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SBA-15 as a Nanostructured Catalyst for Preparation of Biodiesel from Rice Bran Oil

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ABSTRACT

Biodiesel resulting from the trans-esterification of oils from plant sources can be blended with diesel and effectively used in automobiles. The efficiency of homogenous catalysts such as sulphuric acid when used for trans-esterification is low and is accompanied by difficulty in handling and separation. This work aims to use mesoporous silica which has high surface area to improve the trans-esterification efficiency of rice bran oil and since this is as a heterogeneous catalyst it may reduce handling and separation issues. Mesoporous silica was synthesized by varying solvent, pH and metal dopants to achieve various grain sizes, surface area and porosity which were characterized using XRD, SAXS, SEM, FT-IR and BET. The catalytic efficiency of each of the mesoporous silica samples was evaluated and the influence of temperature, reactant to catalyst ratio and reaction time on the biodiesel yield was investigated and compared with conventional catalysts. The optimal reaction conditions were identified as 1:15 oil to methanol ratio with 0.1 g of the catalyst at 70°C for one hour (reaction time). The high surface area of the mesoporous catalysts arising due to its porous morphology facilitated considerable improvement in the biodiesel yield up to 91%. The biodiesel product was characterized using FT-IR and GC-MS. The shelf life of biodiesel was found to be good and there was no fungal growth after long periods of storage. Moreover, the use of mesoporous silica also enabled easy recovery of the catalyst.

Key words: Biodiesel, SBA-15, rice bran oil, trans-esterification

INTRODUCTION

The combination of dwindling oil reserves and the climate change due to carbon dioxide emission has necessitated the development of clean, sustainable energy supplies. Most of the global energy requirements are satisfied by petroleum, coal and natural gas. These energy sources are non-renewable and are available only in limited quantities. Biodiesel, a mixture of alkyl esters, having similar combustion properties as fossil fuels, may aid in reducing the dependence on fossil fuels. Along with non-toxicity and biodegradability, the exhaust gas emissions of biodiesel contain lesser amount of CO, particulate matter and no So_x (Yan *et al*., 2009). Being environment friendly, biodiesel is a potential alternative to fossil fuels and can be used in compression-ignition engines with little or no modifications (Ngamcharussrivichai *et al*., 2008).

Oils derived from plant and vegetable sources have similar long chain hydrocarbons. The highly viscous nature of these oils renders them incapable of being used in engines because of injection problems and the incomplete combustion associated with it. The reduction in viscosity is possible by various methods such as dilution, micro-emulsification, pyrolysis and trans-esterification (Bak *et al.*, 1996). Biodiesel is generally produced by the trans-esterification of refined oils with short chain alcohols. Biodiesel is produced along with glycerin by the reaction between triglycerides and monohydric alcohol in the presence of a catalyst. The stoichiometry of the reaction requires the use of three moles of alcohol for every mole of triglyceride to produce three moles of alkyl ester and one mole of glycerol. The process involves a three-step reversible reaction where diacylglycerols and monoacylglycerols are formed as reaction intermediates (Vicente *et al.*, 2004). These stoichiometric amounts are difficult to employ in practice because of the volatile nature of methanol and the reversible nature of the reaction. Hence methanol in excess of the stoichiometric amounts is needed to shift the equilibrium toward the production of Fatty Acid Methyl Esters (FAME).

The conventional catalysts employed for trans-esterification reaction include strongly basic or acidic solutions such as sodium hydroxide, potassium hydroxide and sulphuric acid. Studies on the trans-esterification of soybean oil have shown that alkali catalysed reaction occurs at a much faster rate than acid catalysed reaction (Freedman *et al.*, 1986). Trans-esterification using alkaline catalysts provides higher conversion percentage even when subjected to lower temperature and shorter reaction times (Ma and Hanna, 1999). The use of these homogenous catalysts reduces the reaction temperature and controls product selectivity (Benjapornkulaphong *et al.*, 2009). However, they are associated with problems such as their sensitivity to free fatty acids and water present in the oil feedstocks and alcohol (Yan *et al.*, 2009). The formation of soap resulting from reaction between free fatty acids and basic catalysts complicates the glycerol separation process thereby significantly affecting the yield of methyl esters. The strong acidic or basic catalysts are highly corrosive and should be removed from the product mixture. The removal of catalyst to purify the product requires the use of large quantities of water leading to the production of waste water (Yan *et al.*, 2009). The employment of a heterogeneous catalytic system involving an environment friendly solid support can answer the problems arising due to the use of homogenous catalysts. The advantages of heterogeneous catalytic system include ease of regeneration, recycling of catalyst, ease in handling and scale-up.

