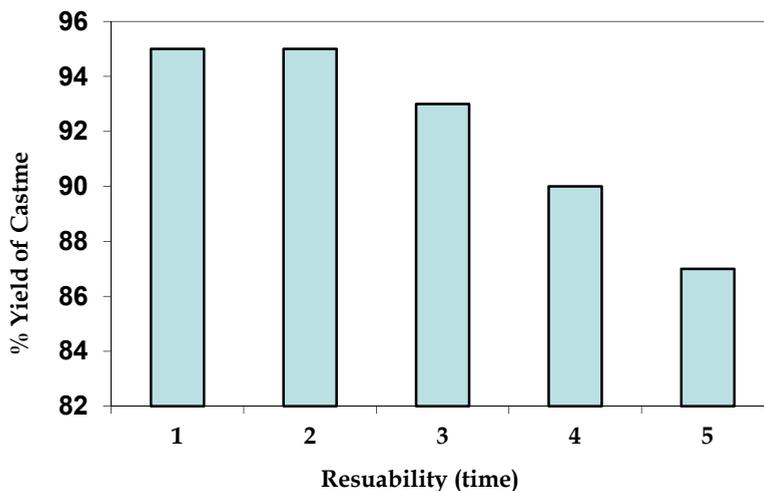


Fig. 11. Catalyst recycling

## 8. Conclusion

Silica gel supported  $\text{KHSO}_4$  acidic catalyst prepared for production of biodiesel from refined castor oil containing 8.4% free fatty acid has been found to be a simple, cheap, ecofriendly and recyclable catalyst system for excellent yield of castor oil biodiesel under mild condition. The activity of the catalyst system is not affected by the presence of free fatty acid. The system is so simple that it does not require any special design compared to other solid supported acidic catalysts.

It may be mentioned in this context that the leading oil companies in the whole world are looking to tap the business opportunities of biodiesel. In the developed process such as the one discussed in this chapter is scaled up to commercial levels by more and more oil companies, it could be a major step towards creation of an eco-friendly transportation fuel that is relatively clean on combustion and provides farmers with substantial income.

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