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Technical Note

Feasibility study of synthesized carbon as catalyst in biodiesel production

Tourangbam RAHUL SINGH[1], Thokchom SUBHASCHANDRA SINGH[1], Tikendra NATH VERMA[2,*], Prerana NASHINE[3], Upendra RAJAK[4]

[1]Department of Mechanical Engineering, National Institute of Technology Manipur, Imphal West, India - 795004
[2]Department of Mechanical Engineering, Maulana Azad National Institute of Technology Bhopal, M.P, India - 462003
[3]Department of Mechanical Engineering, National Institute of Technology Rourkela, India - 769001
[4]Department of Mechanical Engineering, Rajeev Gandhi Memorial College of Engineering and Technology, Nandyal, India - 518501

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ABSTRACT

The thrust in biofuel production has pushed researchers in finding more of environmentally friendly materials for use as catalyst in the biofuel production process. Commercially available catalyst materials are not sustainable, and they generally incur higher cost of operation. In the present study, locally available native woods species of Manipur, India namely, Yenthou (*Arundo donax.L*) and Uningthou (*Phoebe hainesiana*) were exposed at elevated temperature of 400°C and variable exposure time of 90 and 120 minutes for possible use as catalyst during biofuel production. Muffle furnace has been employed for production of catalyst and characterization techniques such as XRD, FT-IR and SEM with EDX are used. XRD analysis shows diffraction peak corresponding to (0 0 2), (1 0 0) and (1 0 1) of the face centered cubic phase at 28.61°, 28.54° and 30.02° respectively while Scherrer equation shows 29.737 nm as average grain size. FT-IR analysis also shows C=C formation from the samples. The SEM & EDX analysis shows good formation of carbon in the catalyst and the weight % of the components are obtained to be 89.18% and 10.82% for C and O respectively. Transesterification of waste cooking oil at 5% (wt%), 10:1, 75°C and 60 minutes for catalyst loading rate, alcohol-to-oil ratio, reaction temperature and reaction time respectively shows conversion rate of 87.4±1.3% with reusability of 3 times.

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***Corresponding author.**
*E-mail address: verma.tikks@gmail.com

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INTRODUCTION

The requirement for sustainable catalyst during biodiesel production is at large. This drives many researchers in pursuing locally available materials for use as feed stock [1-3] and catalyst materials [4-7]. This is due to increased cost in biodiesel production due to usage of chemicals as catalyst materials. A study on biodiesel prepared by the process of transesterification for Rapeseed (RA) and Mahua (MU) biodiesel through equivalent volume of 1:1 is performed for 100% of RA, MU and dissimilar blends of rapeseed-mahua (RM) along with diesel. The results portrayed optimal performance for BL20 blends, and the results are closer to diesel. Similar emission characteristics are also observed for BL20 blend, such as reduction in carbon monoxide, hydrocarbons and smoke during full loading situations at 20.66%, 8.56% and 6.9% respectively, compared to diesel. The oxides of nitrogen are obtained to be slightly greater by 3.77% than diesel [8].

An investigation on transesterification of waste vegetable oil using eggshell as heterogeneous catalyst where the calcination of eggshells took place at 800°C in a furnace shows that the catalyst has large pore diameters of 92.1A and higher surface area of 30.7 m^2/g. Optimization of various parameters was performed by central composite RSM (95% confidence level) and an optimum yield of 91% was obtained at operating factors of 65°C, 22.5:1, 5h 30min and 3.5 (wt.%) for temperature, methanol-oil ratio, reaction time and catalyst respectively [9]. A study aimed to synthesize biodiesel from castor oil using homogenous alkaline transesterification results in optimal yield of 95 wt. %. Gas chromatography was used for characterizing the FAME. Castor oil biodiesel: petro-diesel blends B5, B10 and B20 have been prepared and the corresponding properties are determined in the study. The results shows that castor oil biodiesel blends have lower cloud point with higher viscosity and hence, it was concluded that they are suitable for extreme winter temperatures [10].

