Improvement of Methyl Ester Production through Modified Rice Bran as a Heterogeneous Catalyst

L. Fereidooni[a,]* and A. Pirkarami[b]

aYoung Researchers and Elites Club, Islamic Azad University, North Tehran Branch, Tehran, Iran
bDepartment of Nanomaterials and Nanocoatings, Institute for Color Science and Technology, Tehran, Iran

The present research investigates the impact assessment of modified rice bran as a heterogeneous catalyst, and also production of biodiesel from rice bran oil (RBO). Several variables including temperature, catalyst concentration, amount of methanol, and reaction time were optimized in order to produce high quality RBO biodiesel with maximum yield. The results showed that the obtained conditions for trans-esterification of RBO with methanol and carbon-based acidic heterogeneous catalyst were 65 °C reaction temperature, 6 h reaction time, 10:1 molar ratio of RBO to methanol and 1.5% (w/w) catalyst. The rice bran oil methyl ester produced could be used as a fuel in engines. Considering the availability and renewability, methyl ester rice bran can be easily produced in large quantities as a sustainable and reliable energy resource for multi-functional applications.

INTRODUCTION

Sustainable energy resources, as the environment-friendly materials, are currently a worldwide challenge [1, 2]. However, increased consumption of fossil fuels and their harmful pollutants are hampering the goals of sustainable energy resources [3]. As a renewable fuel, biodiesel which is considered as an alternative to diesel fuel has notably progressed during the recent decades [4] to bring a useful solution to the problem of diesel pollutants [5]. As a viable alternative biofuel, biodiesel can be produced from edible or non-edible source [6]. Research has shown that 70-75% of the overall green diesel production cost is spent on feedstock [7]. The use of economically viable feedstock can significantly reduce the cost of biodiesel production. Therefore, selecting an inexpensive raw in biodiesel production is a crucial requirement [8]. Biomass sources, particularly non-edible oils, that are locally produced from agriculture and plant resources have been considered as an

alternative energy source due to their renewability, and non-toxicity [9,10].

However, rice bran oil (RBO) is available in large quantities in rice cultivating countries [11]. In addition to its availability in rice-producing countries as an agricultural waste, one of the main advantages of rice bran is its low cost for biodiesel production [12]. Although massive crude RBO is abundantly available, only a small portion (<10%) is converted into edible oil due to the difficulties in the refinement process such as high content of free fatty acid (FFA). The development of the two-step process is restricted by the complex operation, high energy consumption and relatively high cost. A practical solution to this problem is one-step methanolysis with simultaneous esterification and trans-esterification converting the oil to biodiesel by a simple process. Although alkali catalyzed trans-esterification reacts with reflux system, the one step mechanism simplifies the conversion process to decrease the units of the procedure as well as the overall process costs [6]. More recently, the heterogeneous catalysts have been improved noticeably. The advantage of using

---

*Corresponding author. E-mail: l_fereidooni@iau-tnb.ac.ir

heterogeneous catalysts lies in removing soap production through neutralizing fatty acid and triglyceride saponification [13].

This experimental study aims at representing free fatty methyl ester (FAME) synthesis from low quality rice bran to propose an economical route for biodiesel production. The utilization of this catalyst in simultaneous esterification and trans-esterification has not been investigated yet. Accordingly, the oil extraction process and the effect of some factors, such as solvent and catalyst dosage on the esterification and trans-esterification process are investigated. The catalytic performance of the carbon-based acidic heterogeneous catalyst in simultaneous esterification and trans-esterification of crude RBO for biodiesel production are studied. The optimal reaction parameters, such as reaction temperature, reactants ratio, catalyst dosage, and reaction time are also studied.

EXPERIMENTAL

Materials and Methods

Rice bran was obtained by a local factory (Tarom, Gilan, Iran). The mechanical impurity was removed through a sieve. Methyl alcohol of 99.5% purity, n-hexane, and anhydrous sodium sulfate were obtained from Merck (Germany).

Extraction of RBO

To extract RBO, 110 g of rice bran was placed in a soxhlet and the solvent (n-Hexane) was added to the flask. Then, the mixture was heated up to the solvent boiling-point which is 65-70 °C. Oil extraction procedure lasted for 5 h, and the sample was then put inside the rotary device at 80 °C and 50 rpm for 75 min to separate the oil and the solvent.

