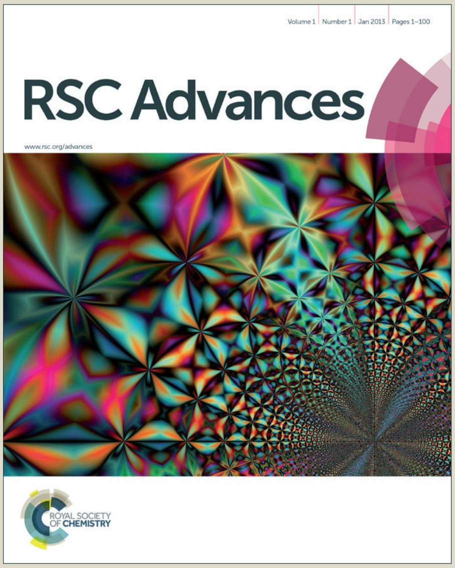
RSC Advances



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Title: Nano sized heterogeneous acid catalyst from *Ceiba pentandra* stalks for production of biodiesel using extracted oil from *Ceiba pentandra* seeds

First Author: Karuppiah Subramanian Parthiban, Department of Chemical Engineering, National Institute of Technology, Tiruchirappalli 620 015, Tamilnadu, India.

Email: ksparthibanks@gmail.com

Corresponding Author: Dr. Muthiah Perumalsamy**,** Department of Chemical Engineering, National Institute of Technology, Tiruchirappalli 620015, Tamil Nadu, India

Phone: 0431 2503112, Email: mpsamy@nitt.edu

Nano sized heterogeneous acid catalyst from *Ceiba pentandra* stalks for production of biodiesel using extracted oil from *Ceiba pentandra* seeds

Karuppiah Subramanian Parthiban, Muthiah Perumalsamy*

Department of Chemical Engineering, National Institute of Technology, Tiruchirappalli 620 015, Tamilnadu, India.

ABSTRACT

Heterogeneous acid catalyst of nano size was prepared by the method of sulfonation of *C. pentandra* stalks and used to convert *C. pentandra* seed oil to biodiesel. The structure of the catalyst was characterized and physicochemical properties of extracted oil as well as effects of different preparation conditions on biodiesel yield were investigated. Scanning electron microscopy (SEM) photograph showed that the catalyst had porous structure which enhanced catalytic ability. From the Brunauer–Emmet–Teller (BET) analysis that the catalyst specific surface area was 714m^2 g^{-1} and average pore size was 4.8 nm. The optimal triglyceride conversion of 99% was attained at a reaction temperature of 220°C, methanol to oil ratio of 18:1M and catalyst concentration of 1.5wt%. Reusability of the catalyst was studied which relieves drastically decrease in energy expenditure and waste generation in the production of biodiesel. Biodiesel viscosity was higher whereas other properties had found similar to that of commercial diesel oil and compared with ASTM D6751 and EN standards.

Keywords: Heterogeneous Catalyst; Ceiba pentandra oil; Transesterification; Biodiesel characterization

---

* Corresponding Author: Dr. Muthiah Perumalsamy**,** Assistant Professor, Department of Chemical Engineering, National Institute of Technology, Tiruchirappalli

1. INTRODUCTION

Crude oil is an exhaustible resource and its price is regulated by its scarcity issues.[1] Biodiesel can replace directly petroleum-derived diesel without engine modifications, derived from either transesterification of vegetable oils or animal fats. Biodiesel is developed through the application of various solid acid catalysts and has gained much attention because of its environmental and technological advantages. Other than its renewability advantages of biodiesel are biodegradability, non-toxicity, low sulfur content and reduced emission of hydrocarbons, particulate matter and carbon-monoxide.[2-3] Combined reaction of esterification and transesterification of oil with methanol are the main chemical pathways for synthesis of biodiesel.[4-5] Total estimated production cost of biodiesel has been potentially accounted for 88% by the usage of refined oils. The use of cheap raw feed stocks such as non-edible oils will improve the economic feasibility of biodiesel.[6-7] Currently; many attempts have also been made to produce biodiesel from non-edible plant oils like jatropha, karanja and mahua.[8]

In conventional biodiesel production, transesterification reaction is achieved by using homogeneous alkali catalysts. However, the synthesis of biodiesel from low-quality oils using base catalyst is challenging because of the undesirable side reactions that occur due to the presence of free fatty acids (FFA) and it gives rise to soap formation, creating serious problems for product separation and ultimately hindering methyl ester yield. For the above reasons, a two-step process is most commonly used to deal with feed stocks having high free fatty acids.[9]Acid-catalyzed pre-esterification is to reduce the FFA concentrations below an optimum threshold limit of < 1 wt %. The second step is the alkali catalyzed transesterification process which converts the oil to biodiesel and glycerol. Homogeneous acid catalysts show better adaptability to FFAs and can simultaneously catalyze esterification and transesterification.[10] However, the separation of the catalyst and corrosion-related problems limit their use.

Development of heterogeneous catalysts has been a recent area of research in biodiesel production. Since heterogeneous catalysts can provide a simple catalyst removal step and can be recycled, utilizing heterogeneous catalysis to produce biodiesel is becoming more popular.[11-12] The implementation of environmentally friendly heterogeneous catalysts in large-scale biodiesel production is preferable to eliminate the drawbacks associated with homogeneous catalysts and improve overall process economics. Heterogeneous catalysts are categorized as solid acid and base. Solid base catalysts include a wide group of compounds in the category of alkaline earth metal hydroxides, alumina loaded with various compounds and zeolites showing high basicity coupled with active basic sites and pore size. Solid base catalysts have been quite successful with high conversion and yield of biodiesel. However, they are sensitive to the presence of free fatty acids and thus solid acids have a preference over solid base catalysts.[13–16]Compared with solid base catalysts, solid acid catalysts have lower catalytic activity but higher stability; they can be used for cheap raw feed stocks with large amount of FFAs without catalyst deactivation.

