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ORIGINAL RESEARCH

Utilization of spray-dried nanoporous gamma alumina support in biodiesel production from waste cooking oil

Faraz Khanbolouk[1] · Mandana Akia[2] · Hamidreza Arandiyan[3] · Farshad Yazdani[1] · Yasin Dortaj[1]

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Abstract Gamma alumina is one of the widely used supports in catalyst preparation, possessing a high specific surface area and good thermal stability. Spray drying is an efficient way to produce narrow particle size distribution and spherical shape powders. In this study, spray drying method has been implemented to prepare microspherical nanoporous gamma alumina with a high specific surface area. The nanoporous gamma alumina support was utilized in the preparation of various heterogeneous base catalysts. The highest biodiesel yield of 99% was obtained at 6 wt% loading of K/γ-Al_2O_3 catalyst, using waste cooking oil as feedstock. The obtained results revealed the great potential of the synthesized nanoporous gamma alumina as an effective support for heterogeneous base catalysts preparation in the transesterification reaction.

Keywords Nanoporous gamma alumina · Heterogeneous base catalyst · Waste cooking oil · Transesterification

✉ Mandana Akia
mandana.akia@utrgv.edu; akia.mandana@gmail.com

✉ Farshad Yazdani
Farshadyazdani@yahoo.com

[1] Chemistry and Chemical Engineering Research Center of Iran (CCERCI), Tehran, Iran

[2] Department of Mechanical Engineering, University of Texas Rio Grande Valley, Edinburg, TX, USA

[3] Particles and Catalysis Research Group, School of Chemical Engineering, The University of New South Wales, Sydney, NSW 2052, Australia

Introduction

In recent decades, the rate of the consumption of fossil fuels increased due to the population growth and industrial development [1, 2]. Reduces in the fossil fuel resources and an increase in environmental pollution are some results of this consumption trend [3]. However, application of renewable sources of energy would be a solution for some of these difficulties. Biodiesel is one of these renewable energy sources that attracted the attention of many researchers in the field. Biodiesel which is a blend of a mono alkyl ester of long-chain fatty acids is generally prepared by transesterification of various renewable sources, such as vegetable oil and waste cooking oil that have triglyceride in their composition [4–7]. According to the reported studies, replacing fossil diesel with biodiesel can reduce the emission of CO, particulate matters and unburned hydrocarbons up to 46.7, 66.7 and 45.2%, respectively; however, NOx emission increases [8].

Triglyceride transesterification has been traditionally performed in batch or continuous reactors using homogeneous catalysts. A basic catalyst such as NaOH, KOH or methoxides, due to their higher catalytic activity and other advantages, are preferred to other homogeneous catalysts like mineral acids and lipases [7]. Although, the catalyst does not remain in the main product, i.e., biodiesel, catalyst can contaminate glycerol by-product. In an industrial production process, it is important to recover glycerol to balance the production costs. For economical and also environmental reasons, it has been tried to replace homogeneous base catalysts with heterogeneous ones [8]. The capability of heterogeneous catalysts and effect of process parameters such as catalyst types, reaction conditions and various feedstocks in biodiesel preparation have been investigated by many scientists. The heterogeneous

catalytic transesterification of soybean has been reported by Sun et al. [2], Nicolas et al. [8] and Xie et al. [9]. They reported biodiesel yields of 87.4, 98.3 and 96% using Al–Ca/K_2CO_3, Na_2ZrO_3 and KI/Al_2O_3 catalysts, respectively. The heterogeneous base catalysts of Sr/ZSM-5 [1] and NaOH/Alumina [10] used in sunflower oil conversion and the biodiesel yields were reported as 87.7% and 96%, respectively. Calero et al. [3] have reported a 100% biodiesel conversion from methanol/oil (molar ratio of 6:1) at 65 °C for 1 h over the heterogeneous base catalyst of CaO. Similarly, Mahesh et al. [5] studied biodiesel preparation from waste cooking oil (WCO) over KBr/CaO catalyst and obtained a yield of 83.6% by applying methanol:oil molar ratio of 12.

Heterogeneous catalysts are widely utilized in two forms, directly or supported on a suitable framework. However, supported catalysts usually have been applied more than the other one. Alumina as a support with different metastable structures is widely used as catalyst framework [11]. The crystalline form of γ-alumina (γ-Al_2O_3) with a high specific surface area, large porosity and suitable thermal, chemical and mechanical stability is the most important structure that has been used as a catalyst and also as a support [12, 13]. There are several methods for alumina preparation. The most common method to produce alumina support is spray drying of a slurry containing alumina, dispersants and binders [14]. In a research work, alumina powders with particle size of 3 μm were synthesized by the precipitation method and the resulted boehmite was spray dried [15]. Tsetsekou et al. [14] prepared alumina with particle size of 50 μm and studied its stability. They produced alumina powders by spray drying of high solid content slurry of alumina. Bertram et al. investigated effects of slurry properties on the morphology of the spray-dried alumina [16]. The microscale size alumina was prepared by Mishra et al. [17] using jet wheel atomizer base spray dryer. Lind et al. [18] produced porous alumina with a surface area of 130 m^2g^{-1}, using primary alumina particles suspension as the feed of the spray dryer and investigated the effects of the spray dryer parameters as well as suspension conditions on the porosity of the product. The influences of slurry properties and dryer conditions on particle size and surface morphology of α-alumina support were studied by Yu et al. [19]. They used commercial α-alumina and polyvinyl alcohol (PVA) as a binder and produced a powder with the particle size between 10 and 45 μm. In a similar research, spherical granules of alumina with 3.5–12.5 μm in size were produced using PVA and commercial alumina and utilizing spray dryer [20]. Cottrino et al. [21] used γ-alumina nanopowder and polyacrylic acids, and prepared γ-alumina granules with a mean particle size of 70 μm. Huang et al. [22] employed phthalic acid and P123, respectively, as interfacial protector and structure-directing agent for synthesis of 2D hexagonal gamma alumina via sol–gel method. The properties of the obtained γ-alumina phase (calcined at 800 °C under air environment) were reported as a surface area of 226.37 m^2g^{-1} and pore volume of 0.31 cm^3g^{-1}.