Synthesis of the Carbon-based Acidic Heterogeneous Catalyst

Synthesis of the carbon-based acidic heterogeneous catalyst was implemented in 2 phases. The first phase was pyrolysis or production of biochar from the rice bran in which 30 g of rice chaff was placed in a 90 °C oven for 24 h to get dried. In a capped container, the rice chaff was placed in a 400 °C furnace for 75 min. Biochar was placed in a capped container made of seamless 316 stainless steel

tubing. The container was capped to prevent interaction of oxygen with the sample during the pyrolysis. When pyrolysis was implemented, the produced biochar was changed into powder. The second phase, biochar sulfonation, was obtained using a dense (98%) sulfuric acid. For each 0.2 g of biochar, 200 ml of acid was added to a long-walled glass container specialized for sulfonation reaction. A glass blade mechanical stirrer at the temperature of 200 °C for 24 h was used to stir the mixture. At the end of the sulfonation reaction, a sintered glass filter was used to separate the acid and the catalyst. Then, 80 °C laboratory-made deionized water (twice distillated) was used to clean the catalyst from the sulfate ions and neutralize the catalyst pH. Finally, the sample was put into a 100 °C oven for 90 min to dry the catalyst.

RESULTS AND DISCUSSION

Catalyst Characterization

As shown in Fig. 1, 200 °C temperature was selected for calcination the digested rice bran to produce the catalyst. The results showed that the acidification and thermal treatment of rice bran could produce the highly purified heterogeneous catalyst. SEM was employed to study the surface morphology of carbon-based acidic as a heterogeneous catalyst calcined at 200 °C. Figure 1 illustrates agglomerated and large size particles (few microns). This difference concerns to the high temperature at which the atoms of small particles diffuse to the boundary and fuse the particles together to make bigger particles as reported by Lee *et al.* [14]. The strong basic strength and high basicity of the catalysts are correlated to the catalytic activity where higher basic strength and basicity usually give more biodiesel yield [15,16].

Biodiesel Production Methodology and Catalyst Removal Process

To carry out the trans-esterification reaction, 1 l of RBO was heated at 65 °C in a round bottom flask. After that, the heterogeneous catalyst was added in methanol (270 ml) and poured into the round bottom flask containing the heated RBO while stirring the mixture continuously. A thermometer was placed in the reacting mixture to measure reaction temperature. The reaction products were allowed to
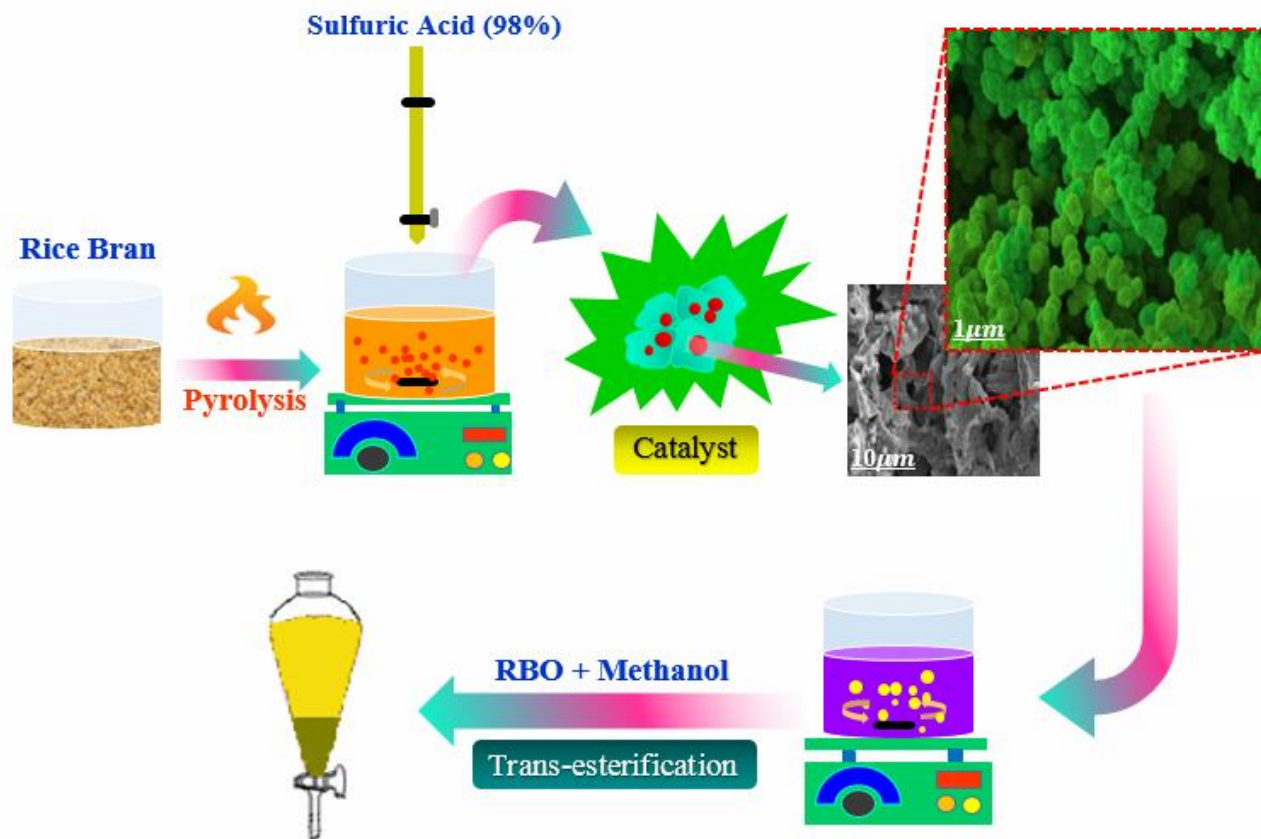
Fig. 1. Schematic representation of RBO trans-esterification reaction with carbon-based acidic heterogeneous catalysts.

