PREPARATION AND APPLICATION OF KOH IMPREGNATED SEPIOLITE AS A SOLID BASE CATALYST FOR BIODIESEL PRODUCTION USING MICROWAVE IRRADIATION

M. HAMDI KARAOĞLU [1], VLADIMIR ZHOLOBENKO [2] AND SEMA ASLAN [1*]

[1]Muğla Sıtkı Koçman University, Faculty of Science, Chemistry Department, 48000 Kötekli / Muğla Turkey.
[2] School of Chemical and Physical Sciences, Keele University, Staffordshire, ST5 5BG, UK.

ABSTRACT

An active basic solid catalyst for biodiesel production was obtained via KOH impregnation onto sepiolite support followed by high temperature calcination. The transesterification of rapeseed oil over the resulting nanocomposite structure was investigated using a microwave reactor. Morphological and structural characterization of sepiolite and KOH impregnated sepiolite was carried out by Fourier transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy and energy dispersive spectroscopy analysis. Optimization of the operational parameters such as methanol to oil molar ratio, catalyst loading, reaction temperature and reaction time were examined. Reusability of the catalyst and the reactions utilizing waste cooking oil were also studied. Obtained results indicated that the basic heterogenous catalysis diminishes the saponification during the transesterification reaction and that microwave heating was very effective at shortening the biodiesel production time. However, the reusability of the KOH impregnated sepiolite catalysts and their structural stability require further investigation.

Keywords: Heterogenous catalysis, KOH, sepiolite, rapeseed oil, microwave assisted transesterification, biodiesel production.

1. INTRODUCTION

The intension of this article is to explain the benefits of the microwave based transesterification process. The advantages of this system can be listed as rapid heating and cooling, cost saving due to energy and time saving, effective and selective heat control opportunities and short reaction times [1-5].

Transesterification (or alcoholysis), is a chemical reaction between an oil or fat with a suitable alcohol to produce esters and glycerol. This process is composed of three consecutive reversible reactions. At first step triglyceride is converted into diglyceride, then diglyceride is converted into mono glyceride and in the last step monoglyceride is converted to fatty acid alkyl ester and glycerol [6-8].

Homogenous or heterogenous catalysts are utilized in these reaction steps [9]. In a typical homogenous catalyst supported transesterification process, the catalyst is dissolved in the medium completely and there is no phase difference between the catalyst and the reaction mixture. On the other hand, heterogenous catalysis is carried out with a catalyst that form another phase such as solid, immiscible liquid or gaseous in the transesterification medium without passing into the same phase [10, 11]. In this case heterogenous transesterification process is attributed to be a green technology issue due to the recycling facilities of heterogenous catalysts, trace amounts of water production during the process that causes the corrosion in the parts of engine during operation and the easy phase separation of biodiesel and glycerol in the end of the reaction [12,13]. Besides, in the homogenous catalytic transesterification, required catalyst amount is vey much, since the salts are reacting with fatty acids before alcohol they yield very high saponification numbers, in the end low quality of biodiesel and glycerol, long term process and distillation are acquired for the excess reactant removal [14-17].

A large scale of heterogeneous catalysts such as alkali metal oxides and their derivatives [18-22] alkaline earth metal oxides and their derivatives [21,23-30], transition metal oxides and their derivatives [31], mixed metal oxides and their derivatives [32], ion exchange resin using [33,34] or sulphated oxide acidic catalysts [35, 36], carbon based catalysts [37], boron group based catalysts [32, 38], waste material using catalysts [39], enzyme based catalysts [40] are in the ascendant in laboratory scale biodiesel production. In a KOH or KOH-bentonite [41] mixture using transesterification study the author claimed that the obtained fatty acid methyl ester (FAME) content, which defines the quality of the biodiesel, increased with the increasing amounts of bentonite proportions [42]. Since the bentonite bares some active groups (such as SiO_2 Al_2O_3 Fe_2O_3 CaO MgO K_2O Na_2O), it chokes the water production and can trigger the presence of catalytically active methoxides during the methanolysis process by shifting the reaction direction in hydroxide/methoxide equilibrium (Eq. (1)) towards the formation of the methoxide, leading to increased amounts of FAME.

$$CH_3OH + OH^- \leftrightarrow CH_3O^- + H_2O \qquad \text{(Eq. 1)}$$

Sepiolite is also a good candidate for this purpose by possessing very much similar active catalytic groups such as SiO_2, MgO or Al_2O_3 and must be used in the same manner with bentonite. Menor et al. reported that MgO presence dominates the basic structure of the bentonite and glycerol production is improved by the combination with Ni impregnation onto this support [43]. We have also enhanced the basic capability of sep. with KOH addition into this unique structure. Additionaly, there are several catalytic studies on sepiolite such as CaO loaded sepiolite used as CO_2 sorbent [44], acid-activated sepiolite using glycerol production study [45] or another report claimed that using the sepiolite as additive into the slurries during catalyst preparation revealed with positive results because of enhancing adherence [46].