Solid acid catalysts do not cause corrosion as found with common acid homogeneous catalysts, such as sulfuric acid.[17] The solid acid catalysts differ in acidity, surface area and thermal stability. For an optimum yield of biodiesel high temperature was required because heterogeneous catalysts are insoluble in the oil and methanol phase. Application of heterogeneous catalysts for production of biodiesel in the industrial outlook deserves for minimal energy requirement. The leaching aspect is another important factor that governs the suitability of particular catalyst.[18] Many researchers have already made good progress on biodiesel production via heterogeneous acid catalysis. Solid acid catalysts, such as Amberlyst-15,[19] SO_4^{2-}/SnO_2,[20] Sulfated zirconia (SO_4^{2-}/ZrO_2) and sulfated titanium oxide (SO_4^{2-}/TiO_2) [21-22] showed high catalytic activity and good stability when used to catalyze esterification and transesterification simultaneously. Incomplete carbonization of D-glucose led to a rigid carbon material consisting of small polycyclic aromatic carbon sheets.[23-24] Sulfonation of such carbon material resulted in very stable solids with a high density of active sites, which was physically robust and displayed no leaching of SO_3H groups during use. A carbon-based solid acid catalyst was prepared by carbonizing vegetable oil asphalt, petroleum asphalt, corn straw and de-oiled canola meal (DOCM). The high catalytic activity observed owing to its high density and stability of acid sites, loose irregular network, and the hydrophobic property of its carbon sheets that prevented the hydration of –OH groups in the presence of water. Besides, this solid showed a remarkable catalytic performance in transesterification.[25-28]

C. pentandra stalk was selected because of its abundant availability and it is under usage. Cotton, the king of natural fibers is mainly cultivated for its lint which is the most sought after textile fiber till date due to its inherent eco-friendly and comfort characteristics. The bulk of the stalk is burnt off in the fields after the harvest of cotton crop. Shells from these trees are leathery, pendulous capsule, 10-25 cm long, and 3-6 cm diameter.[29] *C. Pentandra* seeds were black in color and reported to have low feeding value due to its high fiber content and presence of tannins.[30] The seeds were picked out of the wool and used to be thrown away and also the natural production of seeds remains underutilized. Moreover it grows in wasteland, which makes it a more attractive feedstock for biodiesel production.

This present study deals with the solid acid catalyst preparation, catalytic activity evaluation for biodiesel production and reusability of the catalyst. The effect of various reaction parameters on biodiesel yield, such as catalyst concentration, reaction temperature and molar ratio of methanol to oil were studied. *C. pentandra* stalks are a mixture of straight chain aliphatic hydrocarbon polymers and will result in having a different catalytic activity and stability. Oil extraction and biodiesel production from the *C. Pentandra* oil was investigated. The fuel properties of *C. Pentandra* oil biodiesel were determined by ASTM D6751 standard methods.

2.1 Materials

Solvents and chemicals used were n-hexane (99%), methanol (99.5%), Conc.H_2SO_4 (99%) and anhydrous sodium sulfate (99%). Products belongs to Merck, Germany and used as received without any further purification.

2.2 Catalyst preparation

Water pre-treatment was required for *C. pentandra* stalks to get rid of impurities present in it. Hot air oven was operated at a temperature about 85°C for drying. After the period of 48h the dried once are broken into chips and crushed into powder form. Grounded powder was allowed to burn in muffle furnace at the temperature of 250º C with an increasing temperature of 50º C every half an hour for 4 h. Then the carbon solids were allowed to grind in a planetary mill with an accelerating speed of 300 RPM for 5h. Sulfonation of the grinded carbon was performed as follows: 20% concentrated H_2SO_4 is added and allowed to react for 24h. It is then diluted using excess water and filtered. The residue is washed completely until the filtrate get neutralized (i.e., pH=7) and dried at 65°C for 3h.Sulfonated carbon (dried) was kept inside a muffle furnace at a temperature of 200°C for carbonization around 2h. The residue after carbonization is allowed to cool and taken out, which is the Sulfonated nanocarbon.

Fig. 1

2.3 Oil Extraction

Shells of *C. Pentandra* were dehulled and seeds were removed from the fiber. *C. Pentandra* seeds collected were dried under sun for a period of one week. Forty grams of seeds was grinded and packed inside a thimble for Soxhlet extraction. Extracting medium n-hexane was poured and filled upto two third volumes of the round bottom flask. The heating mantle was adjusted to about 60-70ºC and the solvent was heated continuously, it starts to evaporate and condenses back into the sample. Extracted oil containing some portion of the solvent was then recycled back to the round bottom flask as it refluxes. The extraction was conducted at the rate of 8 cycles per hour and continued for 16 h. Whatman filter paper No. 4 was used to filter the extract and rinsed with the same to complete the transfer. Solvent present was restored by simple distillation. The oil yield obtained was expressed in terms of mass percentage and calculated as

$$\text{Oil yield (wt \%)} = [\text{mass of oil extract (g)} / \text{mass of seed kernel (g)}] \times 100 \qquad (1)$$

The determination of density and viscosity are carried out using a hydrometer and Redwood viscometer. The iodine value and saponification value were determined according to AOCS Official Methods [31].

2.4 Biodiesel Production

Transesterification reaction was performed in an autoclave of 100 mL with Teflon lining. Temperature controller was used to maintain reaction temperature in the range of 180-260°C. After 3h esterification and transesterification reaction were stopped; decanter was used for separation of two distinct phases, the oil phase (biodiesel) and the aqueous phase (Glycerol). It took nearly 4h for phase separation but time requirement was 10min only, because biodiesel layer was translucent. Biodiesel phase became transparent once separation was completed. The lower glycerol layer was decanted. Ester phase was washed five times with 100 mL of warm distilled water. An impurity like residual catalyst, methanol, glycerol and soaps were removed by water washing. Anhydrous sodium sulfate was used for drying of ester phase.

Conversion of *C. Pentandra* oil to biodiesel was predicted using ^{1}H NMR spectroscopy (BRUKER AVANCE III), at 300K choosing a 5 mm probe head and $CDCl_3$ as the solvent. The conversion was calculated using the equation [32]

$$\text{Conversion (\%)} = (2A_{ME}/3A\alpha_{ME}) * 100 \qquad (2)$$

A_{ME} = integration value of the protons of the methyl esters.

$A\alpha_{ME}$ = integration value of the methylene protons.