settle under gravity for 6 h in a separating funnel. The products of the trans-esterification process, including rice bran oil methyl ester and glycerol, form the upper and lower layers, respectively. The reaction was carried out under atmospheric pressure. Heterogeneous catalyst was used under the similar conditions. After gravity separation of the glycerol, water washing of biodiesel is carried out to remove the impurities of the product. The remaining glycerol in biodiesel production can cause problems during storage and damage the fuel system and other components of the engine. To remove the remained catalyst, the biodiesel product was washed with 10% (v/v) of warm (70 °C) distilled water settled under gravity in the separating funnel. Two layers were formed including the upper layer of biodiesel and the lower layer of water and impurities. This process was repeated until the lower layer had a pH similar to the distilled water pH to confirm that the biodiesel is free of catalyst. Some ester was lost due to emulsion formation

during the process of catalyst removal. Fortunately, it was insensitive to the initial moisture and FFA contents of the bran to eliminate any further pretreatment. Because of the high FFA content of RBO, conventional biodiesel production method using base catalyst is unsuitable since the base reacts with FFA forming soap that decreases FAME yield and complicates the purification process [17]. After methanolysis of RBO, a gas chromatography (GC) analyzer was used to determine the fatty acid composition in the RBO (Table 1).

Effect of Molar Ratio between Methanol and RBO

Alcohol/oil molar ratio is one of the most important parameters affecting the yield of ester [18]. Due to its low price and chemical and physical advantages, methanol is the most commonly used alcohols used for trans-esterification [19]. Methanol is the most polar and shortest chain alcohol. Since methanol can easily react with triglycerides, leading

Table 1. Fatty Acid Composition in RBO Determined by Using GC Analyzer

Details of GC analysis	
GC type	Agilent HP 6890
Column	HP 1 crosslinked methyl siloxane
Detector	Flame ionization detector
Initial temperature	125 ℃
Temperature ramp	15 ℃/min for 10 min
Final temperature	275 ℃
Fatty acid	Composition (%)
Palmitic acid (C16:0)	22.8
Linoleic acid (C18:2)	29.5
Oleic acid (C18:1)	46.1
Arachidic acid (C20:0)	0.8
Myristic acid (C14:0)	0.8
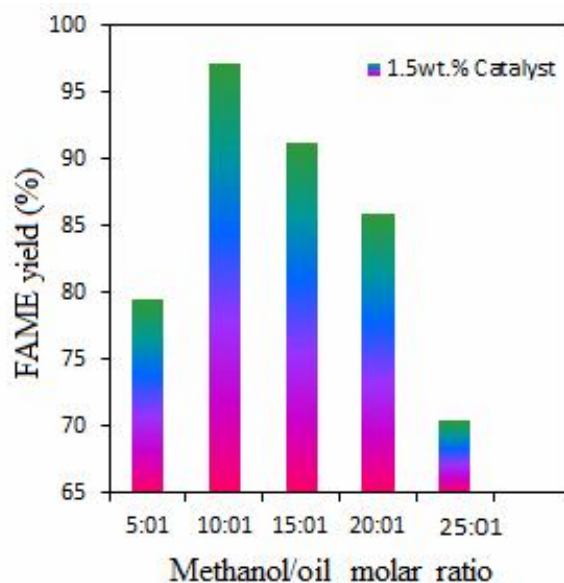
Fig. 2. Effect of molar ratio between methanol and crude RBO.

