Namrata D. Gaikwad and Parag R. Gogate*

Synthesis and application of carbon based heterogeneous catalysts for ultrasound assisted biodiesel production

Abstract: In the present work, carbon based heterogeneous acid catalysts have been prepared using various synthesis approaches based on the use of sustainable starting materials. The properties of the catalysts have been investigated using Fourier transformed infra-red (FTIR), scanning electron microscopy (SEM), temperature-programmed desorption (NH_3-TPD), X-ray diffraction (XRD) and thermogravimetric analysis (TGA). The screening studies for catalytic activity in biodiesel production have established that a catalyst prepared by the approach of hydrothermal carbonation followed by sulfonation from the commercial cellulose showed the best catalytic performance and hence was used in a detailed parametric study for the ultrasound assisted (low frequency 20 kHz horn with power of 120 W) synthesis of biodiesel. The study also involved the use of palm fatty acid distillate (PFAD) as the sustainable feedstock. The obtained optimum conditions were a molar ratio of alcohol to oil of 6:1, catalyst concentration of 3 wt%, temperature as 333 K and power dissipation of 120 W with a reaction time of 3 h. Use of different co-solvents (0.2% of PFAD feedstock) was investigated where THF was found to be the best co-solvent. Overall the novelty of the work can be established in terms of the use of sustainable approaches for catalyst synthesis and its subsequent application for biodiesel synthesis based on the use of sustainable feedstock as a PFAD.

Keywords: biodiesel; esterification; heterogeneous catalyst; intensification; ultrasound.

DOI 10.1515/gps-2014-0079
Received October 26, 2014; accepted January 1, 2015

***Corresponding author: Parag R. Gogate,** Institute of Chemical Technology, Chemical Engineering Department, Matunga, Mumbai 40019, India, e-mail: pr.gogate@ictmumbai.edu.in
Namrata D. Gaikwad: Institute of Chemical Technology, Chemical Engineering Department, Matunga, Mumbai 40019, India

1 Introduction

Increase in the worldwide population and industrialization have also simultaneously increased energy demands and hence fossil fuel consumption leading to continuous speculations about how long these fuel sources can last. Also use of conventional sources leads to significant air pollution either from coal-fired thermal power stations or petro-diesel engine based vehicular emissions [1], and greater environmental concerns in recent years have prompted research into alternative clean, sustainable and affordable fuels. One of the environment friendly alternatives is biodiesel, which can also offer advantages such as sustainability, biodegradability, lower sulfur and aromatic content as well as lower emissions. Biodiesel also has certain disadvantages such as higher viscosity, higher cloud point and pour point, higher nitrogen oxides (NO_x) emissions, higher cost of production, injector coking and engine compatibility problems [2].

Biodiesel is generally produced using transesterification or esterification of various feedstock such as edible oil [3], non-edible oils [4, 5], waste cooking oil, etc. [6–9] based on the use of different catalysts such as acid or alkali both in homogenous or heterogeneous forms. Although much of research has been done in terms of biodiesel production, the process has not been successful on a commercial scale mostly because of the higher cost of raw materials and separation issues. The raw material cost typically contributes to about 70–80% of the total cost of production for biodiesel and hence researchers are focusing their attention on the low cost feedstock [1]. In order to lower the cost of biodiesel, there is need for using non-edible and inexpensive feedstock as well as applying process intensification concepts. The fatty acid cut can be an alternative, cheaper starting material though not much work has been carried out using fatty acid cuts. The present work investigates the use of palm fatty acid distillate (PFAD), which is generated as a byproduct during the refining of palm oil [10, 11], as the feedstock for the synthesis of biodiesel. There have not been many studies based on the use of this

sustainable feedstock especially using the heterogeneous catalysts.

Biodiesel production can be carried out using homogeneous, heterogeneous or enzymatic catalysts [12, 13] although homogeneous base catalysts, such as sodium hydroxide (NaOH) or potassium hydroxide (KOH) have been generally used due to low temperature requirement, higher conversions and faster reaction rates [14, 15]. Base-catalyzed reactions give significant processing problems for feedstock, having higher contents of free fatty acids [16] and also the presence of water decreases the methyl ester yield due to hydrolysis of the triglycerides to diglycerides forming free fatty acid [2]. Heterogeneous catalyst is beneficial over homogeneous catalyst in terms of ease of the separation of the catalyst from the reaction mixture and the possibility of reusability of the catalyst. Alkali metal oxides like CaO are mostly used due to their relatively high basic strength, low solubility in methanol and the fact that they can be synthesized from cheap sources such as limestone and calcium hydroxide [17, 18]. However, CaO [18] gives processing problems such as leaching into the reaction mixture, rapid hydration and carbonation in the air leading to reduced activity and also permanent poisoning due to adsorption on the active sites. Another disadvantage of the heterogeneous catalyst is that the heterogeneously catalyzed reaction requires extreme reaction conditions and higher methanol to oil ratios in order to increase the yield of biodiesel and reduce the required reaction time, leading to energy intensive operation and significant downstream separation problems [14, 18, 19]. Enzyme catalysts offer significant disadvantages such as higher cost of enzyme, slow reaction rate and enzyme deactivation in the presence of an alcohol [20]. Thus, the approach of using a sustainable heterogeneous acid catalyst with some intensification mechanism appears to be the optimum approach for biodiesel synthesis from sustainable feedstock such as PFAD. The present work has investigated the use of a sustainable carbon based catalyst prepared using cellulose in the biodiesel synthesis process which is also intensified using ultrasound. The work also investigated the use of waste paper as a source for the synthesis of carbon based catalysts for the first time. In the typical synthesis of carbon-based catalysts, carbohydrates are carbonized and then activated with sulfonic groups [21]. Takagaki et al. [22] reported that SO_3H group did not leach in FFA giving operational advantages. The carbon based catalyst shows larger-pore volume and pore size, allowing better access for reactants and higher acid sites [23] as well as providing a good degree of reusability.

Since heterogeneous catalyst based reactions can give slower reaction rates due to the mass transfer limitations, intensification aspects have been investigated based on the use of ultrasound [24], which gives cavitational effects in terms of local hot spots and liquid circulation coupled with intense turbulence. For the case of biodiesel synthesis, the physical effects caused by shock waves and microstreaming generated during asymmetric cavity collapse is expected to give dominating effects for the intensification [25]. In heterogeneous liquid/liquid reactions, cavitating conditions result in the formation of very fine emulsions, which increases the surface area available for the reaction between the two phases giving increased rates of reaction [9].

Overall, it can be said that the use of heterogeneous catalyst slows down the process due to mass transfer limitations and hence the application of intensification approaches is required. Study of the synthesis of sustainable heterogeneous catalyst that can be applied for the biodiesel production as well as the use of low cost feedstock is also important to make the complete process environmentally friendly and economical. Considering these aspects, the selected system for the present work is intensified biodiesel production (using ultrasound) from sustainable raw material, like PFAD, in the presence of a heterogeneous catalyst synthesized from cellulose. The work also compared the different approaches for the synthesis of a catalyst from different raw materials based on the activity for biodiesel synthesis, which has not been investigated in any of the earlier works to the best of our knowledge.

2 Materials and methods

2.1 Materials

PFAD was obtained from Godrej Ind. Ltd. (Mumbai, India) as a gift sample. The typical composition of PFAD was palmitic acid (41.6%), oleic acid (33.5%), stearic acid (3.8%), linoleic acid (6.7%), myristic acid (1%), eicosanoic acid (0.4%), eicosenoic acid (0.1%), palmitoleic acid (0.2%), triglycerides (4.5%), diglycerides (3.7%) and monoglycerides (2.6%). Cellulose powder (AR grade), sulfuric acid (98%), potassium hydroxide (AR grade), methanol, hydrochloric acid (HCl), sodium hydroxide (NaOH), oxalic acid (AR grade), potassium bromide (KBr) (spectroscopic grade), tetrahydrofuran (THF), n-Hexane, dimethyl sulfoxide, toluene and amberlyst-15 were procured from S.D. Fine Chemicals Pvt. Ltd. (Mumbai, India).

2.2 Methods

2.2.1 Catalyst preparation

2.2.1.1 Hydrothermal carbonization: Experiments of hydrothermal carbonization were performed using an autoclave procured from Amar Autoclaves and Equipments (Mumbai, India). Autoclave

used in the work has a capacity of 0.0001 m^3 and was made up of hastelloy®. The autoclave was equipped with a 45° inclined pitched blade turbine impeller, temperature controller, pressure indicator and speed regulator. Cellulose powder (0.010 kg), deionized water (0.080 kg) and sulfuric acid (0.0002 kg) were mixed and heated to 453 K for 4 h in an autoclave. After the completion of the reaction, the mixture was cooled to room temperature and subjected to vacuum filtration to obtain a brownish black carbon material. The collected solid was further utilized in sulfonation [26].