In this study, as a new procedure, commercial gibbsite, PVA and phthalic acid were utilized for the synthesis of microspherical nanoporous γ-Al_2O_3 support through spray drying method. The effects of different slurry solid content, PVA wt% and temperature are investigated to achieve the highest BET surface area for the synthesized gamma alumina. The obtained support was employed for the preparation of various heterogeneous base catalysts and applied in biodiesel preparation from WCO.

Experimental

Materials

The commercial gibbsite and PVA were obtained from Petrochemical Company of Iran as initial materials for gamma alumina preparation. Other chemicals including potassium hydroxide, lithium nitrate, sodium hydroxide, phthalic acid, gamma alumina and methanol were purchased from Merck Company. WCO, a mixture of soybean and sunflower oil, was provided from Chemistry and Chemical Engineering Research Center Institute (CCERCI) restaurant.

Support and catalyst preparation

In a typical method for support preparation, PVA and phthalic acid, as a binder and interfacial protector, respectively, were dissolved in distilled water and then gibbsite was added under the stirring condition to achieve a slurry solution. In this investigation, different weight percentages of PVA (1, 2.5 and 4 wt%) and various slurry solid content (40, 50, 60 wt%) at three drying temperatures of the spray dryer (170, 200 and 230 °C) were employed while the content of phthalic acid was kept constant at 5 wt%. The samples were fed to the spray dryer (APV ANHYDRO A/S, Denmark) at the condition of inlet temperature between 170 and 230 °C and an outlet temperature of 90 °C. Then the obtained powders were calcined at 600 °C for 5 h to attain nanoporous γ-alumina.

The support was applied in different heterogeneous base catalyst preparation using the wet impregnation method. A metal content of 10 wt% from KOH, $LiNO_3$ and NaOH precursors was applied for the catalysts preparation. The samples were dried and calcined at 125 °C for 8 h and 400 °C for 4 h, respectively.

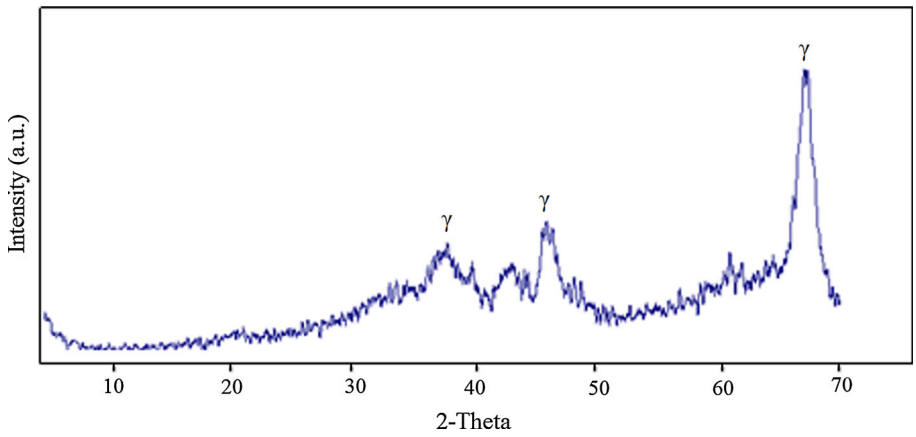


Fig. 1 XRD pattern of the alumina sample (S1) spray dried at a temperature of 200 °C and calcined at 600 °C

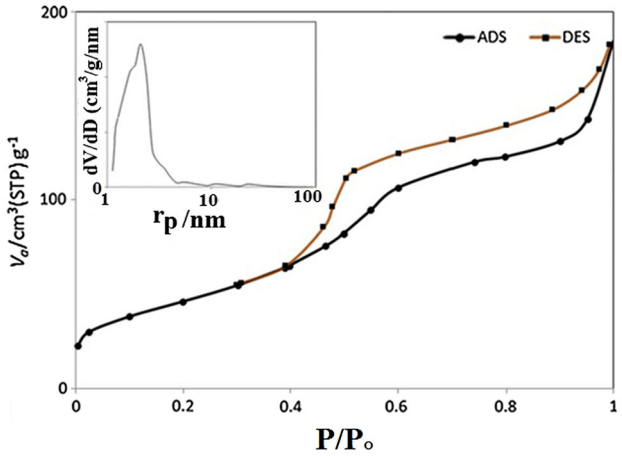


Fig. 2 Nitrogen adsorption/desorption isotherm and pore size distribution (*upper inset*) of sample S1

Transesterification reaction

In a typical preparation of biodiesel, waste cooking oil was filtered and centrifuged and the saponification number, acid value and molecular weight of WCO were measured as 231.9 mg KOH/g oil, 0.53 mg KOH/g oil and 727.2 g mol^{-1}, respectively, based on the standards methods [23]. Transesterification reaction is carried out using WCO, methanol and heterogeneous catalyst under the conditions of 8–1 molar ratio of methanol to WCO, a temperature of 60 °C, at a specified catalyst loading and a certain reaction time. After completion of the reaction, the desired methyl ester product was removed from glycerol phase as the upper layer in a separatory funnel.

At the first series of experiments, different catalysts of K/γ-Al_2O_3, Li/γ-Al_2O_3 and Na/γ-Al_2O_3 with a loading of 4 wt% were utilized in the transesterification reaction of WCO with time duration of 6 h. Then different loadings of K/γ-Al_2O_3 catalyst (4, 6 and 8 wt%) were implemented in the transesterification reaction with the same duration time.

Characterization methods

XRD analysis was performed on a Phillips diffractometer with CuKα radiation ($\lambda = 1.5418$A) to specify the crystallinity of the prepared alumina sample. Nitrogen adsorption/desorption isotherms were obtained at 77.4 K using a Quantachrome NOVA 2200 model. TGA analysis was carried out by a thermogravimetric analyzer (NETZSCHTGA 209 F1) with a constant ramp rate of 10 °C min^{-1} in an atmosphere of nitrogen. Infrared spectra were recorded on a Bruker IFS 66 Fourier transform infrared (FTIR) spectrophotometer. Scanning electron microscopy (SEM) was performed with TESCAN VEGA 3-LM operated at 30 kV. Particle size analyzer was carried out using HELOS particle size analysis. Nano-ZS (Red badge) model ZEN 3600 was employed for zeta potential analysis. H NMR spectra of the synthesized biodiesel were acquired at 400 MHz using a Bruker Avance DPX 300 spectrometer.