The source of the oil also determines the quality of the biodiesel obtained and thereby determines its suitability as a fuel. Biodiesel had been produced for the past three decades from various sources of oil such as castor, palm, soybean, sunflower, coconut, rapeseed, rice bran and tung oil (Jothiramalingam and Wang, 2009). Rice bran oil has been found to be advantageous in the production of biodiesel since it is produced in high quantities in South Asian countries such as China, India. Rice bran is a byproduct obtained from the outer layers of the brown rice kernel during milling to produce polished rice. It is not a common source of edible oil compared to other cereal or seed sources such as corn, cotton or soybean. The presence of lipase in the rice bran causes hydrolysis and leads to the production of fatty acids which makes consumption of crude rice bran oil deleterious (Ju and Vali, 2005). The stabilization of rice bran oil for consumption is an expensive process. Degummed and dewaxed rice bran oil is sufficient for the production of biodiesel making it an inexpensive raw material (Ju and Vali, 2005). Biodiesel obtained from rice bran oil can be used without any modifications to the engine (Saravanan *et al.*, 2009).The inherent high free fatty acid content of rice bran can further aid the trans-esterification reaction. Due to the superior qualities of biodiesel derived from rice bran oil, it may be advantageous to identify novel catalytic strategies to improve yield, quality, reduce time and cost which can aid in offsetting the looming global energy crisis. However, research on use of nanostructured catalysts for conversion of rice bran oil to an effective biofuel has not yet taken off and this forms the main crux of this work.

In this study, maximum yields of bio-diesel were successfully obtained using mesoporous SBA-15 silica material as heterogeneous catalyst. The synthesized mesoporous SBA-15 silica material possessed well-ordered narrow hexagonal pores with a tunable size ranging between 5 and 15 nm. In addition, it offers higher surface area and more number of active sites which may enable maximum conversion of oil to biodiesel. The presence of numerous active centers may also serve to improve the rate of the trans-esterification reaction tremendously. This catalyst can be recycled and reused because of its heterogenic nature. Production of biodiesel using SBA-15 reduces the complications associated with homogeneous catalysts to a great extent.

MATERIALS AND METHODS

Materials: Commercially available brand of rice bran oil,(Oryza, Kaleeswari refinery Pvt. Ltd.) was used without further purification. Methanol and sodium hydroxide were purchased from Merck India. PluronicsP-123 and Tetra Ethyl Orthosilicate (TEOS) were purchased from Sigma-Aldrich Pvt. Ltd., USA and all were used as such without further purifications.

Preparation of SBA-15: SBA-15 was synthesized using the procedure reported by Gandhi *et al.* (2010). Briefly, five grams of P-123 tri-block copolymer was taken in 60 mL of deionized water and the pH was maintained at 2 by adding 60 mL of 2N HCl. Nine grams of TEOS was added to the reaction mixture as the silica source. Then it was stirred for 24 h followed by refluxing at 80°C for another 24 h for aging. The precipitate obtained was filtered, washed with 2 L of deionized water and dried at 100°C for 12 h. Finally, calcination was done at 550°C for 6 h to obtain mesoporous SBA-15.

Trans-esterification: Biodiesel (FAME) was produced using trans-esterification reaction (Fig. 1) after optimization of time and reactant quantities by studying their effect on the reaction yield. Initially the oil was heated well in order to remove the moisture content, if any. A small quantity of NaOH was dissolved in specific quantities of methanol and stirred along with SBA-15 and 100 g of oil at about 70-80°C for 1 h. The biodiesel and the glycerol layers were separated using separating flask. The respective layers were subjected to further characterization to confirm their identity.