2.2.1.2 Sulfonation: Sulfonation was carried out in a 25×10^{-5} m^3 glass reactor of 0.08 m internal diameter provided with a six blade stirrer of 0.02 m diameter and a condenser to achieve reflux operation. A guard tube filled with calcium chloride was also provided to absorb the moisture. Inert atmosphere was maintained using nitrogen gas. Constant reaction temperature was maintained using an oil bath procured from Ganesh Scientific Industries (Mumbai, India). During the actual sulfonation process, the obtained carbon material (0.005 kg from hydrothermal carbonization) was heated in 0.0002 m^3 of concentrated H_2SO_4 (98%) at 423 K under nitrogen atmosphere. After heating for 15 h and subsequent cooling to room temperature, 0.001 m^3 of distilled water was added to the mixture to form a black precipitate. The precipitate was washed repeatedly in hot distilled water (above 353 K) until neutral pH was obtained in the wash water. The catalyst was obtained after drying at 393 K overnight in an oven [21–23].

2.2.1.3 Procedure for the preparation of starting material for catalyst synthesis from waste paper: The use of paper in different applications is increasing day by day and the generated waste after use is generally landfilled or incinerated which creates significant environmental issues and hence alternate approaches for reuse needs to be developed. Considering this, one of the sustainable approaches has been investigated in the current work demonstrating the use as a possible source for the preparation of the catalyst. Delignified waste paper, obtained as per the process reported in earlier work of Subhedar and Gogate [27], was used as a cellulosic raw material for the synthesis of the catalyst. Mechanical crushing of delignified paper in the presence of distilled water was performed initially followed by overnight drying and subsequent mechanical crushing to get a solid material with large surface area. The prepared material was used for hydrothermal carbonization followed by sulfonation as per the process described in the earlier sections.

In addition, commercially obtained cellulose was also used as a feedstock for the synthesis of the catalyst using different approaches based on carbonization and sulfonation such as only hydrothermal carbonization, only sulfonation, sulfonation followed by hydrothermal carbonization and hydrothermal carbonization followed by sulfonation. The aim was to get optimum catalyst with the best possible catalytic activities based on the feedstock and the approach of synthesis.

2.2.1.4 Catalyst characterization: Fourier transformed infrared (FTIR) spectra of untreated and pretreated solid materials were recorded on a Perkin Elmer FTIR spectrometer. Data were collected over the 400–4000 cm^{-1} wavelength range with 256 scans for each sample at 4 cm^{-1} resolution. About 2×10^{-6} kg samples were mixed with 1.2×10^{-4} kg of spectroscopic grade KBr followed by pressing in a hydraulic press using a pressure of 27.57 Pa to produce pellets for the analysis.

The thermal stability of the catalyst was checked by thermogravimetric analysis (TGA) using the METTLER TG50. The catalyst (approximately 5×10^{-7} kg) was heated in the sample compartment over the temperature range of 323–773 K at a constant rate of 10°C/min using the METTLER TOLEDO TC15 TA controller.

The surface morphology of the catalyst was analyzed at 1000 times magnification using 5 kV of accelerating voltage over the 10–20 μm scale at a focal distance of about 10 μm. The scanning electron microscope used for analysis was JEOL/JSM 6380 LA.

The acidity of the catalyst was determined using 10% NH_3-temperature-programmed desorption (NH_3-TPD) analysis using the Micrometrics AutoChem II 2920 V4.03 analyzer. The catalyst (approximately 2×10^{-5} kg) was charged into a U-shaped quartz sample tube and heated at 453 K under the flow of helium for degasification. After cooling to an ambient temperature of 303 K, ammonia was injected into the sample for saturation. The thermal desorption of ammonia was recorded under the flow of helium by raising the temperature at a rate of 5°C/min up to 453 K.

The X-ray diffraction (XRD) analysis of the catalyst was also performed to determine the extent of the crystalline nature of the molecules. Sample was taken in a sample container and X-rays were passed through the sample in the 2θ scale over the range of 5–80° at temperature of 298 K, using the Bruker/D8 Advance instrument.

2.2.2 Synthesis of biodiesel

The synthesized catalyst was used in actual biodiesel production studies based on the sustainable feedstock and intensification using ultrasound. The process of esterification of PFAD used in the investigation consists of two steps: hydrolysis followed by esterification. Hydrolysis was required to eliminate any triglycerides present in the feedstock which can interfere in the esterification (reversible nature) to give possibly lower reaction rates.

2.2.2.1 Hydrolysis: The PFAD obtained from the local industry contained triglycerides (4.5%), diglycerides (3.7%) and monoglycerides (2.6%). The addition of water leads to the hydrolysis of triglycerides, which increases the FFA content in the feedstock so that esterification can be effectively performed. The hydrolysis reaction was carried out in a reactor (0.08 m internal diameter) of volume 25×10^{-5} m^3 equipped with a six blade turbine impeller rotating at 20 rps. First, 0.1 kg of PFAD was melted in the reactor at 363 K within 600 s. Water (0.025 kg) and sulfuric acid (0.5% w/w) as a catalyst, were added to the melt. The reaction mixture was vigorously agitated at 20 rps for 1800 s in an oil bath. After the reaction, the reaction mixture was kept in the oil bath for 300 s to separate into two phases. The organic phase was separated from the aqueous phase and further used for the esterification reaction [11].

2.2.2.2 Esterification

2.2.2.2.1 Conventional method: Esterification using conventional approach was performed in a 15×10^{-5} m^3 reactor (0.05 m

diameter) equipped with reflux condenser. The reactor was kept in a water bath procured from Ganesh Scientific Industries (Mumbai, India) to maintain constant temperature. An overhead six blade glass stirrer having one inch (2.54 cm) diameter was used to achieve uniform mixing of the reactants. 0.050 kg of organic phase from the hydrolysis stage was placed in the reactor at 333 K and kept under these conditions for 1200 s. The reaction was started by the addition of 0.018 kg methanol and solid acid catalyst at loading of 3% w/w of PFAD. The reaction mixture was maintained at 333 K in an oil bath for 3 h with stirring at 20 rps to eliminate the effect of the external mass transfer limitations. Samples were taken at regular intervals from the liquid reaction mixture and quenched for termination of reaction. Subsequently, the mixture was separated from the solid acid catalyst by centrifugation at 100 rps for 20 min and used in the analysis to monitor the progress of the reaction.

2.2.2.2.2 Ultrasound assisted approach: The ultrasound assisted approach was based on the use of an ultrasonic horn procured from Dakshin Pvt. Ltd (Mumbai, India). The ultrasonic horn operates at a frequency of 20 kHz with a power rating of 120 W and has a tip diameter of 0.01 m. The horn was immersed at a depth of 0.01 m into the reaction medium in the 15×10^{-5} m^3 glass reactor, which was kept in a water bath to maintain constant temperature. Magnetic stirring was also used to provide additional stirring. All the reactants were quantitatively similar to that described in the conventional method and, also the approach for the monitoring of the reaction progress was the same as used in the conventional method.

2.2.2.3 Analysis of the esterification reaction: Reaction samples were collected after the specific time intervals. The withdrawn reaction mixture was separated from the solid acid catalyst by centrifugation at 100 rps for 1200 s. The organic layer was separated from the aqueous layer, followed by the addition of sodium sulfate in the organic phase to remove the residual moisture content. The acid value of the samples in esterification reaction was determined by the acid base titration method. A sample of 0.0005 kg of organic layer was dissolved in 20×10^{-5} m^3 of neutralized methanol followed by heating at 333 K for 600 s to get a clear solution and titrated against alcoholic potassium hydroxide using phenolphthalein as an indicator. All the acid values were measured twice to confirm reproducibility and average values were used for the calculations. The conversion was calculated from the initial and final acid values for the reaction mixture. The acid value can be calculated from equation (1) as follows:

$$AV = \frac{\text{Burette reading} \times \text{mol.wt.KOH} \times \text{normality of KOH}}{\text{Wt. of oil}} \quad (1)$$

For the analysis of the properties of biodiesel, the removal of the residual methanol and THF, in the case of the experiments involving a co-solvent, was achieved using the rotavap at 343 K. The moisture content was measured by direct coulometric Karl Fischer titration according to ASTM D 6304. The flash point temperature of diesel fuel is the minimum temperature at which the fuel results into flashing momentarily upon application of an ignition source. The flash point was determined according to the ASTM D93 standard test method. The density of the prepared biodiesel was calculated using a density bottle of capacity 1×10^{-5} m^3 using the standard process of measurements. Viscosity of the biodiesel was measured using the Ostwald Viscometer. A viscometer was first filled with biodiesel, which was then sucked till the marked level. The time required for the movement of the biodiesel from one point to the other was noted and the procedure was repeated for the distilled water. Viscosity was calculated twice to confirm reproducibility and average values were reported.