Results and discussion

Gamma alumina support

A gamma alumina sample was prepared at the conditions of 2.5 wt% PVA, 5 wt% of phthalic acid and slurry solid content of 50% at temperature of 200 °C which is denoted as S1. As it can be seen in Fig. 1, the formation of gamma phase has been confirmed. The nitrogen adsorption–desorption isotherm in Fig. 2 represents type IV of isotherm according to the IUPAC classification. Figure 2 (upper inset) demonstrates a narrow pore size distribution.

The SEM image in Fig. 3 exhibits microspherical gamma alumina. The average particle size of the sample is less than 40 μm according to the results of particle size analyzer. The sample showed very good followability that is attributed to the physical properties of the material and

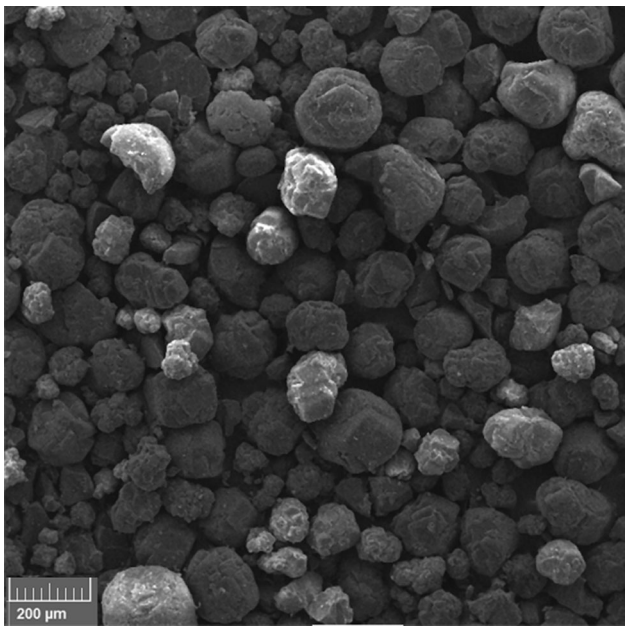


Fig. 3 SEM image of the prepared gamma alumina sample (S1)

the drying method. As it is shown in Fig. 4a, b, FTIR and TGA analyses were employed to confirm the sufficiency of calcination temperature of 600 °C for complete removal of additives and stable phase formation, respectively.

The BET surface area, pore radius and pore volume of the sample were 172.7 m^2g^{-1}, 4.2 nm and 0.3 cm^3g^{-1}, respectively. To investigate the effects of various parameters to obtain the highest surface area, 27 experiments were carried out at various conditions with the changes of two parameters while the other parameter was kept constant at a specified medium value (PVA of 2.5 wt%, 50 wt% slurry solid content and inlet temperature of 200 °C).

As it can be seen in Fig. 5a, the effect of different slurry solid content, PVA wt% and temperature on the surface area depicts the highest surface area at the lowest slurry percentage and medium conditions for temperature and PVA value. The results exhibit no certain relations between these parameters. Other graphs in Fig. 5b, c show almost a maximum or minimum point. It must be noted, besides the high surface area the main criteria for choosing the best conditions for nanoporous gamma alumina preparation have been based on two factors, higher alumina yield and higher slurry stability. Although, the highest slurry solid content resulted to a higher amount of alumina production, the Zeta potential results showed that the sample with 50 wt% of slurry solid content with a zeta potential of −88.3 mv provides the most stable slurry among the other samples. In addition, the pore size and pore diameters almost changed smoothly with the changes in various parameters, as a result, the lowest percentage of PVA was preferred for nanoporous gamma alumina preparation.

The best conditions to attain the highest BET surface area of 214.8 m^2g^{-1} were specified at a temperature of