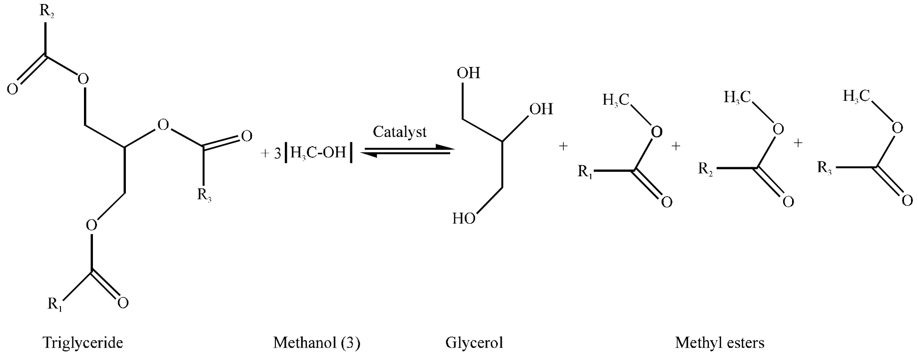

Fig. 1: Trans-esterification reaction involved in the production of biodiesel

Characterization techniques: The products obtained from trans-esterification were subjected to FTIR (Fourier Transform Infrared Spectrometry) (Spectrum 100, Perkin Elmer, USA). The biodiesel sample was also analyzed using GC-MS (Clarus 500, Perkin Elmer, USA). The sample was introduced at a split ratio of 1:20 in the temperature range 50 to 300°C in order to confirm the conversion percentage.

The morphology of the SBA-15 was characterized using field emission scanning electron microscopy (JSM 6701F, JEOL, Japan). The sample was placed on a brass stub using a double-sided carbon tape and sputter coated with a thin layer of platinum before being introduced in the specimen chamber for imaging. The transmission electron micrographs were obtained using a field emission transmission electron microscope (JEM 2100F, JEOL, Japan) after dispersing the sample on a copper grid. The FTIR spectrum was recorded between 4000-400 cm^{-1} using the KBr pellet mode. The crystalline phases of the catalyst were identified using X-ray diffraction (D8 Focus, Bruker, Germany). The small angle x-ray diffraction patterns were recorded between 0.5 to 10° and the x-ray diffraction pattern between 2θ values of 10 to 60° with a step size of 0.001 and scan rate was 1 step/second. The powdered sample was irradiated with Cu-Kα radiation to record the XRD pattern. The surface area of the SBA-15 was recorded using BET technique (ASAP 2020, Micromeritics, USA).

RESULTS AND DISCUSSION

Characterization of the catalyst: The mesoporous SBA-15 catalyst was synthesized using a modified thermal process (Gandhi *et al.*, 2010) and the catalyst was characterized by electron microscopy. Figure 2 shows the scanning and transmission electron micrographs of the SBA-15 which reveals the presence of highly ordered hexagonal pores with tubular morphology.

The surface area of SBA-15 was found to be 623 m^2/g which was in agreement with the values reported earlier (Gandhi *et al.*, 2010). The FT-IR spectrum showed peaks at 1086, 800 and 3459 cm^{-1} due to vibrations of the Si-O-Si, Si-OH and -OH bonds (Gandhi *et al.*, 2010). The XRD pattern of the SBA-15 samples showed peaks at 2θ values 0.7, 1.2 and 1.8° indicating the formation highly oriented mesoporous SBA-15 (Chong *et al.*, 2004).

The trans-esterification of rice bran oil was carried out as shown in the schematic diagram (Fig. 3).The biodiesel produced should be in agreement with the required quality standards and

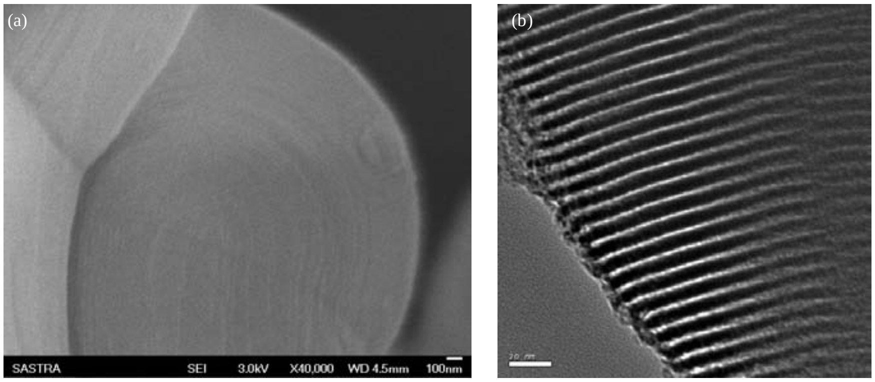

Fig. 2(a-b): (a) Scanning electron micrograph of SBA-15 and (b) Transmission electron micrograph of SBA-15