A bench-scale recycling transesterification reactor was developed in a study with capacity for producing 3 litres of biodiesel. Full factorial method was used to optimize the operating parameters used during the transesterification reaction. The products were characterized using gas chromatography and liquid analysis for determining the contents of ester and calcium concentrations. A maximum yield was observed (almost 100%) for operating conditions of 6:1, 75 min, 3 wt.% for methanol: oil molar ratio, reaction time, and concentration of catalyst [11]. Another study performed an experiment to produce biodiesel using river snail shell as catalyst (calcium oxide). The shell were calcined at 800˚C for 4h in a muffle furnace for obtaining calcium oxide. The parameters considered for the experiment are: methanol/oil molar ratio (6:1, 9:1, 12:1); catalyst amount (1-3 %); reaction time (1-3 h); reaction temperature (65°C). And the final optimal factors were: 9:1 methanol/oil molar ratio, 3 wt. % catalyst and 1h reaction time. This approach achieved a yield of 92.5% biodiesel [12].

An investigation was conducted using impregnation of Na-ZSM-5 on the activated calcium oxide extracted from crab shell, obtained after calcination at 900°C and additional calcination at 550°C for 10h. The resulting catalyst was characterized by; XRD, SEM and BET. The influence of various parameters on the final yield of trans-esterified neem biodiesel was studied and optimized. Produced biodiesel was also characterized by NMR spectrometry. The yield was found to be 95% at 15% CaO impregnated n Na-ZSM-5 at 75°C (reaction time 6h, temperature 75°C, methanol/oil ratio 12:1, catalyst dosage 0.2, catalyst concentration of 15 %) [13]. CaO has been used as an alkaline catalyst for performing transesterification at 95˚C reaction temperature and 2h reaction time. The acid value of Zanthoxylum bungeanum seed oil (ZSO) with high FFA was further reduced to 2 mg KOH/g by single-step esterification using methanol to FFA molar ratio of 4.91:1, ferric sulfate 9.75%. RSM was applied for optimizing the operating parameters. The conversion to biodiesel reached above 96% during the optimal conditions obtained through RSM (11.69:1 alcohol to oil; 2.52% catalyst concentration; 2.45h reaction time) [14].

Waste cork (Quercus suber) was employed in a study as heterogeneous catalyst for biodiesel production from WCO (Canola oil). The study revealed maximum fatty acids methyl esters (FAMEs) conversion of 98% when the catalyst was synthesized at 600°C and operating conditions of 25:1, 1.5% wt.%, 65°C for alcohol: oil ratio, catalyst loading and reaction temperature. The obtained biodiesel greatly composed of fatty acid methyl esters in orders of C18:1 > C18:2 > C16:0 > C20:0. The tested properties were evaluated to be cetane number of 50.56, higher heating value of 39.5 MJ/kg, kinematic viscosity 3.9 mm^2/s and density 0.87 kg/m^3[15].

A study was conducted on biochar catalyst obtained from peat and analyzed by using the instruments and characterization methods and hammett indicator. During the experiment, it was observed that the surface area and pore volume of the peat biochar has been significantly increased which has been achieved through KOH chemical activation treatment [16]. The increasing cost of oil process has tremendously moved researchers in finding different alternate ways for substituting conventional fossil fuels in power generation. Alternatives such as plastic oil, algae, sunflower oil and other various types of non-edible oils were generously tested of their characteristics in internal combustion engines [20-25].

Therefore, the authors in the present study have attempted to study the feasibility of using native woods as carbon materials for use as catalyst in biodiesel production. The catalyst was tested using different testing methods such as XRD, FT-IR, SEM and EDX to analyze the synthesized catalyst material. A confirmation test will also be conducted in checking effectiveness of the newly synthesized carbon

catalyst. The present study has been conducted in view of the arising demand of cheaper and cost-effective materials for use as catalyst in biodiesel production. The present study well yields important results and confirmation for possible use as heterogeneous catalyst.