However, there is not any study about KOH impregnated sepiolite based heterogenous catalysis based on direct biodiesel production with the combination of microwave assistance. There are several methods for the biodiesel production but the crucial point is the choice of the best system avoid to time, energy, yield and quality wasting processes. It is reported that microwave assisted system using production times are lowered up to 6 folds compared to the traditional heating processes [47]. Here we also obtained satisfactory results after 20 min. operation times compared to the previously used 3h. heating process. On the other hand, as we take a deep look into kinetics of this catalyst it can be said that according to the transesterification reaction (Eq. 2) the limiting step is methoxide formation step. In this step the excess amount of methanol addition into the medium doesn't effect at all the order of the reaction. So the calculations can be carried out according to 1st order reaction equation. After the optimization studies reusability and waste rapeseed oil transesterification performances of the present system was tried. This study can be evaluated as a demo of the improvable performance of the presented system, the results can be improved by the incubation of final biodiesel-glycerol mixture for phase separation.

2. EXPERIMENTAL

2.1. Chemical Reagents and Equipments

Magnesium sulfate (99.00 % pure), n-hexane (99.00 % pure), methanol (99.80 % pure), and potassium hydroxide (99. 00 % pure) were purchased from Merck Co. Sepiolite was supplied from Sigma-Aldrich, edible rapeseed oil was bought from a local market. FTIR spectra were collected using a Thermo iS10 spectrometer, XRD patterns which were recorded on a Bruker D8 Advance diffractometer TM3000 (Hitachi) scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDX, Bruker) was utilised to obtain the elemental composition of the sepiolites, biodiesel reaction studies were performed in a Biotage microwave system (Biotage Initiator+).

2.2. Catalyst Preperation and characterization

The first step of the KOH impregnated sepiolite catalyst sythesis is the choice of the KOH/sepiolite ratio. It was defined as 1:4, then the aqueous solution of KOH salt was added into sepiolite containing three-necked flask. Modification of the catalyst was performed with wet impregnation method in which, aqueous

*Corresponding author email: sozcan87@gmail.com

solution of potassium hydroxide salt applied onto the sepiolite support. A round bottom three-necked flask (500 mL) was utilized in the synthesis of the catalyst. The flask was donated with a reflux condenser to keep the solvent inside, a thermometer to measure the temperature during the reaction and a mechanical stirrer to mix the suspension with a magnetic bar. The impregnation of sepiolite with KOH was achieved under continuous stirring for 24 h at a temperature of 60 °C. After the impregnation process, obtained catalyst was centrifuged, filtrated and calcined at 400 °C for 5 h. Then, these samples were cooled to room temperature in a desiccator and stored at dark medium when not in use [48].

2.3. Transesterification reaction and analysis methods of biodiesel

Transesterification is the key step of the whole biodiesel production process. Especially, if the methoxy formation step does not processed well, FAME yield of the produced biodiesel will be lower than it is expected. In the microwave assisted method, methanol, canola oil and a defined amount (optimal amount) of the catalyst were added into the flask and transferred into the reactor. The mixture was stirred continuously and irradiated at defined (optimal) temperature during the optimum time. Then the resulting biodiesel and glycerol containing mixture was cooled down to the room temperature. Subsequently, it was centrifuged for 15 min at 5000 rpm. The supernatant solution, mainly biodiesel containing part of the sample was separated and washed. In order to remove the remaining humidity in the biodiesel, a spatula of magnesium sulphate anhydrous salt was added into the vessel and centrifuged again. Finally, the sample was analyzed by GC–MS to define the total FAME ingredient and concentration [49].