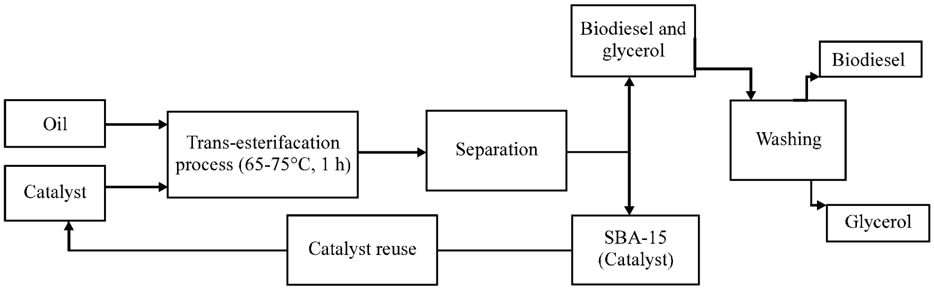

Fig. 3: Scheme for the production of biodiesel

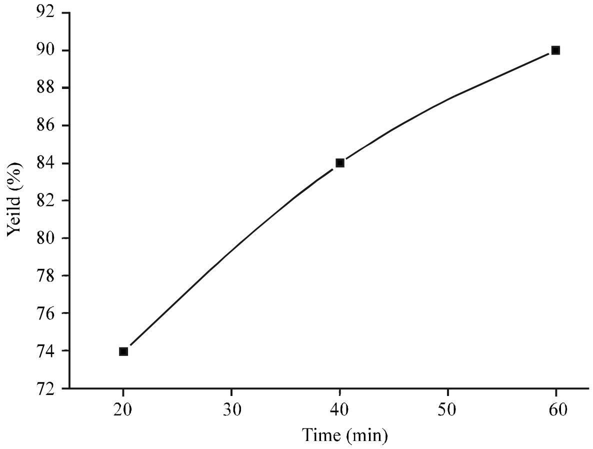

Fig. 4: Dependence of FAME yield on time

hence it is necessary to minimize the amount of unreacted oil, monoglycerides and diglycerides. Optimal reaction conditions for the above mentioned trans-esterification reaction using SBA-15 needs to be studied by conducting batch type reactions to evaluate the effect of parameters namely molar ratio of the reactants, the catalyst amount and time of reaction.

Effect of catalyst amount, reaction time and methanol on FAME yield: The effect of catalyst amount on the yield of trans-esterification reaction was studied by employing three different catalyst amounts 0.05, 0.1 and 0.2 g. It was found that catalyst amount of 0.1 g exhibited the maximum catalytic activity and could produce nearly 91% yield. The analysis of the reaction products at various time intervals to quantify the yield of methyl ester revealed that within 20 min of the reaction, the yield reached almost 74% showing that the increased amount of fatty acids inherently present in rice bran oil allowed faster conversion to their methyl esters. A maximum yield of 91% was obtained after a reaction time of around 1 h and hence the optimal time for the reaction was decided to be one hour. Figure 4 shows the increase in yield with respect to time.

Effect of methanol on FAME yield: The influence of methanol was examined by employing varying oil:methanol ratios. The catalyst amount of 0.1 g was used with different oil:methanol ratios such as 1:5, 1:10, 1:15, 1:20, 1:25 and the trans-esterification reaction was carried out at 70-80°C. Figure 5 represents the effect of reactant mole ratios on the yield of FAME. Molar ratio