MATERIALS AND METHODS

Sample Collection and Preparation

Woodchips which are easily available in the market were collected from the locality of Imphal, India. Fig 1 shows the process of catalyst preparation from raw materials. The steps involve includes- drying of the woodchips in a microwave oven for about 1 hour ensuring no moisture is left within the sample. This is followed by pre-crushing of the chips into smaller size before carbonization for ease in fitting the samples inside the crucible in a muffle furnace. The samples are subjected to an elevated temperature of 400°C. The samples being kept at microwave oven, weighing and finally being kept at the crucible are shown in Fig 2. The samples after carbonization are then crushed using a mortar and pestle, shown in Fig 3. The samples are then kept tightly inside an airtight container.

The transesterification was conducted using the synthesized catalyst using optimal conditions from Singh and Verma (2019) [2].

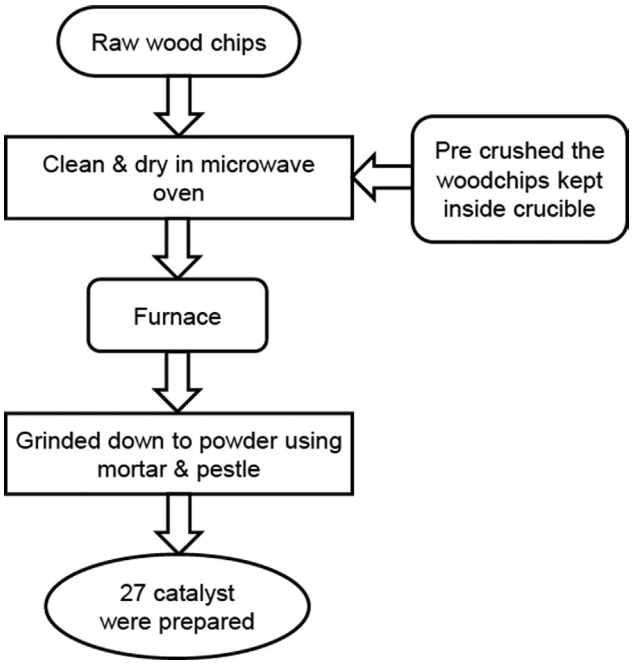

Figure 1. Procedure of preparation of catalyst (C) derived from wood chips.

Figure 3. Grinding of the samples.

Figure 2. Wood chips placed inside microwave oven for drying, weighing and crucible inside a muffle furnace.

Table 1. Calculation of crystal size

2 theta (deg)	FWHM (deg)	Theta (deg)	Theta (rad)	FWHM (rad)	Crystal size (nm)
28.61257	0.160471	14.30629	0.249692	0.002801	51.09039
28.54693	1.1251	14.27347	0.249119	0.019637	7.285877
30.02264	0.26673	15.01132	0.261997	0.004655	30.83631
Average crystal size: 29.73 nm					