According to ASTM D6751 and EN standards biodiesel properties of *C. Pentandra* were obtained.[33]

3. RESULTS AND DISCUSSION

3.1 Catalyst Characterization

Carbonized *C. Pentandra* stalks exposed a loose irregular network structure and the pores became larger when obtained carbon precursor was treated by concentrated H_2SO_4. From the Fig.2 the catalyst was granular and porous with evenly distributed granules and abundant large pores. The granules were made up of several smaller granules which formed a porous net-like structure. The larger quantities of pores and larger pore size would enhance the accessibility of sulfuric acid into the carbon powder bulk. Average pore size of the sulfonated *C. Pentandra* stalks is 4.8 nm and demonstrated that the catalyst is a *sulfonated nanocarbon* catalyst. Reactants can very quickly diffuse into the inside of the catalyst and enables them to make contact with more acid sites. The data from nitrogen adsorption–desorption isotherms demonstrated that the catalyst was porous and having surface area of 714 m^2 g^{-1} indicated that many of the sulfonic acid groups were in the inner surface on the catalyst. The high specific area and large pore size are the major reason for the high catalytic activity and also increased transesterification efficiency.

Fig.2

C. Pentandra stalks catalyst revealed that the contents of carbon, sulfur and oxygen were 47, 18.09 and 34.91 wt. % using EDAX results. FTIR spectroscopy was the effective tool for semi-quantitative estimation of structural information and functional groups in the sulfonated *C. Pentandra* stalk catalyst. From the Fig.3 it confirms the presence of sulfonic acid sites by showing peaks at 1345-1450 cm^{-1}. *C. Pentandra* stalks catalyst showed high catalytic activity because of the H_2SO_4 treatment at 200°C and it leads to extensive covalent sulfonation.[34]

Fig. 3

The Raman spectrum can be used to analyze the graphitic structure. Two bands, located at 1350 and 1540 cm^{-1} exhibiting the presence of D band and G band (Fig. 4). The band at 1540 cm^{-1} is observed in graphitic materials, which is due to the vibration mode corresponding to the movement in opposite directions of two neighboring carbon atoms in a single crystal graphite sheet. The band at 1350 cm^{-1} was commonly associated with the presence of defects in the graphite layer.[35] The carbon catalyst can be deduced to have more defects since the difference in the D/G intensity ratios can be attributed to the change in surface functionalities resulting from breaking C–C bonds.[36] The C–C bond breaking also can help the non-graphitic carbon to couple with the sulfonic acid group to form a stable covalent structure and this catalyst can maintain good stability at high reaction temperature.

Fig. 4

3.2 Comparison of the non-catalytic and catalytic process

3.2.1 Catalyst concentration

In order to investigate the catalytic effect on the conversion of triglyceride, we carried out the simultaneous esterification and transesterification with and without addition of a solid acid catalyst. The conversions of triglyceride in these two processes were compared. The amount of catalyst also affects the conversion efficiency of the process. The effect of catalyst concentration on the conversion of methyl ester with reaction temperature of 200°C and molar ratio of methanol to oil as 12:1M was studied (Fig. 5). With increase in catalyst concentration from 0.5 to 1.5wt%, the conversion of methyl ester increased markedly from 84 to 95%. The effect of without catalyst usage on the biodiesel yield was studied at 200°C with 12:1 methanol to oil ratio. Fig. 5 displayed that with the increase in time it can be seen that the biodiesel conversion increased progressively from 20 to 40%. Hence, it can be concluded that with the addition of a solid catalyst, the esterification and transesterification can be accelerated greatly. The current experiment shows that the optimal usage of the catalyst is 1.5 wt% for further studies.

Fig. 5

3.2.2 Molar ratio of methanol to oil

Since the esterification and transesterification are reversible reactions, excess methanol shifts the equilibrium in the direction of ester formation. Also, methanol increases the solubility of phases, thus encouraging a smooth reaction. The effect of methanol to oil ratio on biodiesel conversion was examined under 1.5wt% catalyst and reaction temperature of 200°C. The biodiesel conversion was affected in a lower methanol to oil ratio. With further increment in methanol to oil ratio, it resulted in a significant effect as shown in Fig. 6b.The conversion rate increased rapidly and reached a higher biodiesel conversion of 97% at 18:1M of methanol to oil ratio. When the methanol to oil ratio was more than 18:1M, the conversion rate was not significantly increased. Effect of methanol to oil ratio on biodiesel yield was examined under without catalyst and reaction temperature of 200°C as shown in Fig. 6a. However, a further increase in the molar ratio of methanol to oil after 18:1 showed very limited effect on the conversion of ester. It also can be noticed that the difference in triglyceride conversion for these two processes is obvious. Hence, an optimal 18:1M methanol to oil ratio is appropriate for this reaction.

Fig. 6(a, b)

3.2.3 Reaction temperature

The influence of the reaction temperature on the biodiesel conversion was evaluated using *C. Pentandra* oil at 190, 200,210 and 220°C with methanol to oil ratio 18:1M and catalyst concentration 1.5wt%. From Fig.7b it could be seen that the conversion rate of biodiesel was increased with the rise of temperature, since the reaction could not reach equilibrium. The reaction rate at 220°C was significantly faster than the reaction rate at 200°C. The highest conversion of triglyceride was obtained as 99% after reaching 2hrs reaction time at 220°C. On the other hand, the reaction carried out without catalyst by varying the reaction temperature from 190-220°C. From the Fig.7a it is observed that methyl ester conversion increases from 20 to 40% by the variation of reaction time from 0.5 to 2 hrs. Biodiesel production cost will be increased if the reaction takes place in the liquid phase because of the reaction carried out at a higher temperature and pressure. It can be seen that the conversion of triglyceride with the addition of a solid catalyst was much higher than the process without a solid catalyst. So, the optimum temperature for this reaction is 220°C.

Fig. 7(a, b)

3.3 Stability

Besides the simple catalyst removal step and being environmental friendly, another main advantage of the solid acid catalyst is reusability. From economic point of view, the cost of the catalyst accounts for a large part of the cost of biodiesel production. The catalyst was recycled to study the reusability. The data of the reusability of the catalysts are presented in Fig. 8. It is observed that catalyst showed reasonable loss of activity with the first recycling, and thereafter a slower progressive loss. From the fresh use run to the completion of 4th reuse run, the yield of ME gradually decrease from 99% to 91% due to catalyst mass loss and it was reduced from 0.5wt % to 0.1wt%.The experimental results indicated that *sulfonated nanocarbon* is a stable catalyst and suitable for long-term use. Consequently the catalytic performance of the proposed catalyst were compared with previously reported carbon-based acid catalysts are presented in the Table 1.