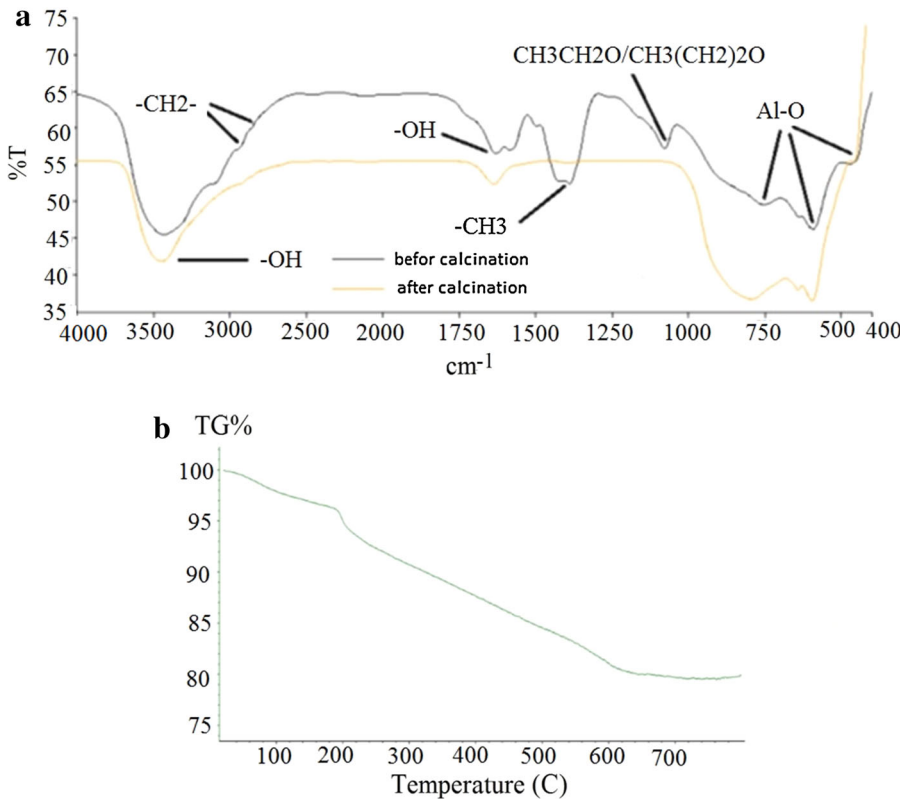
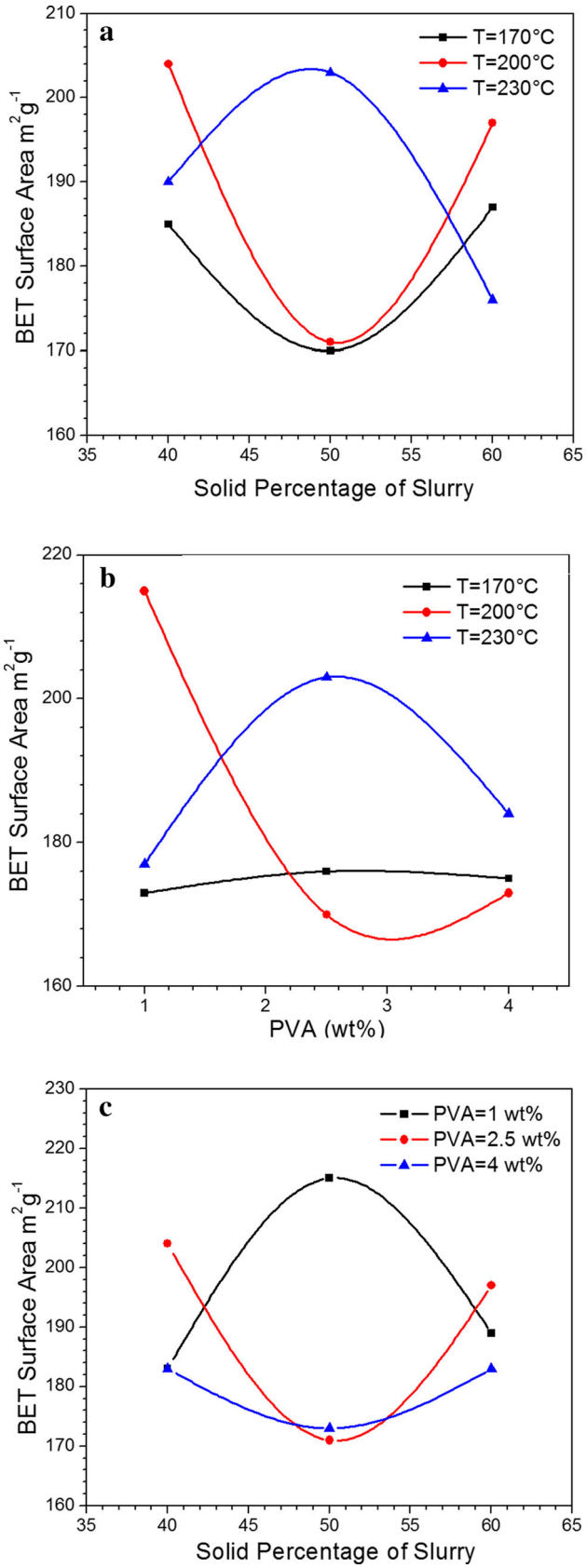


Fig. 4 FTIR results before and after calcination (**a**) and TGA analysis (**b**) for the synthesized gamma alumina support calcined at 600 °C



◀**Fig. 5** Effect of various operating parameters on the BET surface area of the prepared gamma alumina. (**a**) Effect of solid percentage of slurry and temperature at constant PVA value of 2.5%, **b** effect of PVA value and temperature at constant solid slurry content of 50% and **c** effect of solid percentage of slurry and PVA value at constant temperature of 200 °C

200 °C, PVA of 1 wt% and slurry solid content of 50 wt% was denoted as SF.

The results of particle size analyzer for sample SF along with two other samples prepared at the same conditions with different temperatures of 170 and 230 °C were, respectively, denoted as Sa and Sb (Fig. 6). The obtained results revealed the particle sizes less than 100 µm for these samples. Almost the same particle sizes were obtained for the other samples.

Heterogeneous base catalysts characterization

The specific surface area, pore size and pore volume of the prepared catalysts using the nanoporous gamma alumina support have been shown in Table 1. The suitable pore size for an effective catalyst should be more than 15A, which is the size of a triglyceride molecule [24]. As it can be seen in Table 1, the pore size of the prepared catalysts is wide enough for triglyceride molecules to get in and out. All the prepared catalyst samples showed a reduction in BET surface area which is usual after applying impregnation method. However, minimum BET surface area and the lowest pore volume was obtained for Li/γ-Al_2O_3 catalyst.

The biodiesel yields were calculated using TGA method as it can be seen in Fig. 7. The TG and DTG graphs of the produced biodiesel sample using 4 wt% of K/γ-Al_2O_3 along with the results for WCO have been presented in Fig. 7. The starting vaporization temperature for the prepared biodiesel was around 200 °C and completed at a temperature around 550 °C. The results of applying TGA method for WCO feedstock clearly indicates a high-temperature difference between vaporization temperatures of WCO and biodiesel sample which is quite enough to distinguish between the methyl esters and triglycerides species [7].

The biodiesel yield for the three catalyst samples during 6 h of reaction time is represented in Fig. 8. It is known that the Li/γ-Al_2O_3 showed the lowest performance compared to the Na/γ-Al_2O_3 and K/γ-Al_2O_3 catalysts.