to faster reaction rates, the solubility of catalyst in methanol is faster compared to other alcohols. The stoichiometry of the trans-esterification reaction requires 1:3 molar ratio to yield 3 mol of ester and 1 mol of glycerol, but most researchers found that excess alcohol is required to complete the reaction [20]. In the present research, methanol was used for biodiesel production. To evaluate the influence of methanol/oil molar ratio of catalytic activity, the reaction was investigated at five different molar ratios of methanol:oil, 5:1, 10:1, 15:1, 20:1 and 25:1 (Fig. 2). It could be found that the FAME yield has a considerable increase from 79.5% to 97.2% as the methanol:oil molar ratio enhances from 5:1 to 10:1. With the further increase of the molar ratio to 15:1, the FAME yield declines. The results clearly depict that the use of high methanol content increases the biodiesel yield, but further excess amount of methanol lowers the FAME yield. The excessive alcohol leads the reaction towards the products, but further excess of methanol saturates the active sites of the catalyst that subsequently hinders the completion of FFA and triglycerides being protonated at the active sites and lower the FAME yield. So, the optimized amount of methanol/oil ratio should be used. In addition, further excess methanol declines the concentration of RBO in mixture and consequently decreases the reaction rate. Further increase in methanol will also enhance the chance of water contamination driving the equilibrium to the back to the FFA side and lowering the FAME yield. Thus, the optimal molar ratio of methanol to crude RBO is found to be 10:1.

Effect of Catalyst Dosage

The advantages of reducing catalyst concentration not only reduce the catalyst costs, but also saves the time for separation and purification stages of the biodiesel production. Lower catalyst amounts lead to easier biodiesel separation from catalyst during water washings, decrease water consumption and consequently lower degree of emulsion formation. In turn, easier emulsion breakdown affects ester yields by decreasing ester losses via entrapment in the emulsions. The homogeneous catalyst reduces the separation time of biodiesel product from alcohol and glycerol. It could be seen that there is a notable enhancement of the FAME yield from 87.5% to 97.2% as the catalyst dosage is increased from 0.5% to 1.5% (w/w) of

the oil and the yield remains the same for further enhancement of the catalyst amount to 1.5% (w/w). It is possibly because of the lack of enough acid sites to activate the reactants at low catalyst dosage. With the increase of catalyst dosage, more active sites are provided to support the activation of the reactants. According to the result, when the catalyst dosage is increased to 1.5 wt%, RBO could be converted to biodiesel completely. Therefore, using 1.5 wt% catalyst is adequate to complete the reaction and the optimal catalyst dosage is found to be 1.5 %w/w of the oil.

Effect of the Reaction Time

Several researchers have shown that the reaction initiates very fast and almost 80% of the conversion takes place in the first 1 h, and after 5 h, almost 93-98% triglycerides is converted into ester [21-23]. Figure 4 illustrates the conversion of RBO yield at various reaction time intervals. It is shown that FAME yield of about 90.2% is obtained at 4 h, and the conversion remarkably increases to 97.2% at 6 h. As the reaction time is prolonged, the FAME yield also. Based on the results, the optimized reaction condition of carbon-based acidic heterogeneous catalyst (wt%), simultaneous esterification and trans-esterification of rice bran oil would be rice bran oil/ methanol molar ratio of to 10:1, catalyst dosage 1.5 wt%, reaction temperature 65 °C and reaction time 6 h, under which acidic catalyst has the highest catalytic activity with the FAME yield of 97.2%.