Fig. 8

Table 1

3.4 Measured properties of the *C. Pentandra* oil and biodiesel

The principal fatty acid profile of the *C. Pentandra* oil are linoleic (37.1%), oleic (26.9%), palmitic (22.3%) and stearic (6.8%) acids. The level of total saturated and unsaturated fatty acid of the *C. Pentandra* oil was 12.5% and 73.9 % respectively. The high content of unsaturated fatty acid makes it a stable liquid at room temperature. The physicochemical properties of C.

Pentandra oil are given in Table 2. Clearly the properties of biodiesel depend very much on the nature of the raw material, as well as the process used for its production. Biodiesel conversion was identified with ^{1}H NMR spectroscopy and the same was presented in Fig. 9. The properties flash point, density, viscosity, cloud point of the *C. Pentandra* biodiesel were measured and compared with ASTM D6751 and EN standards for biodiesel and presented in Table 3.

Fig. 9

Table 2

Table 3

4. Conclusion

The present study showed that the *sulfonated nanocarbon* was effective solid acid catalyst for biodiesel production from *C. Pentandra* oil. It is inexpensive and environment friendly, has high catalytic activity. The high activity of the catalyst was described to the high acid site density and the bonded hydrophilic functional groups that allowed more methanol to contact with the carbonyl group of triglyceride. It is porous with particle size of 4.8 nm, which increase catalytic activity and stability. The high specific surface area and large pore size are favorable for contact between catalyst and substrates, which effectively improved efficiency of transesterification. The maximum conversion was achieved as 99% at 220°C, 18:1 molar ratio of methanol to oil and 1.5 wt% of catalyst. The properties of the biodiesel derived were found to meet the biodiesel standards of ASTM D6751 and EN and also the commercial diesel.

Reference

1 R.A. De Santis, Crude oil price fluctuations and Saudi Arabia’s behavior, *Energ Econ,* 2003, 25, 155–173.

2 S. Angina and P. Ram, Triglycerides-based diesel fuels, *Renew Sust Energ Rev,* 2000, 4, 111–133.

3 J.V. Gerpen, Biodiesel processing and production, *Fuel Process Technol,* 2005, 86, 1097–1107.

4 E. Lotero, Y. Liu, D.E. Lopez, K. Suwannakarn, D.A. Bruce and J.G.Goodwin, Synthesis of biodiesel via acid catalysis, *Ind Eng Chem Res* 2005, 44, 5353–5363.

5 Y. Liu, E. Lotero, J.G. Goodwin, and X. Mo, Transesterification of Poultry Fat with Methanol Using Mg-A1 Hydrotalcite Derived Catalysts, *Appl Catal A-Gen,* 2007, 138, 331.

6 S. Behzadi and M.M. Farid, Review: examining the use of different feedstock for the production of biodiesel, *Asia-Pac J Chem Eng,* 2007, 2, 480–486.

7 A.S. Ramadhas, S. Jayaraj, and C. Muraleedharan, Biodiesel production from high FFA rubber seed oil, Fuel, 2005, 84, 335–340.

8 S.V. Ghadge, and H. Raheman, Biodiesel production from mahua (Madhuca indica) oil having high free fatty acids, Biomass Bioenerg, 2005, 28, 601–605.

9 S. Zullaikah, C.C. Lai, S.R. Vali and Y.H. Ju, A two-step acid-catalyzed process for the production of biodiesel from rice bran oil, Bioresour Technol, 2005, 96, 1889–1896.

10 Y. Wang, S.Y. Ou, P.Z. Liu, F. Xue and S.Z. Tang, Comparison of two different processes to synthesize biodiesel by waste cooking oil, J Mol Catal A: Chem, 2006, 252, 107–112.

11 G.R. Petersonm and W.P. Scarrah, Rapeseed oil transesterification by heterogeneous catalysis, J Am Oil Chem Soc, 1984, 61, 1593–1597.

12 M.D. Serio, M. Ledda, M. Cozzolino, G. Minutillo, R. Tesser and E. Santacesaria, Transesterification of soybean oil to biodiesel by using heterogeneous basic catalysts, Ind Eng Chem Res, 2006, 45, 3009–3014.

13 Z. Helwani, M.R. Othman, N. Aziz and J. Kim, Solid heterogeneous catalysts for transesterifi cation of triglycerides with methanol: A review, Appl Catal A-Gen, 2009, 363, 1–10.

14 M.K. Lam, K.T. Lee and A.R. Mohamed, Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: A review, Biotechnol Adv, 2010, 28, 500–518.

15 M. Zabeti, W.M.A.W. Daud and M.K. Aroua, Activity of solid catalysts for biodiesel production: A review, Fuel Process Technol, 2009, 90, 770–777.

16 A.A. Kiss, A.C. Dimian and G. Rothenberg, Solid acid catalysts for biodiesel production towards sustainable energy, Adv Synth Catal, 2006, 348, 75–81.

17 S. Zheng, M. Kates, M.A. Dube and D.D. McLean, Acid-Catalyzed Production of Biodiesel from Waste Frying Oil, Biomass Bioenerg, 2006, 30, 267.

18 F.E. Kiss, M. Jovanovic and G.C. Bošković, Economic and ecological aspects of biodiesel production over homogeneous and heterogeneous catalysts, Fuel Process Technol, 2010, 91, 1316-1320.

19 S.P. Chavan, Y.T. Subbarao, S.W. Dantale and R. Sivappa, Transesterification of ketoesters using Amberlyst-15, Synth Commun, 2001, 31, 289–294.

20 S.P. Chavan, P.K. Zubaidha, S.W. Dantale, A. Keshavaraja, A.V. Ramaswamy, and T. Ravindranathan, Use of solid superacid (sulphated SnO2) as efficient catalyst in facile transesterification of ketoesters, Tetrahedron Lett, 1996, 37, 233–236.

21 S. Furuta, H. Matsuhashi H and K. Arata, Catalytic action of sulfated tin oxide for etherification and esterification in comparison with sulfated zirconia, Appl Catal A-Gen, 2004, 269, 187–191.

22 S. Furuta, H. Matsuhashi H and K. Arata, Biodiesel fuel production with solid superacid catalysis in fixed bed reactor under atmospheric pressure, Catal Commun, 2004, 5, 721–723.

23 M. Hara, T. Yoshida, A. Takagaki, T. Takata, J.N. Kondo, S. Hayashi and K. Domen, A carbon material as a strong protonic acid, Angew Chem Int Edit, 2004, 43, 2955–2958.