To confirm the TGA method for methyl ester yield calculation, the (^{1}H) NMR analysis was carried out for 4 wt% of K/γAl_2O_3 catalyst sample as it is shown in Fig. 9. Based on the equation $C = 100\,\frac{2A1}{3A2}$ [C is the percentage of

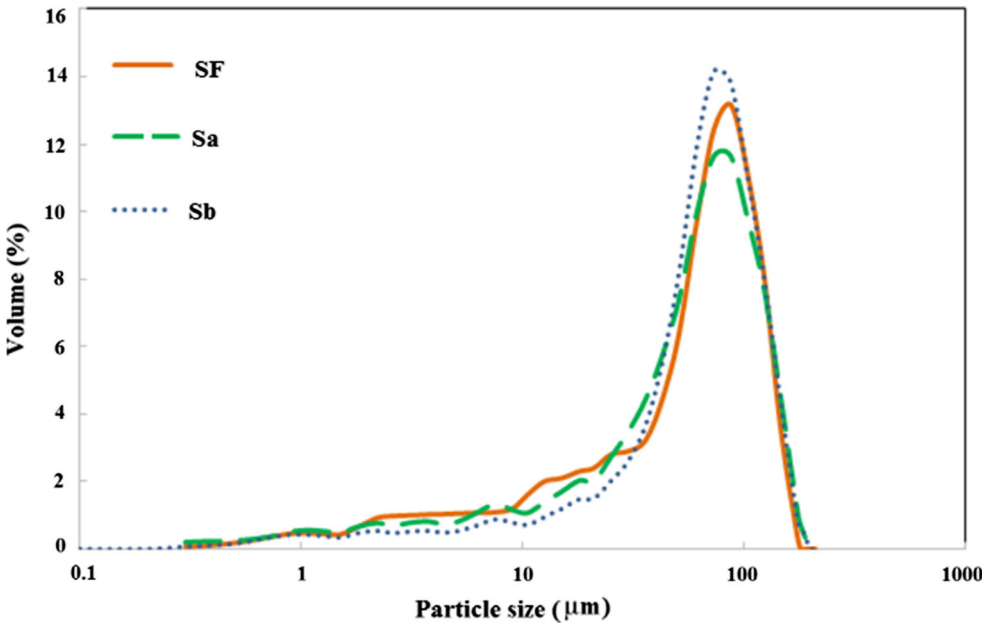


Fig. 6 Particle size distribution of different gamma alumina samples prepared at PVA of 1 wt%, solid slurry content of 50 wt% and various spray-dried temperatures. (**a**) Sample SF at a temperature of 200 °C, **b** sample Sa at a temperature of 170 °C and **c** sample Sb at a temperature of 230 °C

Table 1 Structural properties of gamma alumina support and prepared heterogeneous base catalysts

Catalyst	Surface area (m^2g^{-1})	Pore volume (cm^3g^{-1})	Pore diameter (nm)
Na/ γ-Al_2O_3	76.6	0.18	9.6
K/ γ-Al_2O_3	65.1	0.18	11.4
Li/ γ-Al_2O_3	19.6	0.06	13.5

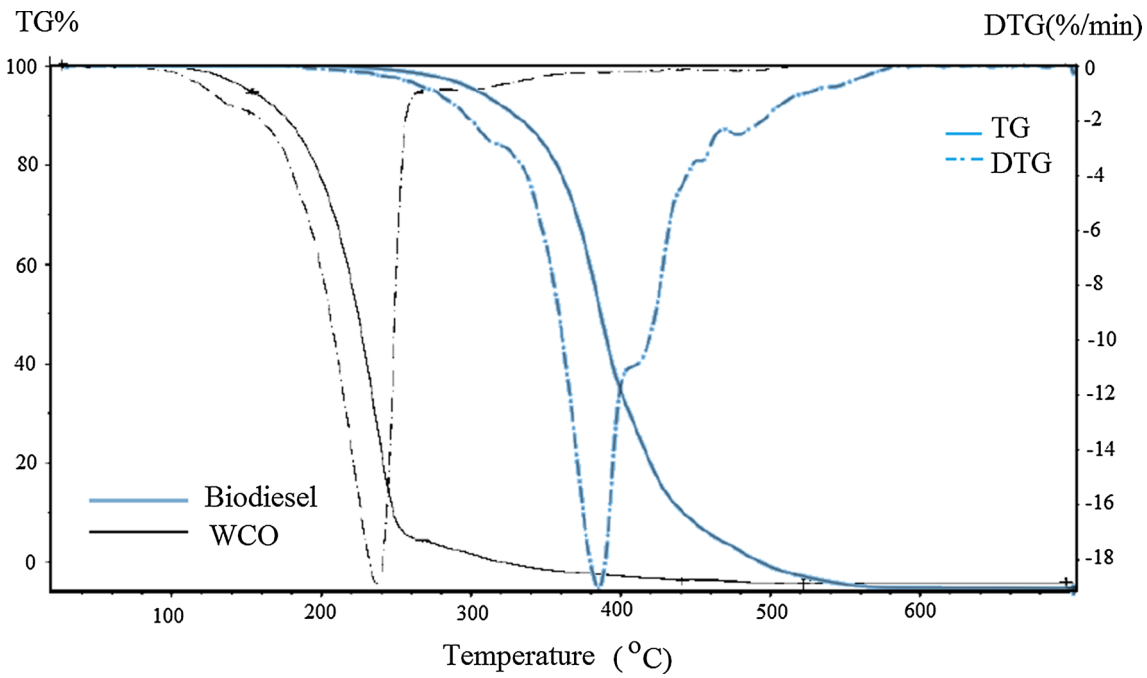


Fig. 7 TG and DTG graphs for biodiesel sample, produced using 4 wt% of K/γ-Al_2O_3 catalyst, and WCO feedstock

triglycerides to corresponding methyl esters, A1 stands for the integration value of protons of the methyl esters (1.000) and A2 is integration value of α-methylene protons (0.723)] [25, 26], the methyl esters yield of 92.21% was calculated for the mentioned sample. The difference between biodiesel yield obtained utilizing TGA method

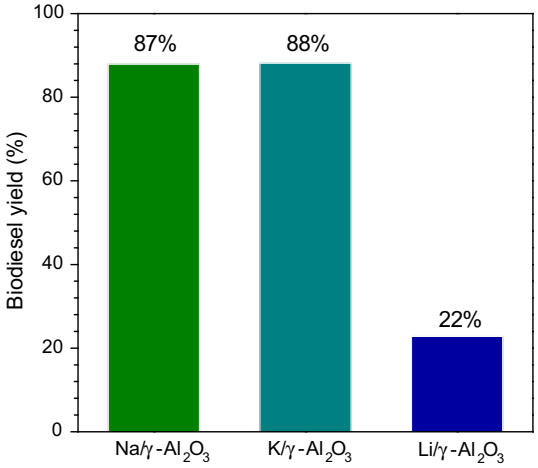


Fig. 8 Effect of different catalysts prepared using synthesized gamma alumina support in biodiesel production from WCO at a reaction time of 6 h

and (^{1}H) NMR analysis was less than 3% which also is lesser than that of the other studies [27].