3. RESULTS AND DISCUSSION

3.1. Structural characterizations of the catalyst

The FT-IR spectra is a conventional method to enlighten the bond formation of the catalysts. Supplementary Figure 1 shows the FTIR spectra of raw sepiolite and KOH/sep. It is clear to indicate that the OH bending peak of the external surface (3558.59 cm^{-1}) (Supplementary Figure 1a) belongs to raw sepiolite was suppressed after the modification (Supplementary Figure 1b). The peak at the 1659.22 cm^{-1} was shifted to the 1648.57 cm^{-1} corresponding the change of the OH vibrations in the sepiolite structure. Also the 1209.98 cm^{-1} peak was diminished due to this recombination of the zeolitic OH group. Finally, the peak shifts in the finger print area (687.65 and 969.72 cm^{-1}) were attributed to the metallic load onto the sepiolite structure and resulted as change in the Si-O-Si plane vibrations [50,51].

Raw and modified sepiolites, discussed above were morphologically studied using SEM-EDX (Figure 1). When SEM images belonging to KOH/sep material are analyzed, it is seen that clear colour removal has occurred and surface pores were doped when compared to raw sepiolite. This colour changes leads us to think that K$_2$O is considerably adsorbed in sepiolite surface and pores (Figure 1a SEM image of the raw sepiolite, b) SEM image of the KOH/sep.). Additionally, the elemental EDX peak of the K in the KOH/sep. structure showed increment after the modification (Figure 1c: raw sepiolite, Figure 1d: KOH/sep.). The impregnation of sepiolite with KOH is evaluated to be successful after these morphological measurement results. Atomic weight percentages of EDX measurements are also given in the Table 1.
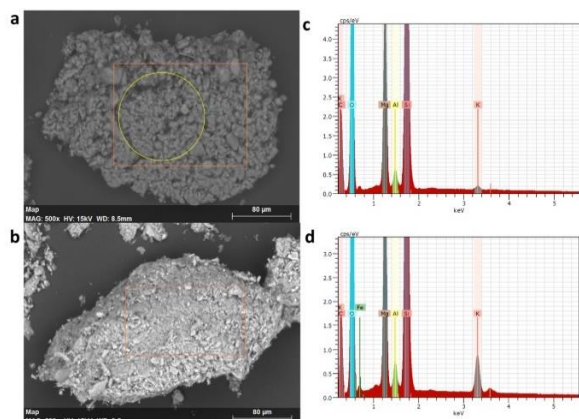

Figure 1. a) SEM image of raw sepiolite, b) SEM image of KOH/sep. c) EDX image of raw sepiolite, d) EDX image of KOH/sep.

Table 1. Atomic weight percentages of EDX measurements

Type of element	Natural sepiolite (wt %)	KOH impregnated sepiolite (wt %)
Si	23.32	21.70
Mg	13.78	11.69
K	3.12	1.14
Al	1.54	0.38

XRD curves of raw sepiolite and KOH/sep. are illustrated in Figure 2. As Figure 2b indicates, the treatment of sepiolite with KOH altered their crystalline structure, since the original crystalline peaks diminished significantly in intensity. XRD pattern of natural sepiolite (Figure 2a) shows the typical diffraction peaks at $2\theta = 7.0°$, $19.55°$, $20.40°$, $23.55°$, $26.55°$, $27.95°$, $34.80°$, $36.40°$, $40.0°$ and $48.20°$. The presence of K$_2$O after the modification (Figure 2b) was indicated by the intensity peaks at 2θ at $6.85°$, $26.30°$, $27.50°$, $34.40°$, 36.40, $39.45°$.$41.25°$, $42.65°$, $45.90°$ and $48.30°$.
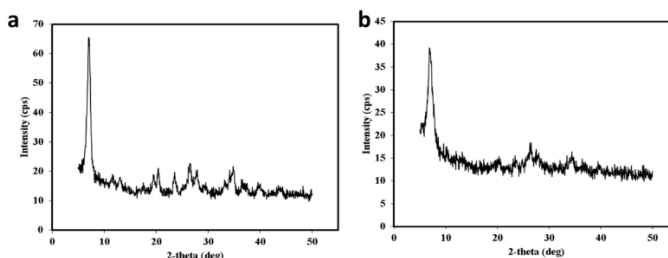

Figure 2. XRD patterns of a) raw sepiolite and b) KOH/sep.