Gas Chromatography–Mass Spectrometry (GC-MS) analysis of Fatty Acid Methyl Esters (FAME) after the removal of methanol and co-solvent by using rotavap was carried out for the qualitative analysis of the final product. The obtained methyl esters were analyzed using a Perkin Elmer (Clarus-500) GC-MS model with a flame ionization detector (FID), equipped with a BPX- 70 capillary column (30 m, 0.25 mm ID, 0.25 μm). Samples were prepared by adding 0.1 ml of FAME to 10 ml of n-hexane (0.1 μl of the samples were injected into column). The injector temperature was maintained at 493 K with a split ratio of 1:100 and the temperature of the detector was 523 K. The parameters for the oven temperature were programmed to increase from 333 K (with 2 min holding time) to 523 K (with 300 s holding time) at the ramping rate of 13°C per min.

3 Results and discussion

3.1 Catalyst characterization

The present work compared the different approaches of catalyst preparation such as 1) only hydrothermal carbonization, 2) only sulfonation, 3) sulfonation followed by hydrothermal carbonization, 4) hydrothermal carbonization followed by sulfonation.

3.1.1 TGA analysis

TGA analysis of the catalyst deals with quantifying the weight loss with increasing temperature. TGA analysis was carried out to study the thermal stability of the prepared catalyst. The characteristics of weight loss with respect to temperature have been shown in the Figure 1. It can be seen from the figure that carbon based heterogeneous acid catalyst prepared from the hydrothermal carbonization followed by sulfonation of the commercially available cellulose, as well as the waste paper pretreated with ultrasonically assisted alkaline treatment as the precursor, showed weight loss of 6–7% up to 573 K followed by gradual weight loss till 773 K establishing the thermal stability of the prepared catalyst. The untreated cellulose shows thermal stability till 593 K with weight loss of 1–2%, but there is a significant weight loss with a marginal increase in the temperature above 593 K. Chabukswar et al. [11] also reported that TGA plots of synthesized catalyst indicated weight loss of only 3–4% up to 543 K

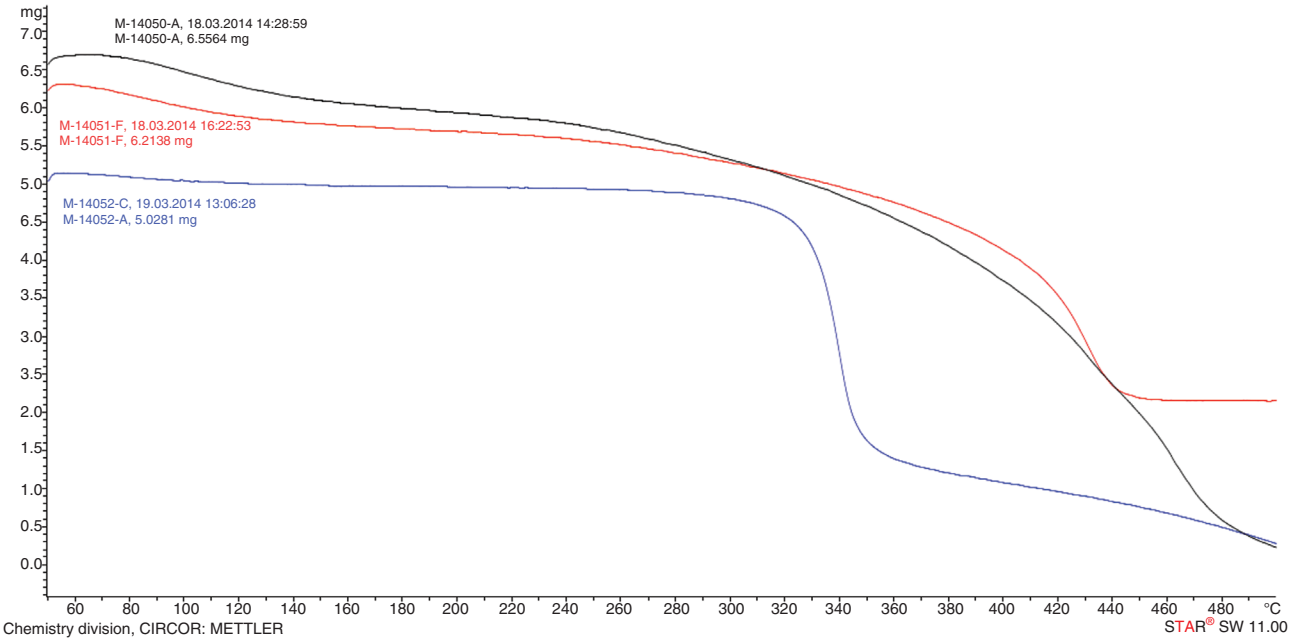

Figure 1 Comparison of different catalysts in terms of TGA. (A) Commercially available untreated cellulose, (B) catalyst obtained from hydrothermal carbonization followed by sulfonation of the commercially available cellulose, (C) catalyst obtained from hydrothermal carbonization followed by sulfonation of the waste paper pretreated with ultrasonically assisted alkaline treatment.

indicating its very good thermal stability. Beyond 543 K, the material showed a gradual weight loss up to 773 K indicating the loss of non-graphite carbon initially and then of the graphite carbon at the higher temperature. Shu et al. [28] also confirmed the thermal stability of carbon-based solid acid catalyst prepared by the sulfonation of carbonized vegetable oil asphalt at 533 K, and reported that initially marginal weight loss was observed due to the water content in the outer matrix of the catalyst.

3.1.2 SEM analysis

SEM analysis was performed to study the structural changes occurring during the hydrothermal carbonization followed by sulfonation of the commercially available cellulose and the waste paper pretreated with ultrasonically assisted alkaline treatment as the precursor and the obtained results are shown in Figure 2 along with the comparison with the basic structure of the feedstock. The images of untreated cellulose showed an irregular network structure and several closely linked long polymer chains, which after hydrothermal carbonization and sulfonation disintegrated to some extent with increased pore size, making more surface area available for the access of the reactant thereby increasing the catalyst activity. Nakajima et al. [29] and Okamura et al. [30] have reported similar structural changes after the treatment used for the synthesis of the catalyst.

3.1.3 NH_3-TPD analysis

NH_3-TPD analysis were also carried out to study the surface acidity in mmol/g of the untreated commercially available cellulose, the carbon based heterogeneous acid catalyst prepared from the hydrothermal carbonization followed by sulfonation of the commercially available cellulose and the catalyst obtained from the waste paper pretreated with ultrasonically assisted alkaline treatment as the precursor using the same route of synthesis as hydrothermal carbonization followed by sulfonation. The surface acidity was found to be 0.19 mmol/g, 1.79 mmol/g and 1.46 mmol/g, respectively, in the same order. Thus, from the surface acidity values, it can be established that the catalyst prepared from the hydrothermal carbonization followed by sulfonation of the commercially available cellulose has the highest acid content which can give higher catalytic effect for the esterification reaction leading to a possible increase in the conversion. Chabukswar et al. [11] reported that the acidity of the catalyst synthesized in the work was 2.5