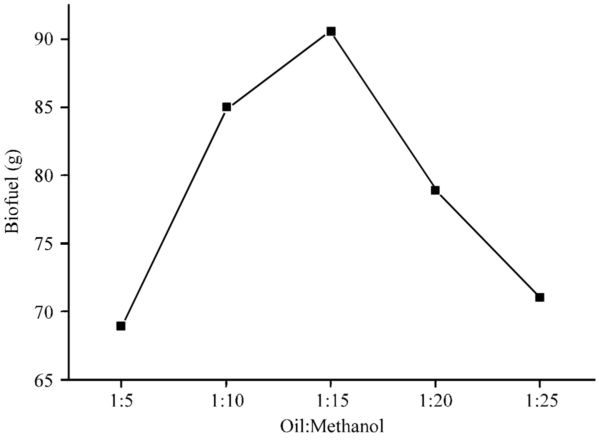

Fig. 5: Effect of methanol on FAME yield

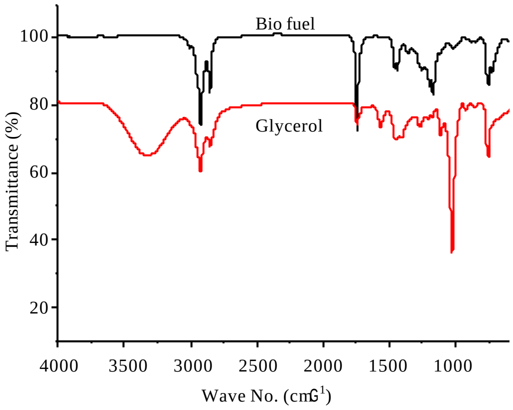

Fig. 6: FTIR spectrum of biodiesel and glycerol

of 1:5 showed a yield of 69%, while the yield increased to 85 and 90.6% when the ratio was increased to 1:10 and 1:15, respectively.

The trans-esterification reactions were performed using the optimum conditions and the product obtained was washed with water. The products obtained after trans-esterification were analyzed using FTIR (Fig. 6). The presence of a strong ester band at 1742 cm^{-1} in the trans-esterified oil fraction confirms the formation of esters and this band is absent in the glycerol fraction. Further, the band at 750 cm^{-1} which may be attributed to the rocking of multiple methylene groups is observed only in the trans-esterified fraction due to the presence of long chain fatty acid esters. The pronounced broad band at 3311 cm^{-1} for glycerol indicates the presence of extensively hydrogen bonded hydroxyl groups. This band is not prominent in the oil fraction. Further confirmation of the extent of trans-esterification was obtained when the trans-esterified oil fraction was subject to GC-MS analysis (Fig. 7). The oil fraction showed 98.6% of methyl esters indicating excellent conversion efficiency achieved by the mesoporous catalyst system. Rice bran oil has been reported to contain a large quantity of free fatty acids that include myristic acid, palmitic acid, palmitoleic acid, stearic acid, oleic acid, linoleic acid, linolenic acid, arachidic acid and behenic acid (Ju and Vali,