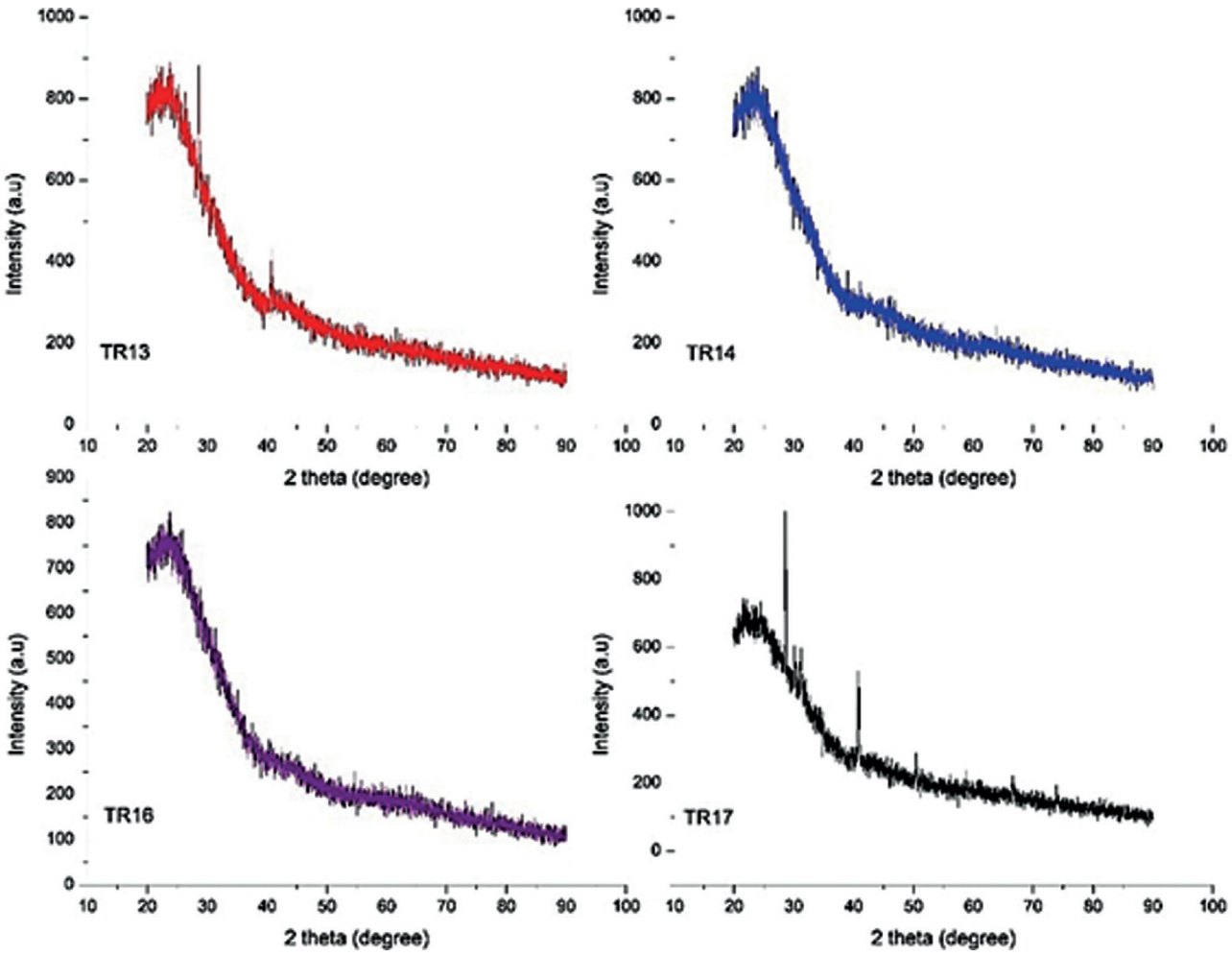

Figure 4. XRD Graph for charcoal of wood chips catalyst.

Sample Analysis and Characterization

The diffracted patterns from the C samples are recorded using X-Ray Diffraction (XRD) instrument.

Then from these data, Scherrer equation have been applied for calculation fo the grain size, the equation being shown in Eq. (1). The sizes of the grain for the different samples obtained after exposure at variations of temperature and exposure time are thereby tabulated in Table 1.

$$\text{Crystal size (D)} = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

Scherrer constant, k = 0.9;

Wavelength of X-ray, λ = 1.5406 Å for Cu-Kα = 0.15406 nm; β = Full width half maxima (radians); θ = Angle of diffraction (degree)

The infrared spectroscopy was measured using PerkinElmer (Spectrum 2) FTIR spectrometer coupled