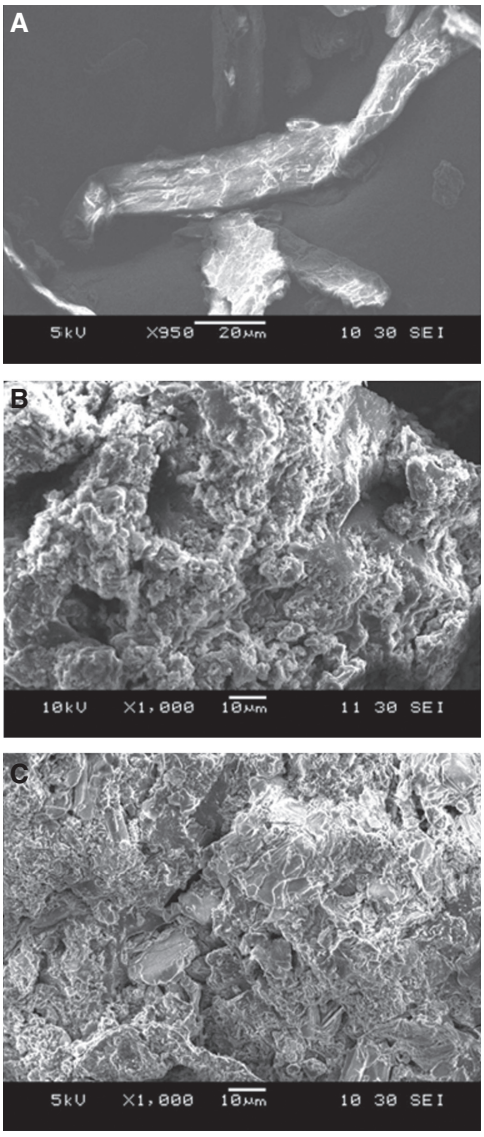

Figure 2 SEM characterization of feedstock and different catalysts. (A) commercially available untreated cellulose, (B) catalyst obtained from hydrothermal carbonization followed by sulfonation of the commercially available cellulose, (C) catalyst obtained from waste paper pretreated with ultrasonically assisted alkaline pretreatment.

mmol/g as compared to 0.8 mmol/g for the Amberlyst-15. Lou et al. [23] reported that for all the four carbohydrate-derived catalysts, the densities of SO_3H groups as main functional sites were in the range of 1.47–1.83 mmol/g. Mar and Somsook [31] reported a surface acidity of 1.53 mmol/g for the catalyst prepared by carbonization at 573 K followed by sulfonation.

Shu et al. [28] have reported that the carbon based catalyst has two distinct desorption peaks from 523 K to 573 K and 773 to 973 K that were assigned to the two types of acid sites as weak and strong acid sites, respectively. A broad desorption peak appeared at 773–973 K, which was due to the presence of strong acid sites. The appearance of weak and strong acidity can be ascribed to the influence of the size of the pore and the position of the acid site. Generally, the weak acidity is related to interactions among ammonia molecules in the pores, whereas the strong acidity is primarily related to interactions between the ammonia molecules and the pore walls of the catalyst.

3.1.4 XRD analysis

XRD analysis was also carried out in order to study how the atoms in a molecule are organized in a crystal structure. The obtained results are shown in Figure 3. The XRD pattern of the commercially available untreated cellulose and the two carbon based heterogeneous acid catalysts established broad and strong diffraction peak at (2θ=10–30°) and a weak diffraction peak (2θ=5–50°), which can typically be attributed to important characteristics in the deciding activity during esterification reactions. Chabukswar et al. [11] have also reported that the XRD spectrum of the synthesized catalyst exhibited one broad and strong diffraction peak attributable to crystalline carbon composed of graphite carbon sheets at an angle (2θ=25°), oriented in a considerably random fashion. Nakajima et al. [29] and Okamura et al. [30] also reported that the XRD pattern for D-glucose based catalyst exhibits a weak and broad diffraction peak (2θ=10–30°) attributable to aromatic carbon sheets oriented in a random fashion. In the case of D-glucose carbonized at 823 K, the diffraction peak (35–50°) due to the graphite structure was observed, which indicates that this sample is composed of larger carbon sheets. Mar and Somsook [31] reported the XRD profiles of the incomplete carbonized vermicelli at different temperatures before and after sulfonation. The broad diffraction peaks (2θ=10–30°) of all XRD patterns were assigned to carbon. After sulfonation, the peak intensities became weaker due to the immobilization of the sulfonic group on the carbon support and it was weaker in the sulfonated samples carbonized at 473 K and 573 K. Further, diffraction peaks for both sulfonic-modified materials were shifted to the larger 2θ values, indicating that the carbonization process occurred during the synthesis process results in smaller polycyclic carbon rings. In the case of material carbonized at 673 K, a weak diffraction peak (2θ=35–60°) of graphite structure could be found. This was probably due to the presence of higher carbonized material, composed of larger and harder carbon materials as a result of plane growth and stacking of carbon sheets.

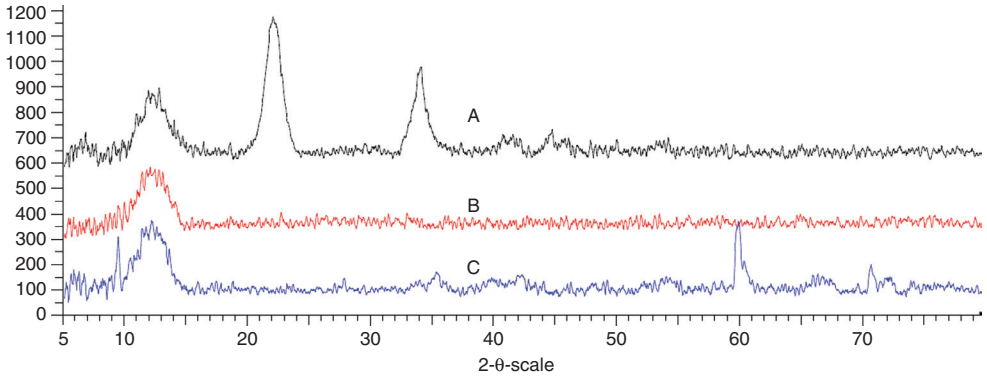

Figure 3 Comparison of different catalysts in terms of XRD analysis. (A) commercially available untreated cellulose, (B) catalyst obtained from hydrothermal carbonization followed by sulfonation of the commercially available cellulose, (C) catalyst prepared from waste paper pretreated with ultrasonically assisted alkaline pretreatment.

3.1.5 FTIR analysis

The qualitative analysis of the obtained catalyst was performed using FTIR spectrometer. It can be seen from the Figure 4 (for the case of catalyst obtained from commercial cellulose), that bands at 1684 cm^{-1} were observed which can be assigned to aromatic-like C=C stretching mode in polyaromatic starch. The band at 3446 cm^{-1} was assigned to the O-H stretching modes of the -COOH and phenolic -OH groups, confirming the presence of -OH group in pre- and post-sulfonation. Stretching in the range of 1100–1300 cm^{-1} band indicated the sulfonic group attachment to the selected base. Similarly, Figure 5 shows the FTIR spectra of the catalyst synthesized from the delignified cellulose raw material, which also showed similar peaks confirming the similar type of catalyst molecular structures.

Guo et al. [32] investigated the FTIR spectra for both sulfonated and raw carbon material, pyrolyzed at 673 K. The bands at 1619 cm^{-1} and 1384 cm^{-1} for the catalyst and its precursor were assigned to aromatic-like C=C stretching mode. The band at 3424 cm^{-1} in raw carbon material and the band at 3429 cm^{-1} in the sulfonated product were assigned to the -OH stretching modes of the -COOH and phenolic -OH groups, confirming the presence of the -OH group in pre- and post-sulfonation. The band at 1702 cm^{-1} was assigned to the C=O stretching mode of the COOH group. The vibration bands at 1035 cm^{-1} ($-SO_2$-symmetric stretching) and 1154 cm^{-1} ($-SO_2$-asymmetric stretching) indicated the presence of $-SO_3H$ group. Shu et al. [28] have also reported similar analysis based on the FTIR spectra of the sugar based catalyst before and after sulfonation.