24 W. Lou, M. Zong and Z. Duan, Efficient production of biodiesel from high free fatty acid-containing waste oils using various carbohydrate-derived solid acid catalysts, Bioresour Technol, 2008, 99, 8752–8758.

25 Q. Shu, J. Gao, Z. Nawaz, Y. Liao, D. Wang and J. Wang, Synthesis of biodiesel from waste vegetable oil with large amounts of free fatty acids using a carbon-based solid acid catalyst, Appl Energ, 2010, 87, 2589–2596.

26 Q. Shu, Z. Nawaz, J. Gao, Y. Liao, Q. Zhang, D. Wang and J. Wang, Synthesis of biodiesel from a model waste oil feedstock using a carbon-based solid acid catalyst: Reaction and separation, Bioresource Technol, 2010, 101, 5374–5384.

27 T. Liu, Z. Li, W. Li, C. Shi and Y. Wanga, Preparation and characterization of biomass carbon-based solid acid catalyst for the esterification of oleic acid with methanol, Bioresour Technol, 2013, 133, 618–621.

28 B.V.S.K. Rao, K. Chandra Mouli, N. Rambabu, A.K. Dalai and R.B.N. Prasad, Carbon-based solid acid catalyst from de-oiled canola meal for biodiesel production, Catal Commun, 2011, 14, 20–26.

29 D. Narahari and R. Asha rajini, Chemical composition and nutritive value of kapok seed meal for broiler chickens, British Poultry Sci, 2003, 44, 505-509.

30 P. Sivakumar, S. Sindhanaiselvan, N. Nagendra Gandhi, S. Shiyamala Devi, S. Renganathan, Optimization and kinetic studies on biodiesel production from underutilized Ceiba Pentandra oil, Fuel, 2012,103,693-698.

31 Official Methods and Recommended Practices of the AOCS, 5th Ed, AOCS Press, Champaign, IL, 1997.

32 G. Gelbard, O. Bres, R.M. Vargas, F. Vielfaure and U.F. Schuchardt, ^{1}H nuclear magnetic resonance determination of yield of transesterification of rapeseed oil with methanol, J Am Oil Chem Soc, 1995, 72, 1239−1241.

33 Standard Test Methods D445, D976, D93, D2500, D97, D86, American Society for Testing and Materials (ASTM), West Conshohocken, PA, 1998.

34 F. Peng, L. Zhang, H.J. Wang, P. Lv and H. Yu, Sulfonated carbon nanotubes as a strong protonic acid catalyst, Carbon 2005, 41, 2397–2429.

35 H.G. Connan, B.J. Reedy, C.P. Marshall and M.A.Wilson, New nanocarbons: rod milling and annealing of graphite in the presence of yttrium, Energy Fuels, 2004, 18, 1607–1614.

36 V.V. Kaichev, V.I. Bukhtiyarov, G. Rupprechter and H.J. Freund, Activation of the C–O bond on the surface of palladium: an in situ study by X-ray photoelectron spectroscopy and sum frequency generation, Kinet Catal, 2005, 46, 269–281.

Figure Caption

Fig. 1. Graphical picture of *Ceiba pentandra* stalks Nano Catalyst

Fig. 2. SEM Images of Nano carbon catalyst

Fig. 3. FTIR Spectrum of Nano carbon catalyst

Fig. 4. Raman Spectrum of Nano carbon catalyst

Fig. 5. Conversion (%) vs. Effect of Catalyst(wt%) (Reaction temperature 200°C, Reaction time 150 min, methanol to oil ratio 12:1M).

Fig. 6. (a) Conversion (%) vs. Effect of Methanol to oil ratio (Reaction temperature 200°C, Reaction time 150 min, Without catalyst) **(b)** Conversion (%) vs. Effect of Methanol to oil ratio (Reaction temperature 200°C, Reaction time 150 min, Catalyst concentration 1.5 wt%),

Fig. 7.(a) Conversion (%) vs. Effect of Reaction temperature (Reaction time 150 min, Methanol to oil ratio 18:1M,Without catalyst), **(b)** Conversion (%) vs. Effect of Reaction temperature (Reaction time 150 min, Methanol to oil ratio 18:1M, Catalyst concentration 1.5 wt%).

Fig. 8. Conversion (%) vs. Number of cycles (Reaction temperature 200°C, Reaction time 150 min, Catalyst concentration 1.5 wt%, methanol to oil ratio 18:1M).

Fig. 9. ^{1}H NMR Spectrum Analysis of *Ceiba pentandra* biodiesel.

Table 1

Catalytic performance of various solid acid catalysts

Acid Catalyst	**Catalyst Concentration (wt%)**	**Methanol to Oil Ratio**	**Conversion (%)**
Vegetable oil asphalt	0.2	16.8	80.5
De-oiled canola meal	7.5	60:1	93.8
Corn straw	7	7:1	98
Ceiba pentandra stalk	1.5	18:1	99

Table 2

Physico-chemical properties of *C. pentandra* oil

Physico-Chemical properties	
Viscosity at 40°C (cSt)	28.45
Density (kg/m^3)	925
Iodine value (g/100 g)	98
Saponification value	193
Free fatty acids (wt. %)	13.4
Unsaponifiable matter (wt. %)	1.5
Refractive index	1.46

Table 3

Fuel properties of *C. pentandra* biodiesel

Characteristic	**ASTM Specifications**	**EN Specifications**	***C. pentandra* Biodiesel**
Phosphorous content (ppm)	≤10	≤10	2
Acid Number	0.5 max	0.5 max	0.12
Flash point (°C)	>130	>101	164
Density (kg/m^3)	880	860 to 900	867
Pour point (°C)	-15 to 10	NA	-2
Cloud point (°C)	-3 to 12	NA	3
Viscosity at 40°C (cSt)	1.9-6.0	3.5 to 5.0	4.3
Lower heating value(MJ/kg)	NIL	35	38.122
Oxidative stability (h)	3 min	6 min	4.12
Cetane Number	47 min	51 min	52