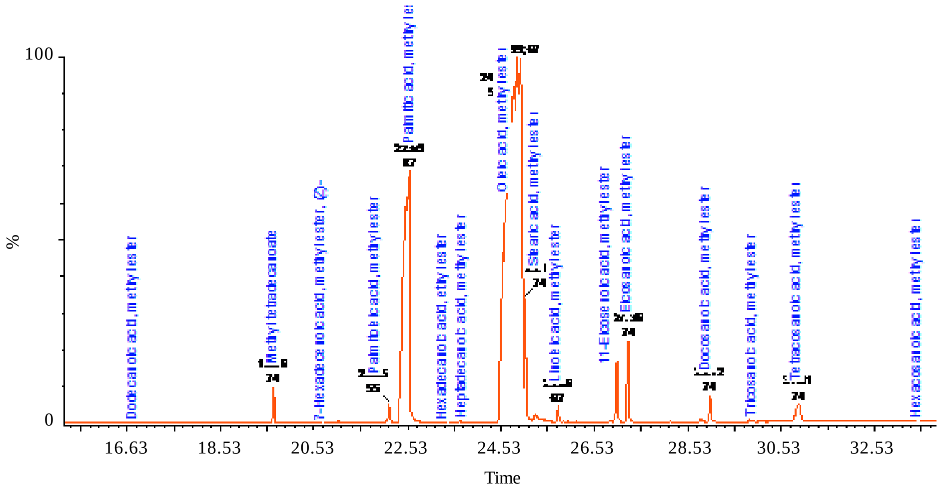

Fig. 7: GC of biodiesel

Table 1: Composition of trans-esterified oil obtained using SBA-15 catalyst

Peak name	Peak area (%)
Dodecanoic acid, methyl ester (lauric acid, methyl ester)	0.0083
7-Hexadecanoic acid, methyl ester (Z)-	0.0148
Methyl tetradecanoate	0.2242
Pentadecanoic acid, methyl ester	0.0160
9-Hexadecanoic acid, methyl ester (Z)-(palmitoleic acid, methyl ester)	0.1153
Hexadecanoic acid, methyl ester (palmitic acid, methyl ester)	17.9897
Heptadecanoic acid, methyl ester,(1.margaric acid methyl ester)	0.0405
9-Octadecenoic acid (Z)-, methyl ester (oleic acid, methyl ester)	75.1399
Octadecanoic acid, methyl ester (stearic acid, methyl ester)	2.1755
9,12-Octadecadienoic acid (Z,Z)-, methyl ester (linoleic acid, methyl ester)	0.2273
Nonadecanoic acid, methyl ester,	0.0104
9,12,15-Octadecatrienoic acid, methyl ester (Z,Z,Z)-(linolenic acid, methyl ester)	0.0201
7,10,13-Eicosatrienoic acid, methyl ester	0.0455
11-Eicosenoic acid, methyl ester	0.6390
Eicosanoic acid, methyl ester	0.9249
13-Docosenoic acid, methyl ester (Z)-	0.0384
Docosanoic acid, methyl ester (behenic acid, methyl ester)	0.3007
Tricosanoic acid, methyl ester,	0.0343
Tetracosanoic acid, methyl ester	0.5078
Heptadecanoic acid, methyl ester	0.0281
Hexacosanoic acid, methyl ester	0.0848

2005). The GC-MS data reveals that all these acids have been converted to their respective methyl esters and Table 1 shows the major components obtained from the GC-MS analysis of the trans-esterified oil fraction.

Comparison of SBA 15 with other catalysts: Different homogenous catalysts namely sulphuric acid, nitric acid and sodium hydroxide have been used for the trans-esterification reaction. It was

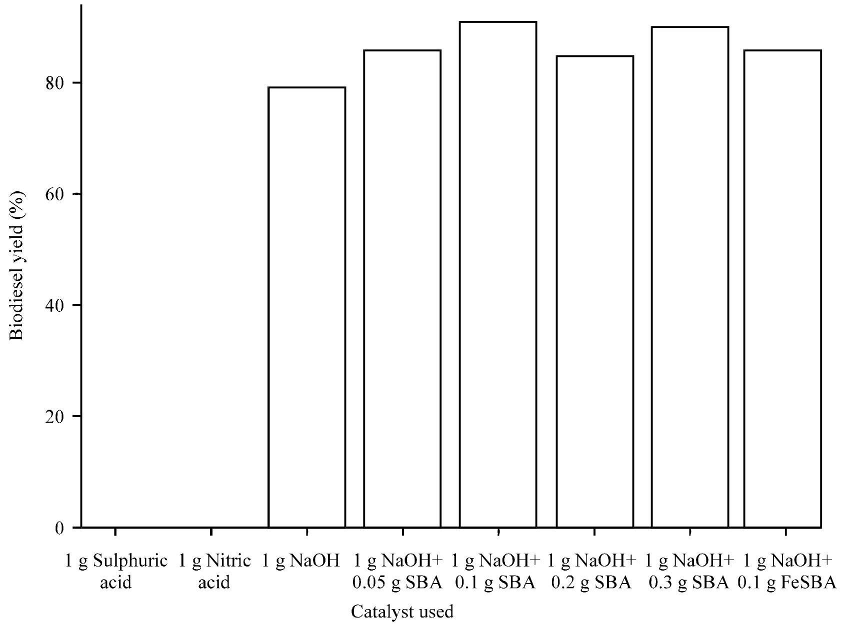

Fig. 8: Comparison of yields obtained using various catalyst

found that after one hour, oil:methanol ratio of 1:15, SBA-15 when used in amounts of 0.1 g gave better yields than other homogenous catalysts (Fig. 8) while the acidic catalysts showed no conversion after 1 h. Thus, the presence of the high surface area with oriented pores served to increase the rate of trans-esterification reaction. This may be attributed to the increase in the number of active sites as well as the proximity of the catalytic groups with the reactant as it gets trapped within the highly ordered pores. Thus, this demonstrates the potential of SBA-15 as a novel nanostructured trans-esterification catalyst.

Analysis of transesterified oil (biodiesel): The properties of the biodiesel obtained using the mesoporous silica were compared with ASTM limits to understand its feasibility for use as an automobile fuel (Table 2). It was observed that the trans-esterified oil fraction had all properties within the permissible limits suggesting that it could be used as an automobile fuel. The presence of 98.6% ester content in the biodiesel sample shows that catalyst system employed is very effective. The absence of both bound and free glycerol confirms the purity of the biodiesel.