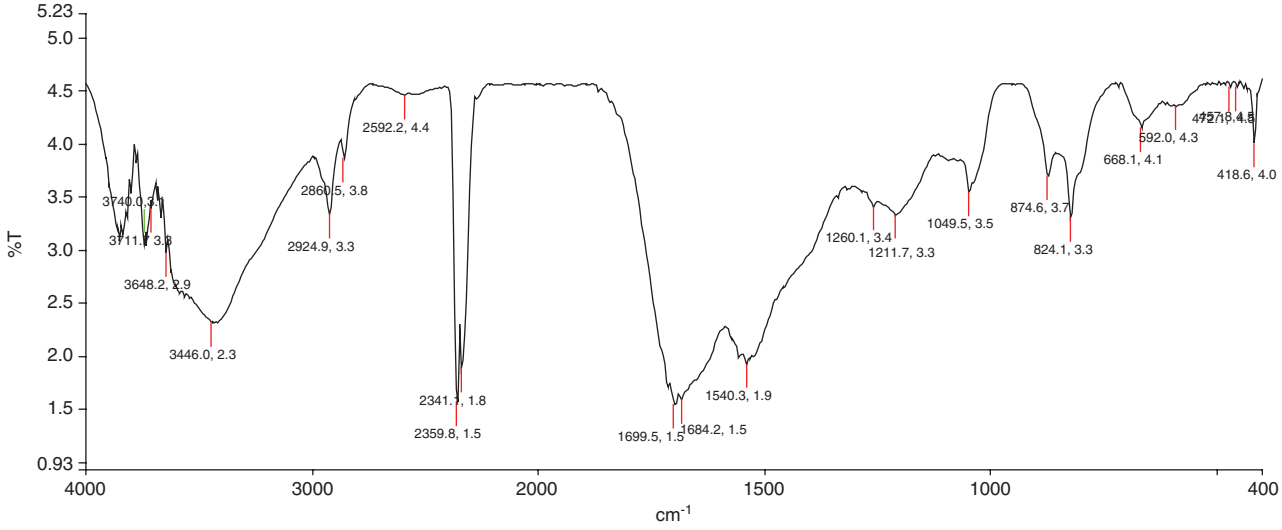

Figure 4 FTIR spectra for catalyst obtained using hydrothermal carbonization and sulfonation of the commercially available cellulose.

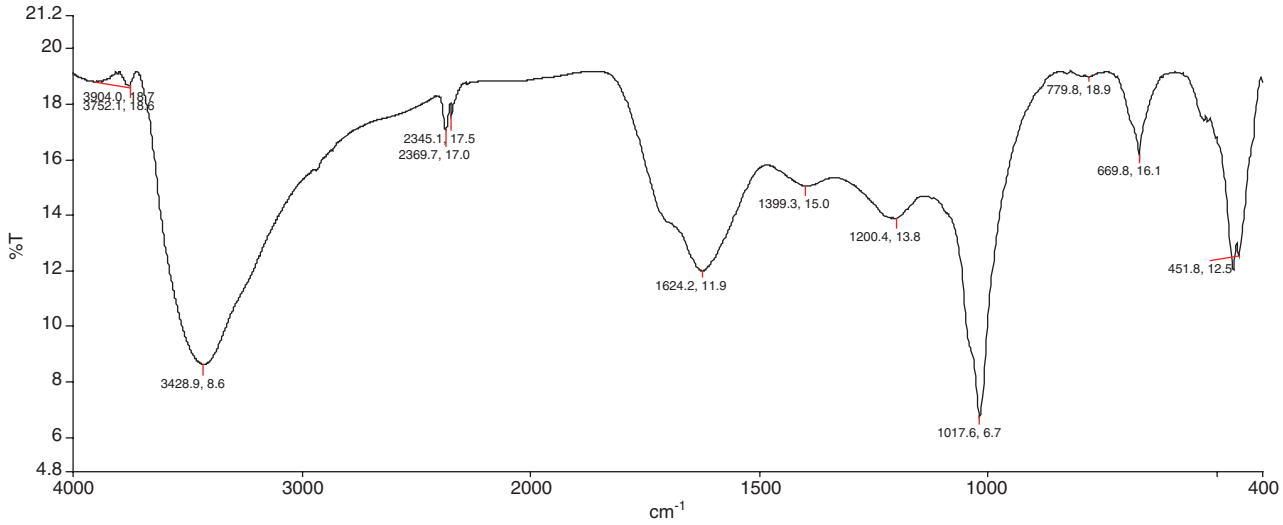

Figure 5 FTIR spectra of hydrothermally carbonized and sulfonated sample of ultrasonically assisted alkaline pretreated delignified paper.

3.2 Biodiesel production

3.2.1 Catalyst screening

The esterification reaction was carried out using the different catalysts prepared by the various methods from commercially available cellulose such as only hydrothermal carbonization, only sulfonation, sulfonation and hydrothermal carbonization and hydrothermal carbonization and sulfonation as well as the catalyst obtained from the waste paper pretreated with ultrasonically assisted alkaline treatment using the route of hydrothermal carbonization and sulfonation. The obtained results were also compared with the widely used amberlyst-15 catalyst based on the performance in conventional synthesis as well as the ultrasound assisted approach. The results obtained for the comparative study are shown in Figure 6 and Table 1. The esterification reaction was carried out under conditions of PFAD: methanol (1:6 mole ratio) and 3% catalyst loading for comparison purpose. It was observed from the table that the catalyst prepared by hydrothermal carbonization followed by sulfonation of the commercially available cellulose gave the highest conversion as 47.9% and 81.2% by conventional and ultrasound assisted approach, respectively, in 3 h at 333 K. The conversion with amberlyst-15 was observed as 47% and 62.8% by conventional and ultrasound assisted approach, respectively. Catalyst prepared by hydrothermal carbonization followed by sulfonation of the commercially available cellulose exhibited remarkable activity giving the highest conversion since the process of carbonization forms small aromatic polycyclic aromatic rings leading to an increase in the surface area giving more active sites available for the sulfonation to take place on the precursor. The enhanced acidity and number of actives sites of the final catalyst helps in giving higher conversion.

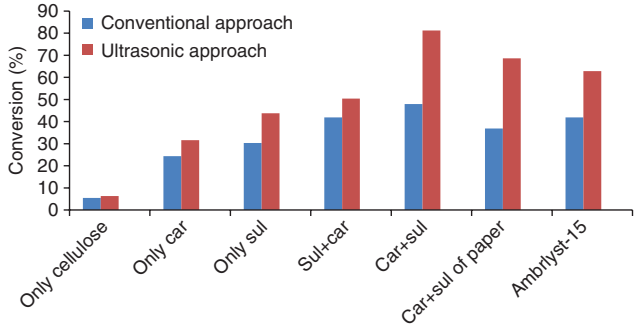

Figure 6 Comparison of different catalysts for the effectiveness in biodiesel production. Reaction temperature 60°C; molar ratio PFAD:methanol 1:6; Time 3 h.

The increase in the percentage conversion in the case of ultrasound assisted approach is attributed to the intense mixing due to the cavitational effects. Activation of the catalyst surface can also occur due to the microjets created by the asymmetric collapse of cavitational bubbles [24]. In heterogeneous reactions containing immiscible phases, the reaction is limited by mass transfer. In the case of ultrasound assisted approach, cavity collapse at or near the interface will cause disruption and mixing, resulting in the formation of very fine emulsions and overcoming the mass transfer limitations. When very fine emulsions are formed, the surface area available for the reaction between the two phases increases, which results in the increased rates of reaction [9]. Thus, ultrasound assisted

Table 1 Comparison of the efficacy of various catalysts in terms of the extent of the conversion for the conventional and ultrasound assisted approach.

Type of catalyst	% Conversion (conventional)	% Conversion (ultrasound)	% Change
Only cellulose	5.43	6.29	15.74
Only hydrothermal carbonization	24.35	31.55	29.56
Only sulfonation	30.33	43.80	44.37
Sulfonation+hydrothermal carbonization	41.88	50.44	20.42
Hydrothermal carbonization+sulfonation of commercial cellulose	47.91	81.24	69.58
Hydrothermal carbonization+sulfonation of paper	36.94	68.59	85.65
Amberlyst-15	35.81	54.43	51.99

approach and catalyst prepared by hydrothermal carbonization followed by sulfonation of the commercially available cellulose was used for the remaining studies of optimization of the reaction conditions.

3.2.2 Effect of molar ratio

Methanol to oil molar ratio is one of the most important parameters in determining the extent of conversion and also the cost of production of biodiesel. The esterification reaction between PFAD and methanol is a reversible reaction and hence higher equilibrium conversion can be obtained if the backward reaction is minimized, which can be done by using one of the reactants in excess (methanol in this case). Experiments were conducted using different molar ratios of PFAD to methanol ranging from 1:1 to 1:9 and the obtained results have been given in Figure 7. It has been observed that with an increase in the molar ratio from 1:1 to 1:6, the extent of conversion increased from 58% to 77% and kinetic analysis revealed that the second order esterification rate constant also increased from 1.36×10^{-07} to 2.06×10^{-07} $(mol/m^3)^{-1}\ s^{-1}$ (as per data of kinetic rate constants shown in Table 2). The results obtained can also be attributed to the higher

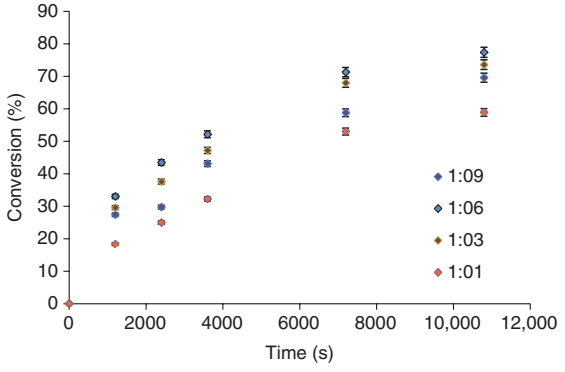

Figure 7 Effect of molar ratio on the percentage conversion.