FT-IR Spectroscopy

FT-IR Nicolet Thermo model 8700 (America) was employed to analyze the chemical composition of the rice bran and the catalyst. Rice bran and catalyst spectra were analyzed in the wave number range of 650-4000 cm^{-1}. The rice bran spectrum is shown in Fig. 5A in which a sharp peak at 792 cm^{-1} to O-Si-O stretching vibrations of silica group is illustrated [24]. The peak shows that the silica was kept in the carbon based materials in the process. Hence, silica proved to maintain the mesoporous structure which caused the carbon composites to collapse [25,26]. A broad band of a peak at 1030 cm^{-1} and a shoulder at 1054 cm^{-1} are shown in rice bran spectrum that are assigned to C-O stretching mode in C-OH and C-O-C stretching between the sugar units in cellulose [27]. Figure 5B shows the prepared
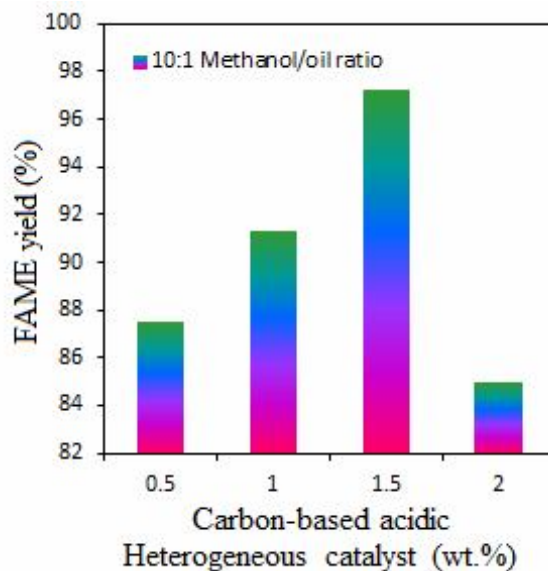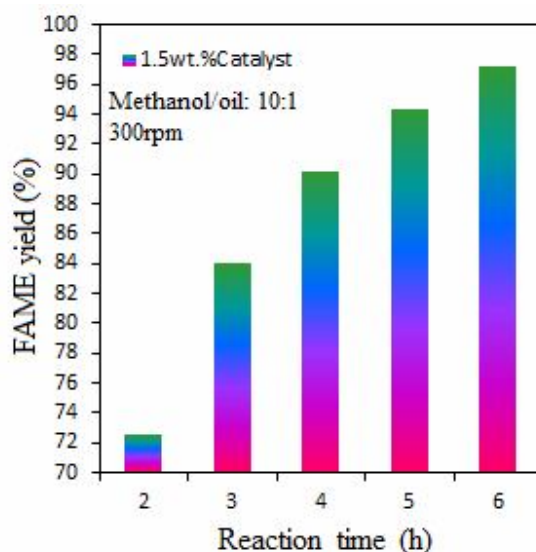
Fig. 3. Effect of catalyst dosage.

Fig. 4. Effect of reaction time.

catalyst at 1040 cm^{-1} and 1080 cm^{-1}. These absorption bands at 1040 cm^{-1} and 1080 cm^{-1} show the asymmetric and asymmetric stretching of S=O bonds of sulfonic acid (SO$_3$-H), respectively [28]. The sulfonation process was obtained by loading of -SO$_3$H to the framework of carbon through substitution of hydrogen in the C-H bond [29]. As

illustrated in Fig. 5A, the C-H vibration in cellulose and C1-O vibration in the syringyl ring derivatives, at 1330 cm^{-1} and the CH$_2$ cellulose plane bending vibrations at 1430 cm^{-1}, are plainly observable in the FT-IR spectrum [30]. In addition, the peak at 1371 cm^{-1} is related to the C-H deformation in cellulose and hemicellulose. Moreover, the
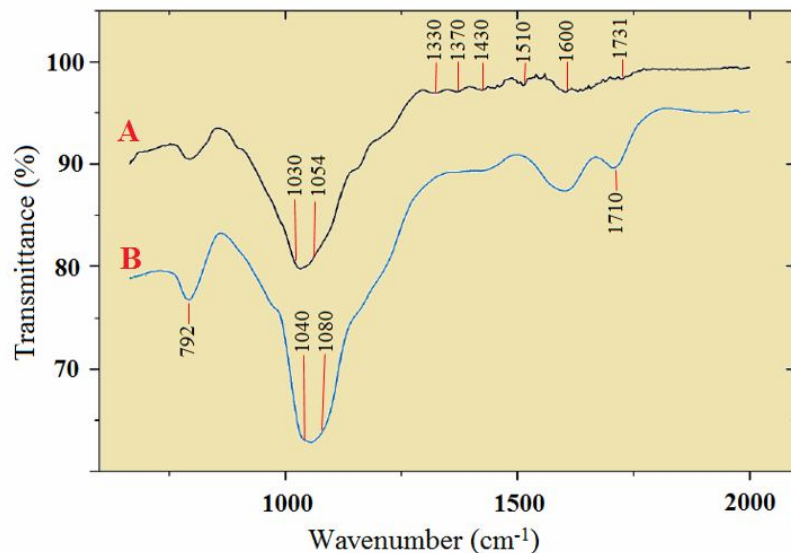
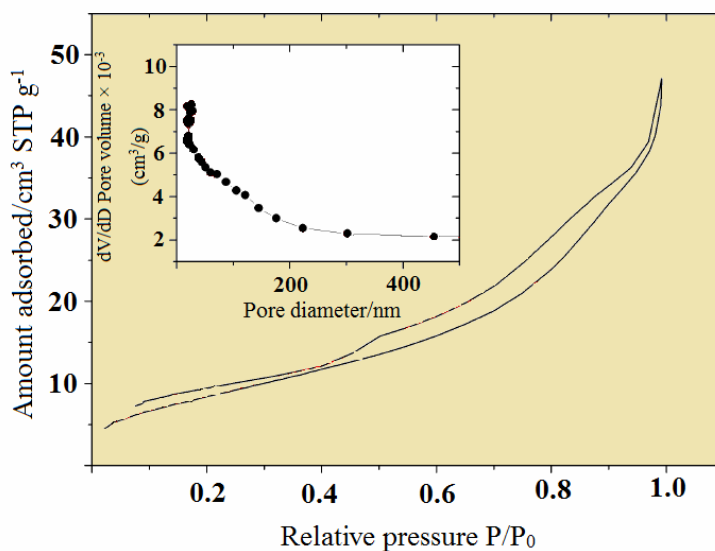**Fig. 5.** FT-IR spectra of (5A) rice bran and (5B) catalyst.