The catalytic performances of K/γ-Al_2O_3 and Na/γ-Al_2O_3 were very close; however, K/γAl_2O_3 catalyst that provided the highest biodiesel yield was chosen as the appropriate catalyst and the impacts of different loadings in transesterification reaction were investigated. As it can be seen in the bar graph of Fig. 10, the impacts of different loadings (4, 6 and 8 wt%) of K/γ-Al_2O_3 catalyst on transesterification reaction were compared. The highest biodiesel yield of 99% was obtained for the sample with 6 wt% of catalyst loading based on the TGA results. The results indicated an increase in the soap formation with an increase in the catalyst concentration.

Utilizing gamma alumina (Merck) as support in heterogeneous catalyst preparation for biodiesel production: comparison of the catalytic performances with other relevant studies

Catalyst K/γAl_2O_3 was prepared using a purchased gamma alumina (Merck) sample and employed in WCO transesterification reaction. The biodiesel yield of 92.3 was obtained at the same operating conditions as described above. As it was demonstrated in Table 2, comparison of the performances between various K/γAl_2O_3 catalysts in different studies clearly revealed the high potential of the synthesized nanoporous gamma alumina support in biodiesel production [37, 38]. As it can be observed in Table 2, WCO feedstock was rarely utilized in biodiesel

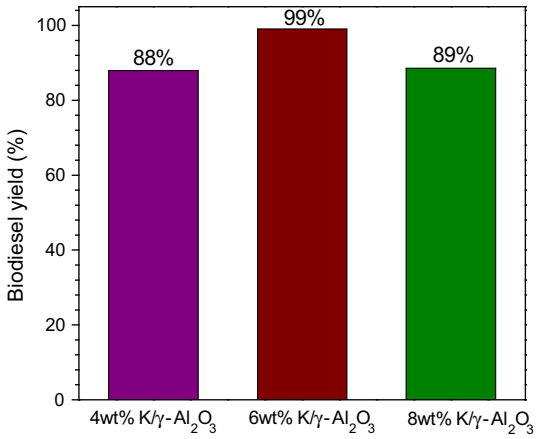


Fig. 10 Effect of different catalyst loading of K/γ-Al_2O_3 in biodiesel production from WCO at a reaction time of 6 h

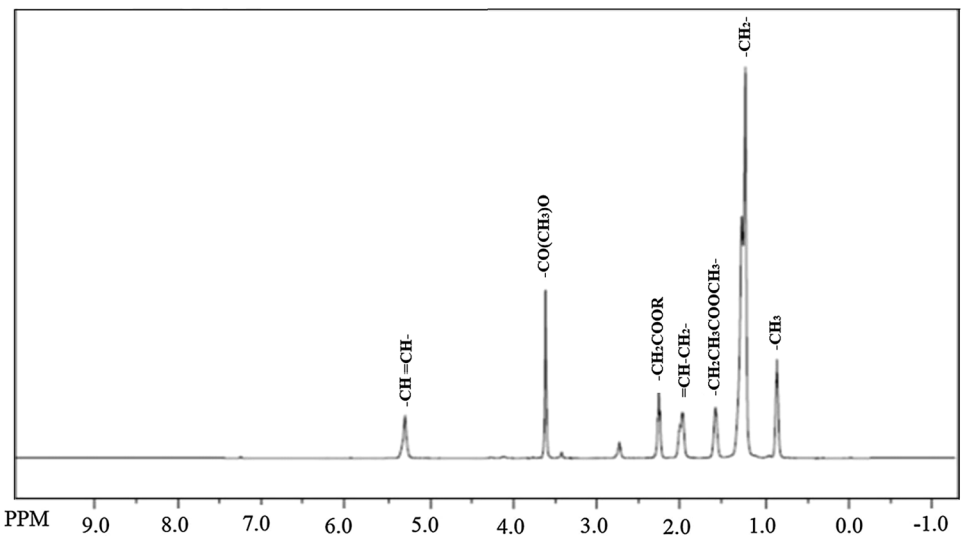


Fig. 9 (^{1}H) NMR spectrum for the biodiesel sample produced using 4 wt% loading of K/γ-Al_2O_3 catalyst

Table 2 Comparison of the obtained results of this work with relevant studies

References	Biodiesel yield (%)	Parameters				Alumina support	Catalyst feedstock	
		Time (hr)	Catalyst concentration (wt%)	Methanol to oil molar ratio	T (°C)			
This study	99	6	6	8	60	Synthesized gamma alumina BET area: 214.81 m^2g^{-1} Pore diameter: 6.56 nm Pore volume: 0.26 cm^3g^{-1}	WCO	K/ γAl_2O_3
This study	92.31	6	6	8	60	Gamma alumina (Merck) BET area: 190 m^2g^{-1} Pore diameter: 10 nm Pore volume: 0.5 cm^3g^{-1}	WCO	K/ γAl_2O_3
Sánchez et al. [28]	92.9	4	4	7.28		BET area: 252.13 m^2g^{-1}	Soybean oil	xK-γAl_2O_3(x = 10wt%)
Noiroj et al. [29]	91.07	3	03-June	15	60	BET area: 208.48 m^2g^{-1}	Palm oil	xKOH/ γ-Al_2O_3 (x = 25wt%)
Ma et al. [30]	84.5	1	4	9	60	BET area: 223.9 m^2g^{-1} Pore diameter: 8.6 nm	Rapeseed oil	K/KOH/Al_2O_3
Tonetto et al. [31]	98.9	6	1	32	120	BET area: 148.5 m^2g^{-1}	Soybean oil	K/ Al_2O_3
Ilgen et al. [32]	89.4	9	3	12	60	BET area: 120–190 m^2g^{-1}	Canola oil	KOH/ Al_2O_3
Ghasemi et al. [33]	76.35	3	4	15	65	BET area: 190.9 m^2g^{-1} Particle size: 4 mm	WCO	xKOH/ Al_2O_3(x = 25 wt%)
Guixia et al. [34]	89.53	5	10	8	60	BET area: 121.02 m^2g^{-1}	Microalgae (biomass)	xKOH/ Al_2O_3(x = 35 wt%)
Wenlei et al. [35]	96	8	2.5	15	65	Particle size: 2–12 μm	Soybean oil	xKI/ Al_2O_3(x = 35 wt%)
Bo et al. [36]	90	3	4	12	65		Palm oil	KF/ Al_2O_3(0.331 wt%)