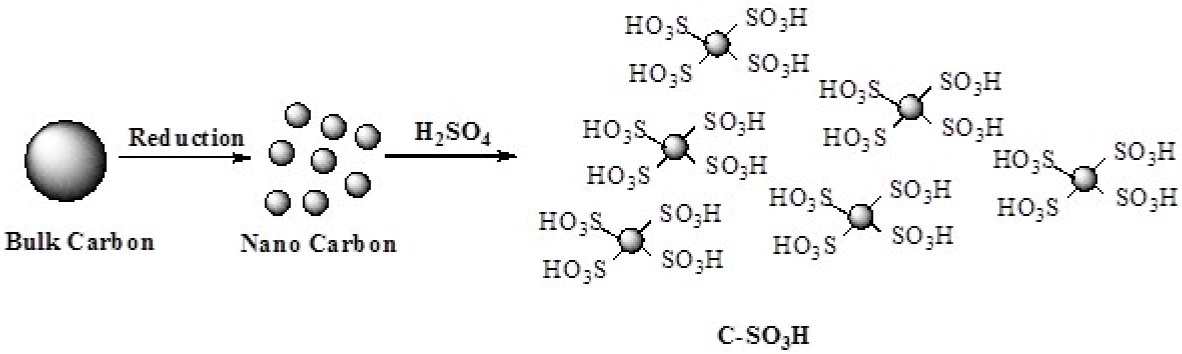

Bulk Carbon
Reduction
Nano Carbon
H_2SO_4
HO_3S
SO_3H
$C\text{-}SO_3H$

Fig. 1

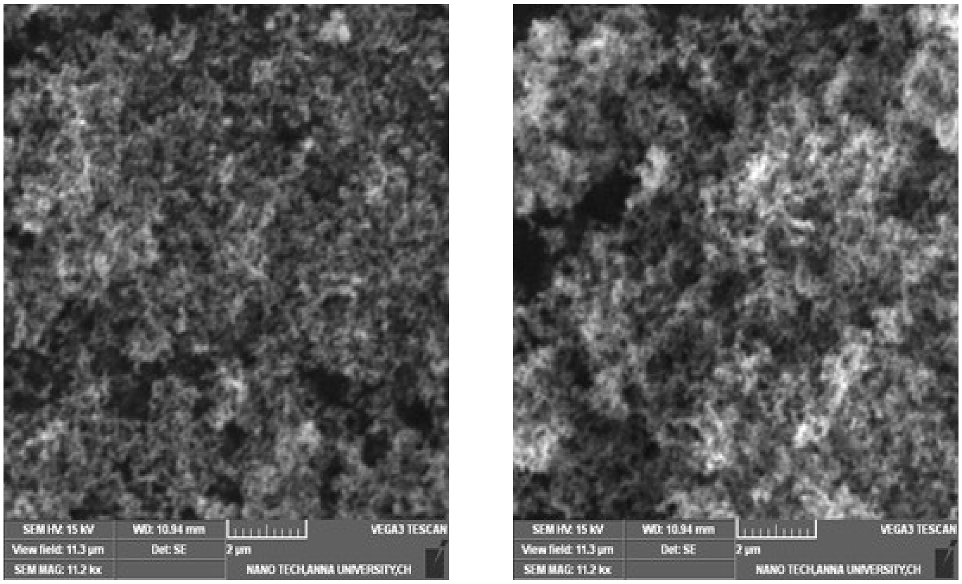

SEM HV: 15 kV
WD: 10.94 mm
VEGA3 TESCAN
View field: 11.3 μm
Det: SE
2 μm
SEM MAG: 11.2 kx
NANO TECH,ANNA UNIVERSITY,CH
SEM HV: 15 kV
WD: 10.94 mm
VEGA3 TESCAN
View field: 11.3 μm
Det: SE
2 μm
SEM MAG: 11.2 kx
NANO TECH,ANNA UNIVERSITY,CH

Fig. 2

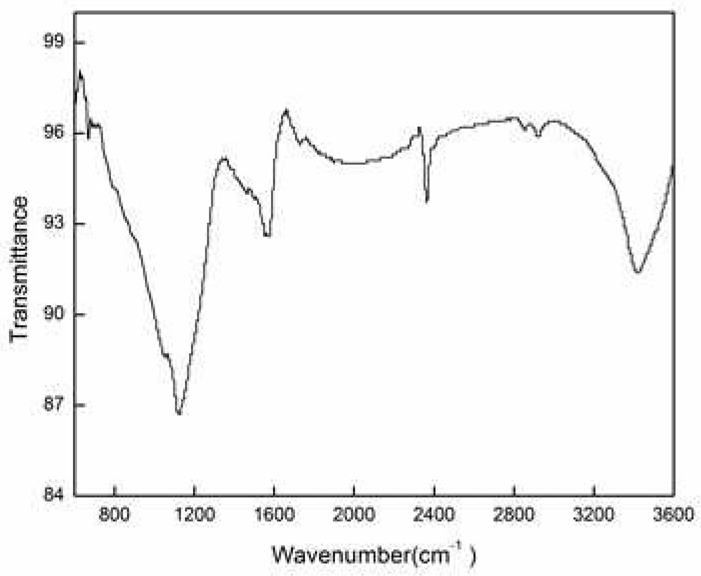

99
96
93
90
87
84
Transmittance
800
1200
1600
2000
2400
2800
3200
3600
Wavenumber(cm^{-1})

Fig. 3

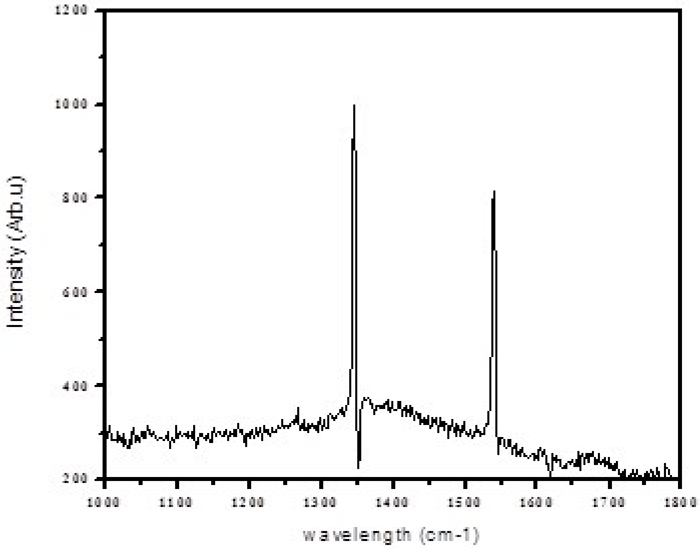

1200
1000
800
600
400
200
Intensity (Arb.u)
1000
1100
1200
1300
1400
1500
1600
1700
1800
wavelength (cm-1)