Fig. 6. N2 adsorption-desorption isotherm and pore size distribution of catalyst.

peak at 1460 cm^{-1} shows -OCH$_3$, the bands at 1510 cm^{-1} and 1600 cm^{-1} represent the phenolic ring vibrations and the peak at 1731 cm^{-1} demonstrates the ester bond (C=O) [31]. The 1614 cm^{-1} band represents alkenes and some newly formed aromatics C=C stretching. The appearance of the peak at 1710 cm^{-1}, related to C=O, as well as the disappearance of the peak at 1731 cm^{-1} in the rice bran suggest the production of a certain amount of weak acid, such as carboxylic acid in sulfonation process.

Table 2. BET Characteristics of Rice Bran and Catalyst

Sample	Surface area ($m^2 g^{-1}$)	Pore diameter (nm)	Pore volume ($cm^3 g^{-1}$)
Rice bran	10.43	5.17	0.025
Catalyst	37.01	6.44	0.018
Glucose derived	4.10	4.00	0.440
Cellulose derived	5.70	5.10	0.520
Starch derived	7.20	8.20	0.810

BET Analysis

N_2 adsorption and desorption isotherms measured at 77 K using a micromeritics surface area and porosity analyzer was applied to determine the specific surface area and pore volume.

The BET method was employed to analyze the carbonised rice bran and the catalyst porosity to obtain further insight into the structural changes. Table 2 lists the surface area, pore volume, pore diameter for rice bran, and carbonised samples. The data of surface area and pore volume were obtained from Barrett-Joyner-Halenda desorption cumulative surface area and volume measured between 17 Å and 3000 Å. As shown in Table 2, the catalyst microporosity pore size ranges from 5-10 nm. The rice bran surface area is 10.43 $m^2 g^{-1}$ showing at least 4-fold increase after carbonisation; following the sulfonation, a further pore size increase of 10-21% is observed. The catalysts, sulfonated for 20 min, demonstrated the largest surface area of 43-48 $m^2 g^{-1}$ resulting the collapse of the carbon based structure in elongated and nearly closed pores that are shown in SEM (Fig. 1). However, the conventional catalyst displays a typical isotherm with a larger hysteresis loop, applicable equally to porous catalysts [32]. At high relative vapor pressures, the adsorption-desorption isotherms of a material rely on the absorption restrictions of pore width. Hence, the isotherm attained at such low pressure is not significantly different from that of the conventional catalyst that is similarly mesoporous, but with a narrower range of pore sizes, < 20 nm.

The morphology of the catalyst showed a highly porous structure, and conventional catalysts presented a dense biomass surface. The current experiment suggests a promising preparation method for producing carbon based solid acid catalyst from biomass material in a timely and -energy-saving manner.

CONCLUSIONS

In this study, base catalyzed trans-esterification was studied with carbon-based acidic heterogeneous catalyst of rice bran for biodiesel production from RBO. Using RBO as feedstock for biodiesel production is economically and environmentally beneficial. In the reaction stage, factors that greatly influenced the yield and the quality of FAME were methanol/RBO molar ratio and catalyst concentration. The effects of several parameters including process temperature, reaction time, molar ratio of alcohol to oil, and catalyst concentration on the ester (biodiesel) yield were investigated. The combination giving biodiesel yield was found to be 10:1 methanol/oil molar ratio, 1.5 wt% catalyst, 65 °C reaction temperature and 6 h reaction time, followed by 3-4 times gentle washing of the biodiesel with 70 °C distilled water (10 %v/v).