3.2. Evaluation of the Catalytic Performance of KOH/sep. modified catalyst using microwave irradiation

According to the interaction of dielectric nature of the materials with microwaves leads to electronic, ionic, dipole or interfacial polarization of the substance. This type of heating mechanism leads to dielectric heating of the substance at each polarization station not likely conventional heating systems (Scheme 1). The usage of microwave irradiation enhances the reaction stations of the triglycerydes.

Methanol is mostly used as solvent in transesterification reactions, known to have high microwave absorption capacity. Since its high polarity feature it can be concluded that oil-methanol-catalyst involved reaction can be effected by microwaves by dipolar polarization and ionic conduction. Ionic or dipole rotation of the molecules ease the collisions between methanol and oil so this interaction results in superheating of the reaction stations of the triglycerides (Scheme 1) [2,8].
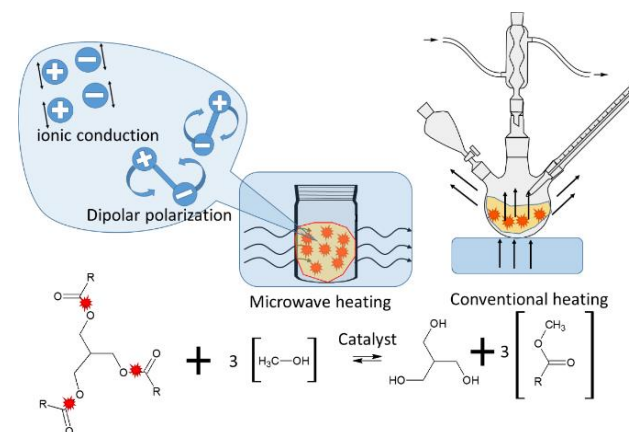
Scheme 1. Conventional and microwave heating mechanisms, molecular polarizations of triglycerides under microwave conditions and transesterification reaction scheme.

The effect of catalyst loading on the biodiesel yield was studied with the different weight percentages of the catalyst (Figure 3a). Here the weights of

KOH/sep. were choosen from 3% to 9% whereas other conditions were maintained as MeOH/oil molar ratio of 1/6, reaction time 20 min. and temperature 80 °C. The biodiesel yields were clearly increased from 0.32 to 57.14 % according to the amount of catalyst increased from 3 to 9 wt%. This increment shows that the collisions between catalyst surface and the triglyceride at 9%, are definitely much more than that of 3% [52].

The temperature is an important parameter in catalytic studies and its effect should be investigated for transesterification reaction that is catalysed by a solid catalyst [53]. The effect of temperature on the esterification using the microwave approach has been investaged by changing the temperature of reaction at different values as 60, 80 and 100 °C (Figure 3b). The MeOH/oil molar ratio of 1/6 and catalyst concentration of 3% (w/w) was kept constant for all the experimental runs related to the effect of temperature. Figure 3 shows the conversion rate of biodiesel increased when the reaction temperature increased from 333 to 393 K.

Biodiesel production from transesterification is a reversible reaction. The biodiesel yield could be improved by introducing excess amounts of methanol to force the reaction towards the formation of biodiesel [53]. The methanol/oil molar ratio ranged from 3:1 to 9:1 were used for biodiesel production at given conditions (Figure 3c) (catalyst amount 3 wt.%, reaction time 20 min and temperature 80 °C). The yield increased from 7.42% to 21.20% with the increase in molar ratio from 3:1 to 9:1.

Effect of reaction time was studied by varying time intervals (Figure 3c). Studies were carried out at different irradiation times, e.g. 5, 10, 20 and 30 minute with 3.0% catalyst and methanol/oil molar ratio: 6/1. The effect of reaction time on the transesterification reaction is presented in Figure 3. The conversion rate of biodiesel increased from 10.53% to 57.21% when the reaction time increased from 5 min. to 30 min..
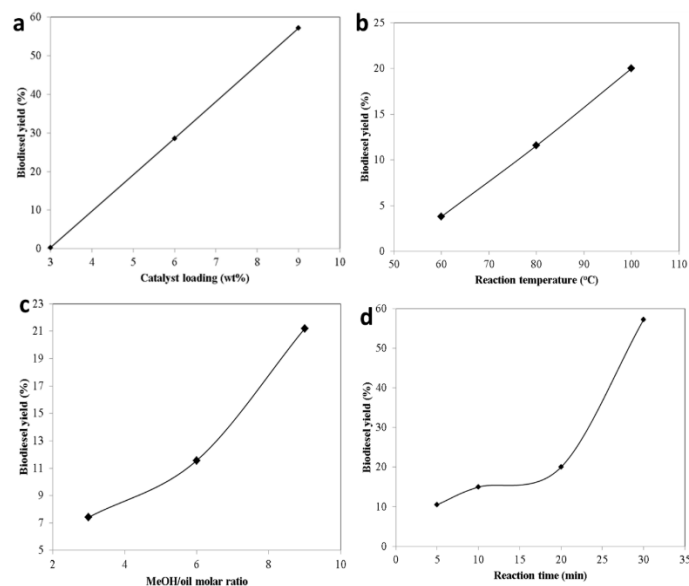