Cetane index is used to identify the quality of combustion and a cetane index of 49 obtained for the biodiesel sample is in accordance with the American Standards. The calorific value of the biodiesel was found to be 38,320 kJ kg^{-1} which is close to that for diesel (42,000 kJ kg^{-1}). Higher calorific values can be achieved when used as blends with diesel facilitating proper combustion in IC engines. Low amounts of sulfur in the biodiesel will also result in reduced SO_x emissions.

Table 3 shows the distillation characteristics of the biodiesel obtained from rice bran oil after trans-esterification using mesoporous silica. The distillation characteristics indicate that the biodiesel possesses a narrow distillation range with nearly 95% recovery achieved by 356°C. Similar narrow distillation ranges have been reported for the biodiesel obtained by trans-esterification of soybean oil (Qi *et al*., 2009).

Table 2: Properties of Biodiesel obtained from rice bran oil using mesoporous catalyst

Parameter	Observed value	Limits as per ASTM: D6751 2001[a]
Water content by KF method	0.2%	≤0.05%
Kinematic viscosity @ 40°C in cSt	5.07	1.9 to 6.0
Sulphated ash	0.002%	0.02%
Flash point PMCC method	168°C	>100°C
Copper strip corrosion @ 100°C for 3 h	Not worse than class 1	Class 3
Acid number as mg of KOH g^{-1}	0.12	≤0.50
Iodine value	96.9	-
Phosphorus as P	Nil	0.001%
Calculated cetane index	49	>47
Alkaline matter (mg kg^{-1})	Nil	<5
Sulphur content	0.04%	<0.05%
Calorific value (kJ kg^{-1})	38320	
Ester content	98.6%	-
Methanol content	Nil	-
Monoglyceride content	Nil	-
Diglyceride content	Nil	-
Triglyceride content	Nil	-
Free glycerol	Nil	≤0.02%
Total glycerol (m/m)	Nil	≤0.24%

[a]Annual book of ASTM standards (American society for testing and materials, Vol. 05.01, WestConshchocken, PA), 1998

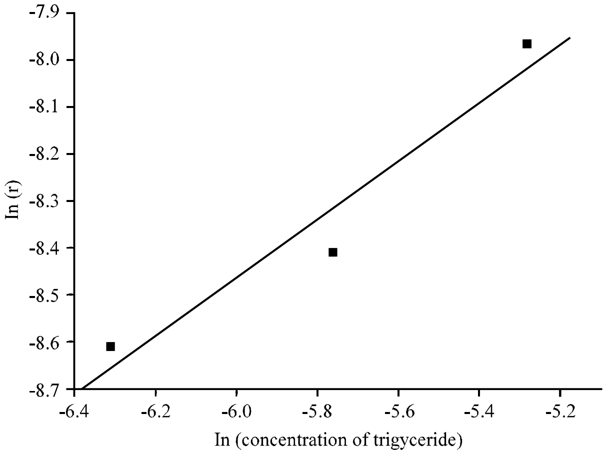

Fig. 9: Reaction fitting to first order kinetics

Kinetic studies: The rate of change of triglyceride concentration with respect to time was found by calculating the amount of FAME obtained at various reaction periods since the FAME obtained would be due to the fatty acid present in the triglyceride. Stoichiometrically, three moles of FAME will be obtained from one mole of triglyceride. Thus from the plot of concentration of triglyceride present versus time the rate of the reaction was determined. Assuming the hydrolysis to be independent of rate kinetics and since the methanol concentration was high, the order of the trans-esterification reaction was found to resemble pseudo first order kinetics (Freedman *et al*., 1986) (Fig. 9).

Table 3: Distillation temperatures of biodiesel from rice bran oil using mesoporous silica catalyst

10% Recovery	336°C
50% Recovery	344°C
90% Recovery	354°C
95% Recovery	356°C
Final boiling point	360°C

CONCLUSION

The biofuel samples obtained by using SBA-15 (0.1 g) have shown best results both in case of qualitative and quantitative aspects from the trials conducted. This fuel when blended with diesel in appropriate proportions has the potential to be used as an automobile fuel. The use of a nanostructured catalyst has been demonstrated to be more superior to conventional catalysts and overcomes many of the shortcomings in the previous methods.

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