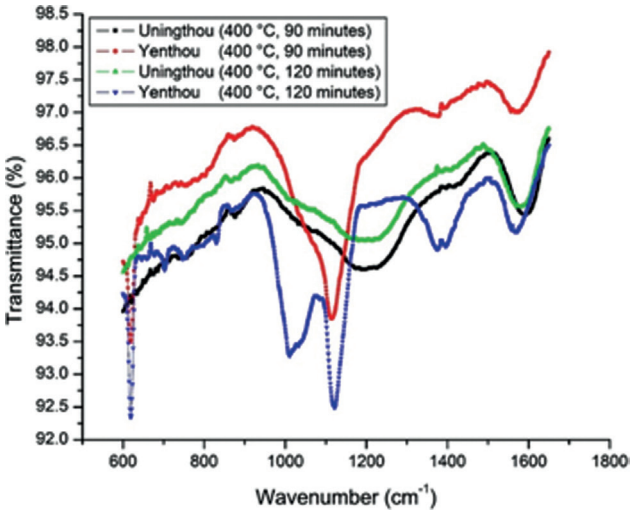

Figure 5. IR spectra for charcoal of wood chips after carbonization.

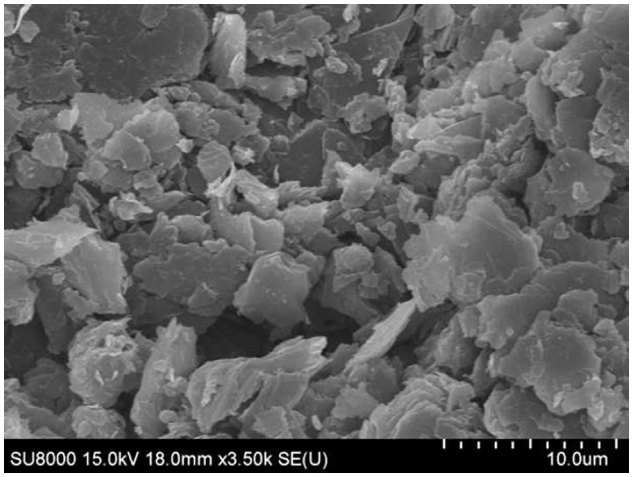

Figure 6. SEM image of Yenthou (400°C for 120 minutes).

with LiTaO3 detector and Spectrum 10TM software. The SEM and EDX analysis were conducted using Nova Nano SEM attached with EDX analyzer.

RESULTS AND DISCUSSION

Figure 4 shows the pattern results of X-ray diffraction for the charcoal of wood chips catalyst samples where TR13, TR14, TR16 and TR17 represents the samples Uningthou (400°C, 90 minutes), Yenthou (400°C, 90 minutes), Uningthou (400°C, 120 minutes) and Yenthou (400°C, 120 minutes). From the figure, it is observed that the pattern of XRD for the numerous samples demonstrates the diffraction peak at 28.61°, 28.54° and 30.02° corresponding to

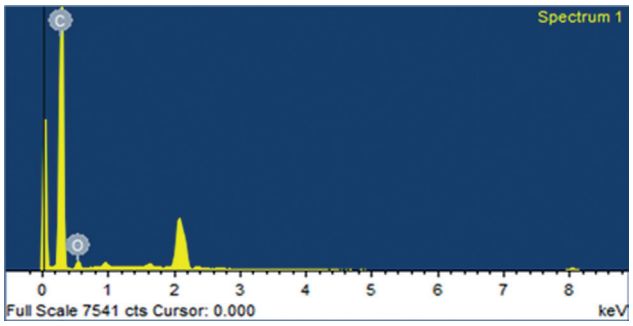

Figure 7. EDX analysis of Yenthou (400°C for 120 minutes).

Table 2. Elemental composition of Yenthou (400°C for 120 minutes)

Sl. No.	Element	Weight %	Atomic %
1	CK	89.18	91.65
2	OK	10.82	8.35

(0 0 2), (1 0 0) and (1 0 1) of the face centered cubic phase respectively, which indicates the formation of carbon. This is coherent to findings of others research [17-19]. The crystal size, which have been calculated using above equation (1), is tabulated in Table 1. These findings will be corelated with the findings of FT-IR.