production and compared to the other presented studies, milder operating conditions have been applied in the present study to achieve a high methyl ester yield of 99%.

Conclusions

In this study, a new route using PVA and phthalic acid was applied for the synthesis of microspherical nanoporous γ-alumina with the implementation of spray drying method. The gamma alumina precursor was chosen from commercial grade which is more economical for the large-scale process. Among the prepared samples at various conditions, the highest surface area of 214.8 m^2g^{-1} was obtained for sample SF at the conditions of 1 wt% PVA, a temperature of 200 °C, slurry solid content of 50 wt% and phthalic acid content of 5 wt%. Different heterogeneous-based catalysts of K/γ-Al_2O_3, Li/γ-Al_2O_3 and Na/γ-Al_2O_3 were prepared using the synthesized support and 4 wt% loading of these catalysts was implemented in biodiesel production process from waste cooking oil. Comparison the performances of three mentioned catalysts, at the same operating conditions, revealed almost the same activity for both K/γ-Al_2O_3, Na/γ-Al_2O_3 catalysts while a low catalytic activity was obtained for Li/γ-Al_2O_3. TGA and (^{1}H)NMR methods were employed for monitoring the produced biodiesel. The effect of different catalyst loadings was studied for K/γ-Al_2O_3 catalyst and the results showed the maximum biodiesel yield of 99% at the conditions of 6 wt% of catalyst content, a temperature of 60 °C, methanol to WCO molar ratio of 8 and a reaction time of 6 h. A purchased gamma alumina support (Merck) was employed for the catalyst preparation and comparison of the results for biodiesel production at the same operating conditions revealed the promising potential of the synthesized gamma alumina support to achieve higher performances. Moreover, compared to the other relevant studies, in our study milder operating conditions were implemented for biodiesel production from WCO.

References

1. Feyzi, M., Khajavi, G.: Investigation of biodiesel production using modified strontium nanocatalysts supported on the ZSM-5 zeolite. Ind. Crop. Prod. **58**, 298–304 (2014)
2. Sun, C., Qiu, F., Yang, D., Ye, B.: Preparation of biodiesel from soybean oil catalyzed by Al-Ca hydrocalcite loaded with K2CO3 as heterogeneous solid base catalyst. Fuel Process. Technol. **126**, 383–391 (2014)
3. Calero, J., Luna, D., Sancho, E.D., Luna, C., Bautista, F.M., Romero, A.A., Posadillo, A., Verdugo, C.: Development of a new biodiesel that integrates glycerol, by using CaO as heterogeneous catalyst, in the partial methanolysis of sunflower oil. Fuel **122**, 94–102 (2014)
4. Feyzi, M., Hassankhani, A., Rafiee, H.R.: Preparation and characterization of Cs/Al/Fe3O4 nanocatalysts for biodiesel production. Energy Convers. Manag. **71**, 62–68 (2013)
5. Mahesh, S.E., Ramanathan, A., Begum, K.M.M.S., Narayanan, A.: Biodiesel production from waste cooking oil using KBr impregnated CaO as catalyst. Energy Convers. Manag. **91**, 442–450 (2015)
6. Sánchez, M., Navas, M., Ruggera, J.F., Casella, M.L., Aracil, J., Martínez, M.: Biodiesel production optimization using γAl2O3 based catalysts. Energy **73**, 661–669 (2014)
7. Hamze, H., Akia, M., Yazdani, F.: Optimization of biodiesel production from the waste cooking oil using response surface methodology. Process Saf. Environ. **94**, 1–10 (2015)
8. Santiago-Torres, N., Romero-Ibarra, I.C., Pfeiffer, H.: Sodium zirconate (Na2ZrO3) as a catalyst in a soybean oil transesterification reaction for biodiesel production. Fuel Process. Technol. **120**, 34–39 (2014)
9. Xie, W., Li, H.: Alumina-supported potassium iodide as a heterogeneous catalyst for biodiesel production from soybean oil. J. Mol. Catal. A: Chem. **255**, 1–9 (2006)
10. Arzamendi, G., Campo, I., Arguinarena, E., Sánchez, M., Montes, M., Gandía, L.: Synthesis of biodiesel with heterogeneous NaOH/alumina catalysts: comparison with homogeneous NaOH. Chem. Eng. J. **134**, 123–130 (2007)
11. Akia, M., Alavi, S.A., Rezaei, M., Yan, Z.F.: Synthesis of high surface area γ-Al2O3 as an efficient catalyst support for dehydrogenation of n-dodecane. J. Porous Mater. **17**, 85–90 (2010)
12. Abd El-Hafiz, D.R., Riad, M., Mikhail, S.: Nano-structured Mn–Al and Co–Al oxide materials for catalytic ethanol conversion. J. Nanostructure Chem. **5**, 393–403 (2015)
13. Aboonasr Shiraz, M.H., Rezaei, M., Meshkani, F.: Microemulsion synthesis method for preparation of mesoporous nanocrystalline γ-Al2O3 powders as catalyst carrier for nickel catalyst in dry reforming reaction. Int. J. Hydrogen Energy **41**, 6353–6361 (2016)
14. Tsetsekou, A., Agrafiotis, C., Leon, I., Milias, A.: Optimization of the rheological properties of alumina slurries for ceramic processing applications Part II: spray-drying. J. Eur. Ceram. Soc. **21**, 493–506 (2001)
15. Xie, Y., Kocaefe, D., Kocaefe, Y., Cheng, J., Liu, W.: the effect of novel synthetic methods and parameters control on morphology of nano-alumina particles. Nanoscale Res. Lett. **11**, 259 (2016)
16. Bertrand, G., Filiatre, C., Mahdjoub, H., Foissy, A., Coddet, C.: Influence of slurry characteristics on the morphology of spray-dried alumina powders. J. Eur. Ceram. Soc. **23**, 263–271 (2003)
17. Mishra, P.K., Nayak, B.B., Mishra, B.K.: Influence of behavior of alumina slurry on quality of alumina powder prepared by jet wheel impact atomization. Powder Technol. **196**, 272–277 (2009)
18. Lind, A., Myrstad, R., Eri, S., Skagseth, T.H., Rytter, E., Holmen, A.: Spray drying of porous alumina support for Fischer-Tropsch catalysis. Stud. Surf. Sci. Catal. **175**, 685–688 (2010)
19. Yu, B., Feng, Y.J., Wohn, L.S., Huang, C., Li, Y.F., Jia, Z.: Spray-drying of alumina powder for APS: effect of slurry properties and drying conditions upon particle size and morphology of feedstock. Bull. Mater. Sci. **34**, 1653–1661 (2011)