REFERENCES

[1] Guabiroba, R. C. d. S.; *et al.*, Value chain analysis of waste cooking oil for biodiesel production: Study case of one oil collection company in Rio de Janeiro-Brazil. *J. Clean. Prod.* **2017**, *142*, Part 4, 3928-3937,

DOI: 10.1016/j.jclepro.2016.10.064.

[2] Pirkarami, A.; *et al*., Contributing factors on the removal of Azo-dyes from industrial wastewater: A comparison of the efficiency of sonocataysis and photocatalysis process. *J. Appl. Chem. Res.* **2016**, *10*, 15-23.

[3] Kaimal, V. K.; Vijayabalan, P., A detailed investigation of the combustion characteristics of a DI diesel engine fuelled with plastic oil and rice bran methyl ester. *J. Energ. Inst.* **2017**, *90*, 324-330, DOI: https://doi.org/10.1016/j.joei.2015.11.005.

[4] Al-Jammal, N.; *et al*., Manufacturing of zeolite based catalyst from zeolite tuft for biodiesel production from waste sunflower oil. *J. Renew. Energ.* **2016**, *93*, 449-459, DOI: http://dx.doi.org/10.1016/j.renene.2016.03.018.

[5] Fu, J.; *et al*., Storage and oxidation stabilities of biodiesel derived from waste cooking oil. *Fuel* **2016**, *167*, 89-97, DOI: 10.1016/j.fuel.2015.11.041.

[6] Fereidooni, L.; Mehrpooya, M., Experimental assessment of electrolysis method in production of biodiesel from waste cooking oil using zeolite/chitosan catalyst with a focus on waste biorefinery. *Energ. Convers. Manage* **2017**, *147*, 145-154, DOI: 10.1016/j.enconman.2017.05.051.

[7] Atabani, A. E., *et al.,* A comprehensive review on biodiesel as an alternative energy resource and its characteristics. *Renew Sust Energ Rev* **2012**, *16*, 2070-2093, DOI: http://dx.doi.org/10.1016/j.rser.2012.03.004

[8] Wu, L.; *et al.,* Bentonite-enhanced biodiesel production by NaOH-catalyzed transesterification: Process optimization and kinetics and thermodynamic analysis. *Fuel* **2016**, DOI: 10.1016/j.fuproc.2015.12.017.

[9] Sinha, S.; *et al.,* Biodiesel development from rice bran oil: Transesterification process optimization and fuel characterization. *Energ. Convers. Manage* **2008**, *49*, 1248-1257, DOI: http://dx.doi.org/10.1016/j.enconman.2007.08.010.

[10] Fereidooni, L.; *et al*., Trans-esterification of waste cooking oil with methanol by electrolysis process using KOH. *J. Renew. Energ.* **2018**, *116* (Part A), 183-193, DOI: 10.1016/j.renene.2017.08.067.

[11] Zullaikah, S.; *et al.,* A non-catalytic in situ process to produce biodiesel from a rice milling by-product using a subcritical water-methanol mixture. *J. Renew. Energ*. **2017**, *111*, 764-770, DOI: https://doi.org/10.1016/j.renene.2017.04.040.

[12] Einloft, S.; *et al*., Biodiesel from rice bran oil: transesterification by tin compounds. *Energ. Fuel* **2007**, *22*, 671-674, DOI: 10.1021/ef700510a.

[13] Vicente, G.; *et al*., Integrated biodiesel production: a comparison of different homogeneous catalysts systems. *Bioresource Technol.* **2004**, *92*, 297-305, DOI: https://doi.org/10.1016/j.biortech.2003.08.014.

[14] Lee, S. L., *et al*., Transesterification of palm oil to biodiesel by using waste obtuse horn shell-derived CaO catalyst. *Energ. Convers. Manage* **2015**, *93*, 282-288, DOI: http://dx.doi.org/10.1016/j.enconman.2014.12.067.

[15] Huang, R., *et al*., Using renewable ethanol and isopropanol for lipid transesterification in wet microalgae cells to produce biodiesel with low crystallization temperature. *Energ. Convers. Manage* **2015**, *105*, 791-797, DOI: http://dx.doi.org/10.1016/j.enconman.2015.08.036.