The IR spectra of the samples are shown in Fig 5. Vibration of C = C bonds of carboxyl acids and the variations of the ketones of lignin & hemicellulose are observed at 1568 cm^{-1}. The charcoal spectra at around 1600 cm^{-1} can be endorsed to the vibration of C = C groups of aromatic rings generally interrelated to the existence of lignin and also to the development of aromatic compounds instigated by the removal of hydrogen and oxygen of aliphatic compounds. This shown formation of good bonds during the process.

The presence of a band at 1500 cm^{-1} (C=C) created due to uneven temperature distribution between 240°C & 380°C indicated the presence of an aromatic rings in the wood and charcoal obtained. This can also be attributed to the loss of oxygenated collections and thermal deprivation of this group in hemicellulose. It can be noted that the findings of FT-IR are well correlated with the findings specified in the x-ray diffraction spectrometer. The findings reported by other researchers in the similar area also concur with the present findings.

The scanning electron microscopy image has been tested for Yenthou exposed at 400°C for 120 minutes since it displays the best possible formation of the catalyst amongst the samples tested. The morphology is shown in Fig 6. The

EDX analysis for the sample is also tested and is reported in Fig. 7 From the EDX analysis, the formation of carbon particles in the samples at high quality can be observed. The percentage composition of the sample, as detected by the EDX is shown in Table 2.

A confirmation test using the synthesis catalyst for possible extraction of methyl esters from waste cooking oil has been conducted. The catalyst Yenthou exposed at 400°C for 120 minutes displays the best possible formation of the catalyst amongst the samples tested. An optimal parameter of 5% (wt.%) catalyst loading, 10:1, alcohol to oil ratio, 75°C reaction temperature and 60 minutes reaction time as reported by Singh and Verma (2019) [19] when employed for performing transesterification reaction. An inverted conical flask was employed for collecting the oil after the transesterification reaction. The transesterified oil was kept cooling in the flask for 3 hrs. Then the glycerol and esters were separated in the flask. The heavier glycerol was then removed using a stop cork.

The experiments were conducted for five times to check for fluctuation in the results. A conversion rate of 87.4 ±1.3% has been observed. The catalyst showed good reusability up to 3 times.

CONCLUSION

The present study has been conducted in using carbon synthesized from wood biomass for possible use as catalyst during biofuel production. The following are important aspects of the present study:

- The patters observed from XRD shows FCC phase corresponding to (0 0 2), (1 0 0) and (1 0 1) at 28.61°, 28.54° and 30.02° respectively. The average grain size of the samples was obtained to be 29.737 nm for the sample by using the Scherrer equation.
- The FTIR analysis of the samples depicts formation of C=C bonds, which is attributed to presence of carboxyl acids, observed at 1568 cm^{-1}, while peaks around 1600 cm^{-1} and 1500 cm^{-1} indicate presene of C=C due to aromatic rings.
- The SEM & EDX analysis of the sample shows good formation of carbon in the catalyst and the weight % of the components are obtained to be 89.18% and 10.82% for C and O respectively.
- Transesterification was conducted using the catalyst (yenthou, 400°C and 120 min) at waste cooking oil at 5% (wt%), 10:1, 75°C and 60 min for catalyst loading rate, alcohol-to-oil ratio, reaction temperature and reaction time respectively.
- The methyl ester conversion rate was observed to be 87.4±1.3% with reusability of 3 times.

The synthesized catalyst proved to be a potential source for use as catalyst during biodiesel production. Therefore, it can be a source of cheap and economically viable candidate for use as heterogeneous catalyst.

NOMENCLATURE

CaO	Calcium oxide
EDX	Energy dispersive x-ray spectroscopy
FAME	Fatty acid methyl ester
FFA	Free fatty acids
FTIR	Fourier transforms infra-red spectroscopy
FWHM	Full wave half maxima
KOH	Potassium hydroxide
RSM	Response surface methodology
SEM	Scanning electron microscopy
XRD	X-ray powder diffraction

AUTHORSHIP CONTRIBUTIONS

Authors equally contributed to this work.

DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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