20. Ramavath, P., Swathi, M., Buchi Suresh, M., Johnson, R.: Flow properties of spray dried alumina granules using powder flow analysis technique. Adv. Powder Technol. **24**, 667–673 (2013)
21. Cottrino, S., Jorand, Y., Adrien, J., Olagnon, C.: Spray-drying of highly concentrated nano alumina dispersions. Powder Technol. **237**, 586–593 (2013)
22. Huang, F., Zheng, Y., Cai, G., Zheng, Y., Xiao, Y., Wei, K.: A new synthetic procedure for ordered mesoporous γ-alumina with a large surface area. Scripta Mater. **63**, 339–342 (2010)
23. Yee, K.F., Wu, J.C., Lee, K.T.: A green catalyst for biodiesel production from jatropha oil: optimization study. Biomass Bioenergy **35**, 1739–1746 (2011)
24. Hoffmann, G.: The Chemistry and Technology of Edible Oils and Fats and Their High Fat Products, pp. 1–28. Academic Press, Cambridge (1989)
25. Tariq, M., Ali, S., Ahmad, F., Ahmad, M., Zafar, M., Khalid, N., Khan, M.A.: Identification, FT-IR, NMR (1 H and 13 C) and GC/MS studies of fatty acid methyl esters in biodiesel from rocket seed oil. Fuel Process. Technol. **92**, 336–341 (2011)
26. Killner, M.H.M., Linck, Y.G., Danieli, E., Rohwedder, J.J.R., Blümich, B.: Compact NMR spectroscopy for real-time monitoring of a biodiesel production. Fuel **139**, 240–247 (2015)
27. Chand, P., Reddy, C.V., Verkade, J.G., Wang, T., Grewell, D.: Thermogravimetric quantification of biodiesel produced via alkali catalyzed transesterification of soybean oil. Energy Fuels **23**, 989–992 (2009)
28. Sánchez, M., Navas, M., Ruggera, J.F., Casella, M.L., Aracil, J., Martínez, M.: Biodiesel production optimization using γAl2O3 based catalysts. Energy **73**, 661–669 (2014)
29. Noiroj, K., Intarapong, P., Luengnaruemitchai, A., Jai-In, S.: A comparative study of KOH/Al 2 O 3 and KOH/NaY catalysts for biodiesel production via transesterification from palm oil. Renew. Energy **34**, 1145–1150 (2009)
30. Ma, H., Li, S., Wang, B., Wang, R., Tian, S.: Transesterification of rapeseed oil for synthesizing biodiesel by K/KOH/γ-Al2O3 as heterogeneous base catalyst. J. Am. Oil Chem. Soc. **85**, 263–270 (2008)
31. Tonetto, G.M., Marchetti, J.M.: Transesterification of soybean oil over Me/Al2O3 (Me = Na, Ba, Ca, and K) catalysts and monolith K/Al2O3-cordierite. Top. Catal. **53**, 755–762 (2010)
32. Akia, M., Yazdani, F., Motaee, E., Han, D., Arandiyan, H.: A review on conversion of biomass to biofuel by nanocatalysts. Biofuel Res. J. **1**, 16–25 (2014)
33. Ghasemi, M., Molaei Dehkordi, A.: Transesterification of waste cooking oil to biodiesel using KOH/γ-Al2O3 catalyst in a new two-impinging-jets reactor. Ind. Eng. Chem. Res. **53**, 12238–12248 (2014)
34. Ma, G., Hu, W., Pei, H., Jiang, L., Ji, Y., Mu, R.: Study of KOH/Al2O3 as heterogeneous catalyst for biodiesel production via in situ transesterification from microalgae. Environ. Technol. **36**, 622–627 (2015)
35. Xie, W., Li, H.: Alumina-supported potassium iodide as a heterogeneous catalyst for biodiesel production from soybean oil. J. Mol. Catal. A: Chem. **255**, 1–9 (2006)
36. Bo, X., Guomin, X., Lingfeng, C., Ruiping, W., Lijing, G.: Transesterification of palm oil with methanol to biodiesel over a KF/Al2O3 heterogeneous base catalyst. Energy Fuels **21**(6), 3109–3112 (2007)
37. Hassani, M., Najafpour, G.D., Mohammadi, M.: Transesterification of waste cooking oil to biodiesel using γ-alumina coated on zeolite pellets. J. Mater. Environ. Sci. **7**(4), 1193–1203 (2016)
38. Heidar, T.H., Tahvildari, K.: Efficient Synthesis of biodiesel from waste cooking oil catalysed by Al2O3 impregnated with NaOH. J. Chem. Pet. Eng. **49**, 143–151 (2015)