Fig. 4

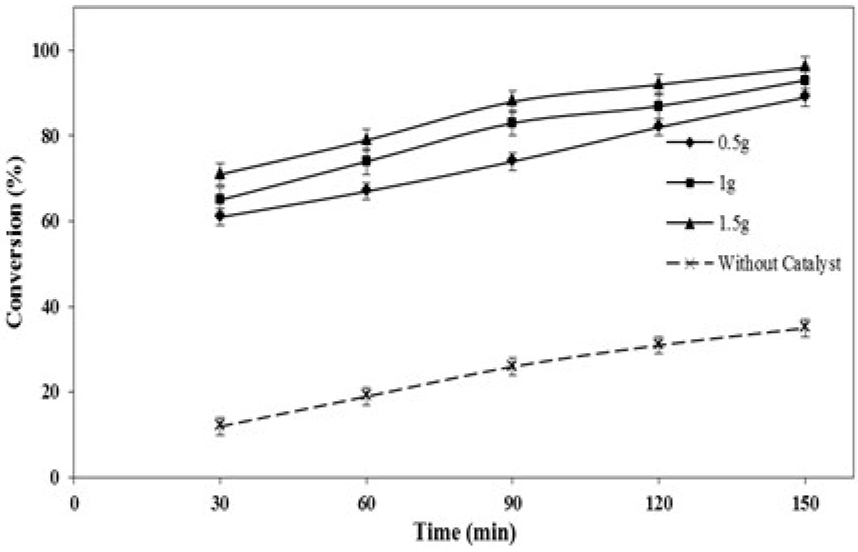

Conversion (%)
100
80
60
40
20
0
0
30
60
90
120
150
Time (min)
0.5g
1g
1.5g
Without Catalyst

Fig. 5

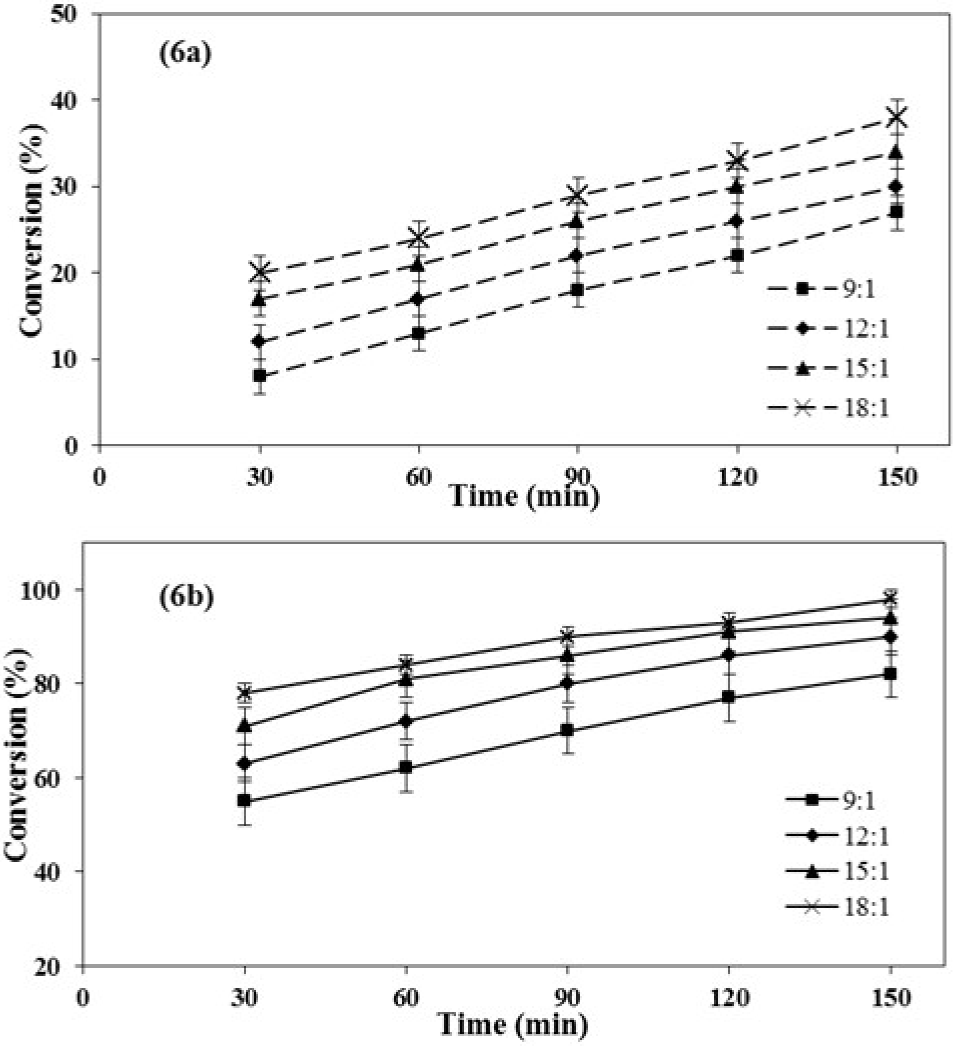

(6a)
Conversion (%)
0
10
20
30
40
50
0
30
60
90
120
150
Time (min)
9:1
12:1
15:1
18:1
(6b)
Conversion (%)
20
40
60
80
100
0
30
60
90
120
150
Time (min)
9:1
12:1
15:1
18:1