Table 2 Kinetic analysis for the effect of molar ratio.

Molar ratio	% Conversion	Rate constant $(mol/m^3)^{-1}\ s^{-1}$	R^2
1:01	58.88	1.36×10^{-07}	0.9854
1:03	73.6	2.64×10^{-07}	0.9891
1:06	77.39	3.20×10^{-07}	0.995
1:09	69.58	2.05×10^{-07}	0.992

cavitational activity due to the presence of higher amount of methanol in the system. Stavarache et al. [33] reported similar results for excess methanol which was attributed to enhanced number of cavitation events and hence the formation of enhanced emulsion providing additional area for the reaction. Excess methanol also favors the removal of water from the reaction as aqueous phase, thereby not hindering the progress of the reaction. It is also interesting to note that the increase in the extent of conversion was only marginal for an increase in the PFAD to methanol ratio beyond 1:6. At the higherst PFAD to methanol ratio of 1:9, the separation of esters from the glycerol layer also becomes difficult and based on these results, oil to methanol ratio of 1:6 was used for further studies related to the effect of operating parameters. Ji et al. [34] and Hingu et al. [35] have also reported similar results of increase in the extent of methyl esters yield with an increase in the reactant ratio till an optimum value.

3.2.3 Effect of catalyst loading

To study the effect of catalyst concentration on the rate of reaction and equilibrium conversion, the reaction was carried out at different catalyst loadings over the range 1.5%–3% of the PFAD. The results obtained are given in Figure 8. It can be seen from the figure that an increase in the catalyst concentration from 1.5 wt% to 3 wt% results

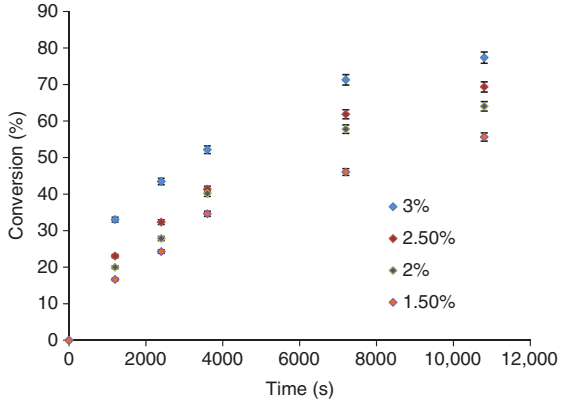

Figure 8 Effect of catalyst loading on the percentage conversion.

in an increase in the conversion from 55% to 77% and also the kinetic studies revealed that the second order esterification rate constant increased from 1.13×10^{-07} to 3.20×10^{-07} $(mol/m^3)^{-1}$ s^{-1}. Table 3 shows the effect of catalyst loading on the kinetic rate constants. The main role of acidic catalyst was in making available protons in the organic phase in sufficient quantity to catalyze the esterification reaction [36]. The water formed during the esterification reaction inhibits the availability of protons in the palm fatty acid phase, slowing the progress of the reaction. A higher catalyst loading increases the availability of the protonic sites, and hence, the overall rate of reaction increases with an increase in the concentration of catalyst. In the present case, the carbon based catalyst was composed of polycylic aromatic carbon sheets. Therefore, the surface of the catalyst is relatively hydrophobic and is less likely to form a water layer on its surface. So the hydrophobic fatty acids or glycerides could readily access the protonic sites of the catalyst [22, 23] leading to the increase in the reaction rate. Also, the microstreaming effect of ultrasound can help in maintaining the catalyst activity by removing the inactive surface formed on the catalyst so that the active acidic sites can easily be available for the reaction of PFAD on the catalyst surface [24].

3.2.4 Effect of temperature

In order to study the effect of the reaction temperature on the esterification reaction, the esterification reaction was carried out under optimal conditions of reactant molar ratio of PFAD to methanol as 1:6 and catalyst loading of 3% at different operating temperatures varying from 318 K to 333 K. The effect of the reaction temperature on the conversion is presented in Figure 9. It can be seen from the figure that there is an increase in the conversion from 50% to 77% with an increase in temperature from 318 K to 333 K and the kinetic studies revealed that the second order esterification rate constant increased from 9.78×10^{-08} to 3.20×10^{-07} $(mol/m^3)^{-1}$ s^{-1} (data shown in Table 4). The increase in the conversion with an increase in the temperature can be attributed to the effects of changes in solubility and extent of cavitation at different temperatures. As esterification is a heterogeneous reaction, two layers of methanol-rich phase and an ester rich phase are observed at lower temperature. The reaction occurs in the ester layer and methanol is less soluble in the ester layer at lower temperature, resulting in the lower conversions. With an increase in the temperature, there in an increase in the solubility of methanol in the ester phase, resulting in an increase in the rate of reaction. Also, with an

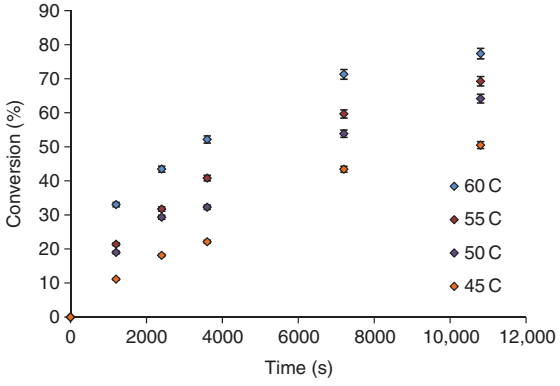

Figure 9 Effect of the reaction temperature on the percentage conversion.

Table 3 Kinetic analysis for the effect of catalyst loading.

Catalyst loading (%)	% Conversion	Rate constant $(mol/m^3)^{-1}$ s^{-1}	R^2
1.50	55.64	1.13×10^{-07}	0.9921
2	64.06	1.69×10^{-07}	0.9895
2.50	69.36	2.13×10^{-07}	0.9957
3	77.39	3.20×10^{-07}	0.995

Table 4 Kinetic analysis for the effect of temperature.

Temperature (°C)	% Conversion	Rate constant $(mol/m^3)^{-1}$ s^{-1}	R^2
45	50.52	9.78×10^{-08}	0.9878
50	64.16	1.64×10^{-07}	0.9933
55	69.26	2.08×10^{-07}	0.9988
60	77.39	3.20×10^{-07}	0.995

increase in the temperature, the solubility of water formed during the reaction in methanol increases overcoming the equilibrium limitations [10]. At significantly higher temperatures, the cavitational intensity decreases due to the cushioned collapse of cavities thereby reducing the degree of intensification.

Considering the effect of temperature on the esterification reaction follows Arrhenius law, the activation energy of the esterification reaction can be determined with the help of the following expression:

$$\ln(k) = \ln(k_0) - \frac{Ea}{RT} \quad (2)$$

where k is reaction rate constant, k_0 is the pre-exponential factor, Ea is the activation energy required for the reaction, R is the molar gas constant, which is equal to 8.314 J/(mol.K) and T is the reaction temperature. To determine the activation energy, an Arrhenius plot was made based on the rate constants obtained at various temperatures. According to the slope of the line presented in Figure 10, the estimated activation energy of the esterification reaction was found to be 66.37 kJ/mol. Freedman et al. [37] have also reported activation energies in the range of 50–85 kJ/mol for acid catalyzed transesterification of soybean oil.