[16] Guo, F.; *et al.,* Calcined sodium silicate as solid base catalyst for biodiesel production. *Fuel Process Technol.* **2010**, *91*, 322-328, DOI: http://dx.doi.org/10.1016/j.fuproc.2009.11.003.

[17] Ju, Y.-H., S.R. Vali., Rice bran oil as a potential resource for biodiesel: a review, **2005**, DOI: http://hdl.handle.net/123456789/5381.

[18] Guldhe, A., *et al*., Conversion of microalgal lipids to biodiesel using chromium-aluminum mixed oxide as a heterogeneous solid acid catalyst. *J. Renew. Energ* **2017**, *105*, 175-182, DOI: https://doi.org/10.1016/j.renene.2016.12.053.

[19] Banković-Ilić, I. B.; *et al*., The effect of tetrahydrofuran on the base-catalyzed sunflower oil methanolysis in a continuous reciprocating plate reactor. *Fuel Process Technol.* **2015**, *137*, 339-350, DOI: http://dx.doi.org/10.1016/j.fuproc.2015.03.023.

[20] Babaki, M.; *et al*., Process optimization for biodiesel production from waste cooking oil using multi-enzyme systems through response surface methodology. *J. Renew. Energ.* **2017**, *105*, 465-472,

DOI: 10.1016/j.renene.2016.12.086.

[21] Maneerung, T.; *et al.*, Sustainable biodiesel production via transesterification of waste cooking oil by using CaO catalysts prepared from chicken manure. *Energ. Convers. Manage* **2016**, *123*, 487-497, DOI: https://doi.org/10.1016/j.enconman.2016.06.071.

[22] Encinar, J. M.; *et al.*, Biodiesel from used frying oil. Variables affecting the yields and characteristics of the biodiesel. *Ind Eng Chem Res* 2005, *44*, 5491-5499, DOI: 10.1021/ie040214f.

[23] Soetaredjo, F. E.; *et al.*, KOH/bentonite catalysts for transesterification of palm oil to biodiesel. *Appl. Clay. Sci* 2011, *53*, 341-346, DOI: 10.1016/j.clay.2010.12.018.

[24] Ludueña, L.; et al., Nanocellulose from rice husk following alkaline treatment to remove silica. *BioResources* **2011**, *6*, 1440-1453, DOI: 10.15376/biores.6.2.1440-1453.

[25] Janaun, J.; Ellis, N., Role of silica template in the preparation of sulfonated mesoporous carbon catalysts. *Appl. Catal. A: Gen* **2011**, *394*, 25-31, DOI: 10.1016/j.apcata.2010.12.016.

[26] Shanks, B. H., Conversion of biorenewable feedstocks: new challenges in heterogeneous catalysis. *Ind. Eng. Chem. Res.* **2010**, *49*, 10212-10217, DOI: 10.1021/ie100487r.

[27] Chen, W. -H.; Tu, Y. -J.; Sheen, H. -K., Disruption of sugarcane bagasse lignocellulosic structure by means of dilute sulfuric acid pretreatment with microwave-assisted heating. *Appl. Energ.* **2011**, *88*, 2726-2734, DOI: 10.1016/j.apenergy.2011.02.027.

[28] Sani, Y. M.; *et al.*, Palm frond and spikelet as environmentally benign alternative solid acid catalysts for biodiesel production. B*ioresources* **2015**, *10*, 3393-3408, DOI: 10.1016/j.biortech.2005.03.014.

[29] Zhang, M.; *et al.*, Catalytic performance of biomass carbon-based solid acid catalyst for esterification of free fatty acids in waste cooking oil. *Catal. Surv. from Asia* **2015**, *19*, 61-67, DOI: 10.1007/s10563-014-9182-y.

[30] Li, H.; Lu, J.; Mo, J., Physiochemical lignocellulose modification in the formosan subterranean termite Coptotermes Formosanus Shiraki (Isoptera: Rhinotermitidae) and potential uses in the production of biofuels. *BioResources* **2011**, *7*, 0675-0685, DOI: 10.15376/biores.7.1.0675-0685.

[31] Li, C.; *et al.*, Comparison of dilute acid and ionic liquid pretreatment of switchgrass: biomass recalcitrance, delignification and enzymatic saccharification. *Bioresource Technol.* **2010**. *101*, 4900-4906, DOI: 10.1016/j.biortech.2009.10.066.

[32] Fagerlund, G., Determination of specific surface by the BET method. *Mater et Constr* **1973**, *6*, 239-245, DOI: 10.1007/BF02479039.