Fig. 6

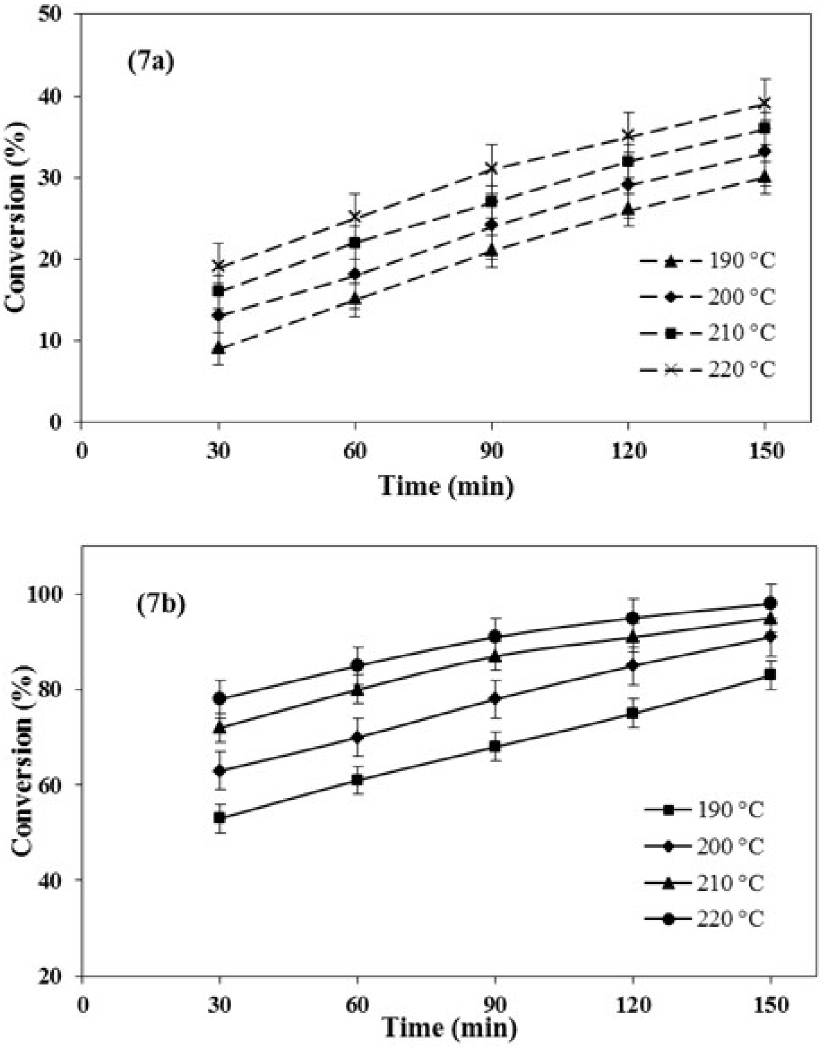

(7a)
Conversion (%)
0
10
20
30
40
50
Time (min)
0
30
60
90
120
150
190 °C
200 °C
210 °C
220 °C
(7b)
Conversion (%)
20
40
60
80
100
Time (min)
0
30
60
90
120
150
190 °C
200 °C
210 °C
220 °C

Fig. 7

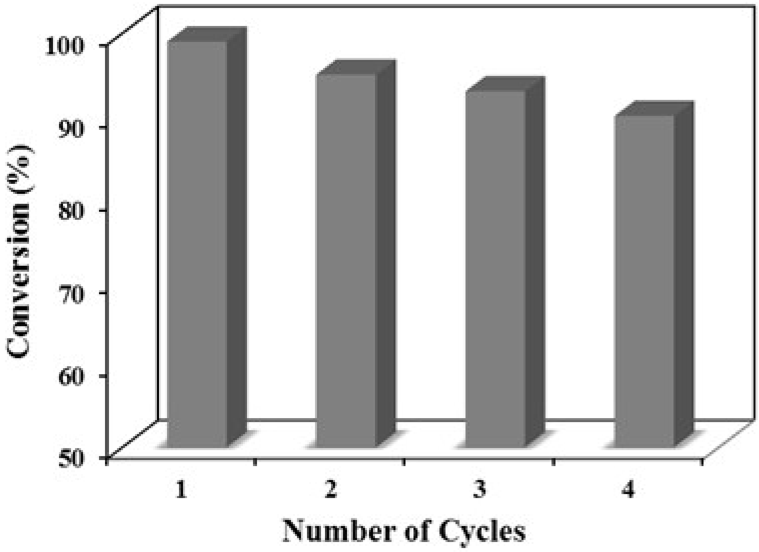


Fig. 8

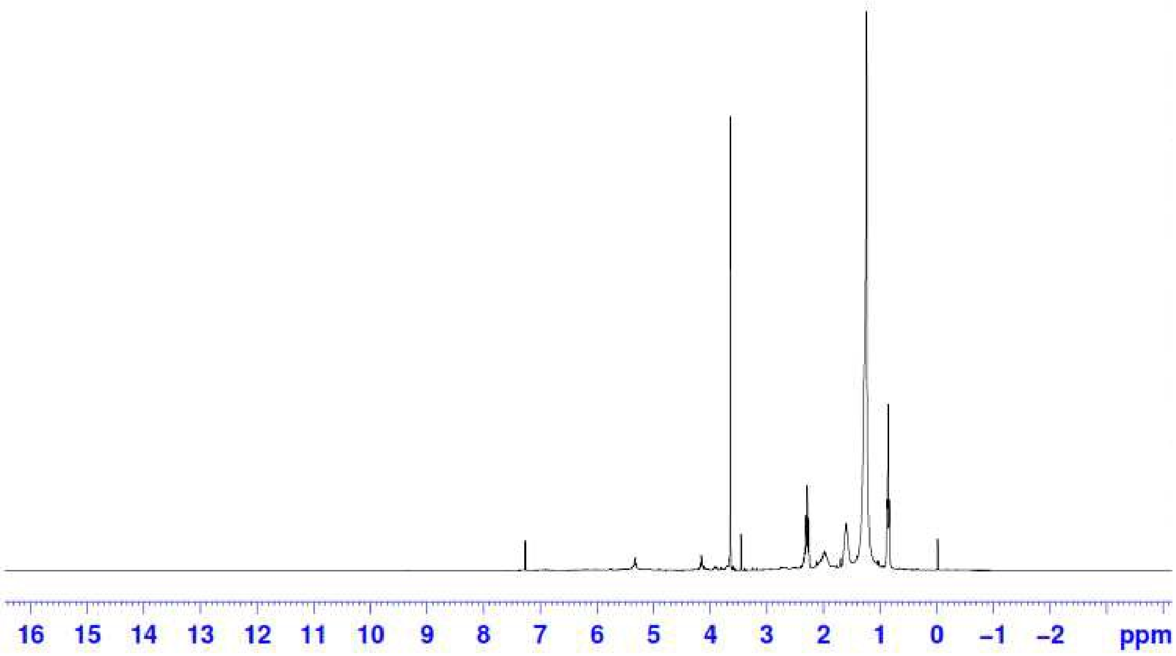


Fig. 9