3.2.5 Effect of ultrasound power

Ultrasonic power dissipation is also an important parameter in deciding the extent of intensification as power dissipation significantly affects cavitational intensity. The optimal parameters such as PFAD to methanol molar ratio (1:6), catalyst concentration (3 wt% of PFAD) and temperature (333 K) were kept constant for the study involving the variation in ultrasonic power dissipation from 60 W to 120 W. The obtained results are shown in Figure 11. It can be seen that the conversion increases from 60% to 77% for

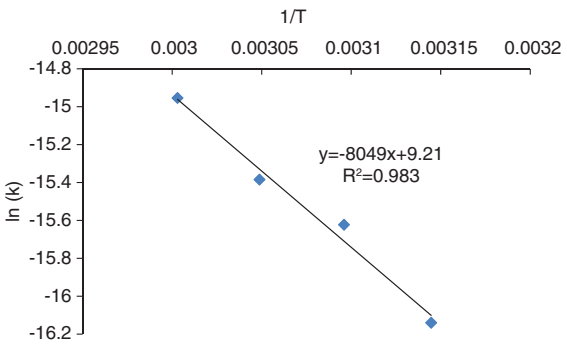

Figure 10 Relationship between ln (k) and 1/T as per Arrhenius' law.

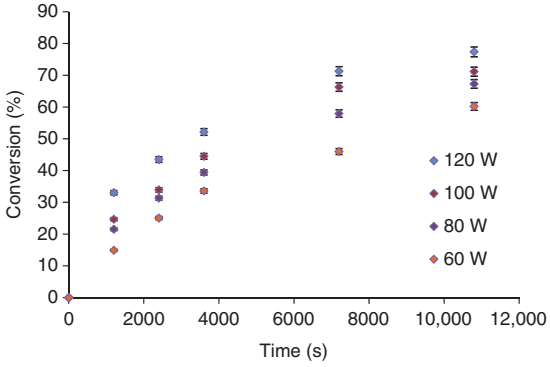

Figure 11 Effect of ultrasonic power on the percentage conversion.

an increase in power from 60 to 120 W and also the kinetic studies revealed that the second order esterification rate constant increases from 1.34×10^{-7} to 3.20×10^{-7} $(mol/m^3)^{-1}\ s^{-1}$. The effect of ultrasonic power on the kinetic rate constants has been shown in Table 5. The increase in the conversion with an increase in the ultrasonic power is attributed to enhanced mixing and emulsification of the two immiscible reaction layers. With an increase in the power dissipation, the cavitational intensity increases providing intense turbulence at the microscale and hence eliminates the mass transfer resistances enhancing the rate of reaction. Enhanced cavitational activity also helps in maintaining the activity of the catalyst by removing any deposition on the surface of the catalyst [9]. A similar behavior for the esterification reaction for biodiesel production has been reported by Ji et al. [34].

3.2.6 Effect of duty cycle

Ultrasonic duty cycle is another important operating parameter affecting the cavitational intensity and is the fraction of time during which an ultrasonic system is operated. For example, duty cycle of 10% means ultrasonic irradiation is on for 1 s followed by 9 s off. The main objective of using pulsed ultrasound is to reduce the net

Table 5 Kinetic analysis for the effect of ultrasonic power.

Ultrasonic power (W)	% Conversion	Rate constant $(mol/m^3)^{-1}\ s^{-1}$	R^2
60	60.22	1.34×10^{-07}	0.988
80	67.3	1.89×10^{-07}	0.9989
100	71.76	2.39×10^{-07}	0.983
120	77.39	3.20×10^{-07}	0.995

power consumption in the system and also to achieve sufficient cooling of the transducers [21] so that better equipment durability is achieved. The optimal parameters such as PFAD to methanol molar ratio (1:6), catalyst concentration (3 wt% of PFAD), temperature (333 K) and power dissipation of 120 W were kept constant. The ultrasonic duty cycle was varied from 5 s ON 5 s OFF to 8 s ON 2 s OFF and the obtained results are depicted in Figure 12, whereas the effect of duty cycle on the kinetic rate constants is shown in Table 6. It can be observed that as the duty cycle increases from 5 s ON 5 s OFF to 8 s ON 2 s OFF the conversion increases from 53% to 77% and also the kinetic analysis revealed that the second order esterification rate constant increased from 1.04×10^{-7} to 3.20×10^{-7} $(mol/m^3)^{-1}$ s^{-1}. Ji et al. [34] and Gole et al. [9] reported a similar effect of ultrasonic pulse which has been attributed to the lower degree of cavitational collapse at or near the interface at lower pulse which gives lower degree of emulsion. The increase in the conversion of PFAD with an increase in the time of exposure of ultrasonic irradiation is attributed to the enhanced cavitational activity similar to that obtained for the case of enhanced power dissipation. Thus, depending on the stability of the reactor in terms of how efficient is the transducer cooling, ultrasonic usage for a continuous period can be decided.

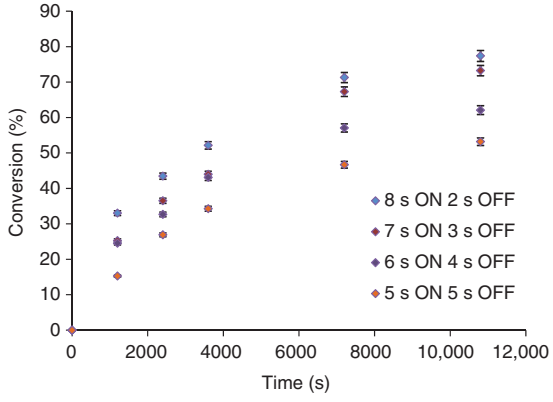

Figure 12 Effect of ultrasonic duty cycle on the percentage conversion.

Table 6 Kinetic analysis for the effect of duty cycle.

Duty cycle	% Conversion	Rate constant $(mol/m^3)^{-1}$ s^{-1}	R^2
5 s ON 5 s OFF	53.19	1.04×10^{-07}	0.9785
6 s ON 4 s OFF	62.1	1.51×10^{-07}	0.9734
7 s ON 3 s OFF	73.25	2.62×10^{-07}	0.9888
8 s ON 2 s OFF	77.39	3.20×10^{-07}	0.995

3.2.7 Effect of co-solvent addition

Biodiesel production is time consuming because of the immiscible nature of oil or fatty acids and methanol, causing mass transfer limitations, especially during the initial periods of the reaction. Co-solvent plays an important role in increasing the yield of biodiesel production. In the present work, different co-solvents such as tetrahydrofuran (THF), hexane, toluene and dimethyl sulfoxide have been used with an objective of improving the miscibility of oil and alcohol phase. Introducing a co-solvent into the process changes the reaction mixture from a two-phase system to a single-phase system due to an increase in the mutual solubility of alcohol and vegetable oil at low reaction temperatures based on the concept of "like dissolves like". The mass transfer rates in the single-phase reaction are expected to be higher compared to those observed in the two-phase reaction, due to an increase in the contact surface, and hence the production of biodiesel can be intensified by the addition of a co-solvent. The co-solvent amount was chosen as 0.2% of the fatty acid weight since Mupanneni et al. [38] reported that the maximum conversion was obtained at co-solvent (hexane and THF) to oil ratio of 0.2%. Figure 13 depicts the obtained results for the effect of addition of various co-solvents. It can be seen from the figure that the use of THF increases the conversion to 86% compared to 77% obtained in the absence of any co-solvent. Kinetic analysis also revealed that the addition of co-solvent changes the reaction order from second order to first order due to the uniform mixing [1] with a rate constant of 0.010 min^{-1} for the case of THF as a co-solvent. Table 7 gives the obtained values of the rate constants for the addition of various co-solvents. Higher conversion was obtained when THF was used as a co-solvent compared to other co-solvents used in the work which can be attributed to the higher polarity of THF.

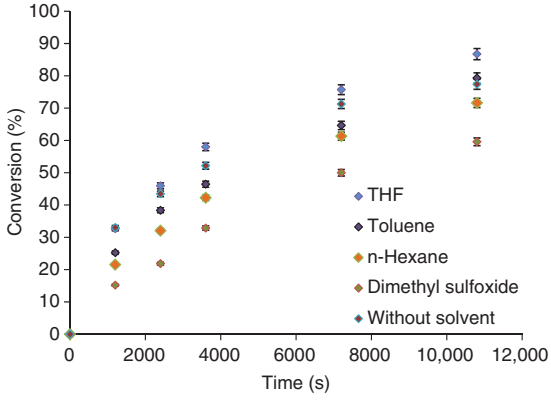

Figure 13 Effect of co-solvent addition on the percentage conversion.

Table 7 Kinetic analysis for the effect of co-solvent addition.

Co-solvent	% Conversion	Rate constant	R^2
THF	86.74	1.78×10^{-04} (s^{-1})	0.9876
Tolune	79.33	1.37×10^{-04} (s^{-1})	0.9895
Without solvent	77.39	3.2×10^{-07} (s^{-1})	0.995
n-Hexane	71.63	1.14×10^{-04} (s^{-1})	0.9848
Dimethyl sulfoxide	59.58	8.31×10^{-05} (s^{-1})	0.9847

Similar results have also been reported by Boocock et al. [39] and Karmee and Chadha [40].

4 Properties of biodiesel

Important properties of the prepared biodiesel were analyzed to check the comparison with the ASTM standards. The moisture content of the biodiesel was found to be 0.23% with density of 828.8 kg/m^3. The viscosity of the biodiesel was observed to be 3.231×10^{-3} Pa.s and the flash point was 403 K. GC-MS analysis of the prepared biodiesel sample was also performed and the obtained spectra confirmed the presence of fatty acid methyl palmeate (C16:0), fatty acid methyl stearate (C18:0), fatty acid methyl oleate (C18:1) and fatty acid methyl linoleate (C18:2) at the retention time of 14, 15.203, 15.26, 15.47 min, respectively. The obtained properties of the biodiesel as well as the GC-MS spectra matched the standard characteristics.

5 Conclusions

Different catalysts synthesized from sustainable sources were characterized using different catalyst testing methods and screened for use in biodiesel production. The catalyst prepared by the hydrothermal carbonization followed by sulfonation of commercial cellulose showed better results compared to the other catalysts because of the formation of higher extent of acidic active sites.

The present work also illustrated the applicability of sonochemical reactors for the intensified production of biodiesel from a sustainable and economical feedstock such as PFAD. The effects of different operating and design parameters on the biodiesel production were evaluated, along with the comparison with conventional stirring method, highlighting clearly the role of ultrasonic field in inducing an effective emulsification and mass transfer to enhance the biodiesel production significantly. It was observed that the optimized conditions were molar ratio of 1:6, catalyst loading of 3%, temperature of 333 K, power dissipation of 120 W, 8 s ON and 2 s OFF duty cycle and THF as a co-solvent, and gave a maximum conversion of 86%. Overall, the present work demonstrated a sustainable approach for the synthesis of catalyst and the subsequent biodiesel production from non-edible cheaper feedstock such as PFAD.

References

[1] Maddikeri GL, Pandit AB, Gogate PR. *Ind. Eng. Chem. Res.* 2012, 51, 14610–14628.
[2] Demirbas, A, Ed. *Biodiesel: A Realistic Fuel Alternative for Diesel Engines*, Springer-Verlag Limited: London, 2008.
[3] Taravus S, Temur H, Yartasi A. *Energy & Fuels* 2009, 23, 4112–4115.
[4] Patil P, Gude V, Deng S. *Ind. Eng. Chem. Res.* 2009, 48, 10850–10856.
[5] Prabhavathi Devi BLA, Reddy T, Vijaya Lakshmi K, Prasad RBN. *Biores. Tech.* 2014, 153, 370–373.
[6] Komintarachat C, Chuepeng S. *Ind. Eng. Chem. Res.* 2009, 48, 9350–9353.
[7] Wang L, Dong X, Jiang H, Li G, Wang M, Dong X, Jiang H, Zhang M. *Fuel Proc. Tech.* 2014, 128, 10–16.
[8] Zhang Y, Dube MA, McLean DD, Kates M. *Biores. Tech.* 2003, 89, 1–16.
[9] Gole VL, Gogate PR. *Ind. Eng. Chem. Res.* 2012, 51, 11866–11874.
[10] Deshmane VG, Gogate PR, Pandit AB. *Ultrason. Sonochem.* 2009, 48, 7923–7927.
[11] Chabukswar DD, Kaur HP, Gaikar VG. *Ind. Eng. Chem. Res.* 2013, 52, 7316–7326.
[12] Xie W, Wang J. *Energy Fuels* 2014, 28, 2624–2631.
[13] Aarthy M, Saravanan P, Gowthaman MK, Rose C, Kamini NR. *Chem. Eng. Res. Des.* 2014, 92, 1591–1601.
[14] Lotero E, Liu YJ, Lopez DE, Suwannakaran K, Bruce DA, Goodwin JG. *Ind. Eng. Chem. Res.* 2005, 44, 5353–5363.
[15] Kulkarni MG, Dalai AK. *Ind. Eng. Chem. Res.* 2006, 45, 2901–2913.
[16] Wang Y, Ou S, Liu P, Xue F, Tang S. *J. Mol. Cat. A: Chem.* 2006, 252, 107–112.
[17] Zabeti M, Daud W, Aroua MK. *Fuel Proc. Tech.* 2009, 90, 770–777.
[18] Lam MK, Lee KT, Rahman A. *Biotech. Adv.* 2010, 28, 500–518.
[19] Atadashi IM, Aroua MK, Abdul Aziz AR, Sulaiman NMN. *J. Ind. Eng. Chem.* 2013, 19, 14–26.
[20] Bajaj A, Lohan P, Jha PN, Mehrotra R. *J. Mol. Cat. B Enz.* 2010, 62, 9–14.
[21] Hara M. *Sustain. Chem.* 2009, 2, 129–135.
[22] Takagaki A, Toda M, Okamura M, Kondo JN, Hayashi S, Domen K. *Cat. Today* 2006, 116, 157–161.
[23] Lou WY, Zong MH, Duan ZQ. *Biores. Tech.* 2008, 99, 8752–8758.
[24] Gogate PR. *Chem. Eng. Proc.* 2008, 47, 515–527.
[25] Mason, TJ, Ed. *Chemistry with Ultrasound*, Elsevier Science Publications, London, UK, 1990.
[26] Liang X, Yang J. *Cat. Let.* 2009, 132, 460–463.
[27] Subhedar PB, Gogate PR. *Ultrason. Sonochem.* 2013, 21, 216–225.

[28] Shu Q, Zhang Q, Xu GX, Nawaz Z, Wang DZ, Wang JF. *Fuel Proc. Tech.* 2009, 90, 1002–1008.
[29] Nakajima K, Hara M, Hayashi S. *J. Am. Cer. Soc.* 2007, 90, 3725–3734.
[30] Okamura M, Takagaki A, Toda M, Kondo JN, Domen K, Tatsumi T. *J. Am. Chem. Soc.* 2006, 18, 3039–3045.
[31] Mar WW, Somsook E. *Procedia Eng.* 2012, 32, 218–212.
[32] Guo C, Fang Baishan F. *Biores. Tech.* 2011, 102, 2635–2640.
[33] Stavarache C, Vinatoru M, Maeda Y, Bandow H. *Ultrason. Sonochem.* 2007, 14, 413–417.
[34] Ji J, Wang J, Li Y, Yu Y, Xu Z. *Ultrasonics* 2006, 44, 411–414.
[35] Hingu SM, Gogate PR, Rathod VK. *Ultrason. Sonochem.* 2010, 17, 827–832.
[36] Einhorn C, Einhorn J, Luche JL. *Synthesis* 1989, 787.
[37] Freedman B, Pryde EH, Mounts TL. *J. Am. Oil Chem. Soc.* 1984, 61, 1638–1643.
[38] Muppaneni T, Reddy HK, Patil PD, Dailey P, Aday C, Deng S. *App. Energy* 2012, 94, 84–88.
[39] Boocock DGB, Konar SK, Mao V, Lee C, Buligan S. *J. Am. Oil Chem. Soc.* 1998, 75, 1167–1172.
[40] Karmee SK, Chadha A. *Biores. Tech.* 2005, 96, 1425–1429.

Bionotes

Namrata D. Gaikwad

Namrata D. Gaikwad received her B Tech in Chemical Engineering from Dr. Babasaheb Ambedkar Technological University, Lonere with distinction in 2010, after which she worked as a lecturer in the Chemical Engineering Department at Finolex Academy of Management and Technology, Ratnagiri for 2 years. This research work is based on her work for Master's degree in Chemical Engineering at the Institute of Chemical Technology, Mumbai. After graduation in July 2014, she joined Aker Solutions, Mumbai as a Trainee Engineer.

Parag R. Gogate

Parag R. Gogate has been a versatile chemical engineer with outstanding research work in the area of use of alternate energy sources, wastewater treatment, and converting waste into value added products. Dr. Gogate has contributed extensively to publishing in journals of high repute with 165 international journal publications along with over 5000 citations (h-index of 40); he has also contributed a total of 15 chapters in edited books. Dr. Gogate has active consultancy projects with many national and international companies and also collaborations with many research groups worldwide. Dr. Gogate has contributed extensively to the development of the profession with the organization of refresher courses/seminars for participants from academic institutes and from industry and also by running competitions for the student community.