Figure 3. The effects of a) amount of catalyst, b) temperature of the reaction, c) Methanol to oil ratio, d) reaction time on the catalytic performance of KOH/sep. catalyst.

CONCLUSION

In this study, biodiesel is produced from canola oil using microwave assisted transesterification process. It is very important to reach effective transesterification yields in a short reaction time. Among the methods developed until today this is an intermediate study that indicates the effectiveness of microwave assistance in the biodiesel production. The optimal reaction levels were defined as a methanol/oil molar ratio of 9:1, amount of catalyst of 9.0 wt.% and reaction temperature at 353 K for a 20 min transesterification reaction. In the end 57.14 % biodiesel yield was achieved. The use of microwave irradiation always shortened the reaction time and was provided higher FAME yields. However, the reusability of the KOH impregnated sepiolite catalysts and their structural stability requires further investigation.

DECLARATIONS

The authors declare that there are no competing interests.

REFERENCES

1. I.K. Hong, H. Jeon, H. Kim, S.B. Lee, *J. Ind. Eng. Chem.* **42**, 107, (2016).
2. I. Fatimah, D. Rubiyanto, J. Nugrah, *Sus. Chem. Pharm.* **8**, 63, (2018).
3. A.T. Hoang, M. Tabatabaei, M. Aghbashlo, *Energy Sour. Part A.* **42**, 2923, (2019).
4. R.S. Pasupathy, T. Mohanraj, *Energy Sour. Part A.* **43**, 172, (2019).
5. M. Tomar, N. Kumar, *Energy Sour. Part A.* **42**, 2944, (2019).
6. F. Ma, M.A. Hanna, *Bioresour. Technol.* **70**, 1, (1999).
7. A. Al-Ani, R. Gertisser, V. Zholobenko, *Appl. Clay Sci.* **162**, 297, (2018).
8. A. Al-Ani, R.J. Darton, S. Sneddon, V. Zholobenko, *ACS Appl. Nano Mater.* **1**, 310, (2018).
9. Y. Wang, X. Wang, Y. Liu, S. Ou, Y. Tan et al. *Fuel Proc. Technol.*; **90**, 422, (2009).
10. Z. Helwani, M.R. Othman, N. Aziz, J. Kim, W.J.N. Fernando. Appl. Catal. A General. **363**, 1, (2009).
11. M. Zabeti, M. Wan, D. Wan. Fuel Proc. Technol. **90**, 770, (2009).
12. A.K. Sarma, J.K. Sarmah, L. Barbora, P. Kalita, S. Chatterjee et al. Recent Patents on Eng. **2**, 47, (2008).
13. J.S. Lee, S. Saka. *Bioresour. Technol.* **101**, 7191, (2010).
14. M. Canakci, J. Van Gerpan. Transactions-Am. Soc. Agric. Eng. **44**, 1429, (2001).
15. M.L. Grandos, M.D. Poves, D. Alonso, R. Mariscal, F.C. Galisteo et al. *Appl. Catal. B: Env.* **73**, 317, (2007).
16. J. Ji, J. Wang, Y. Li, Y. Yu, Z. Xu. *Ultrason.* **44**, 411, (2006).
17. K.S. Kumar, C. Anju. *Bioresour. Technol.* **96**, 1425, (2005).
18. T. Ebiura, T. Echizen, A. Ishikawa, M. Kazuhito, T. Baba. *Appl.Catal. A: General.* **283**, 111, (2005).
19. W. Xie, P. Hong, C. Ligong. *J. Mol. Catal. A: Chem.* **246**, 24, (2006).
20. D. Fabbri, V. Bevoni, M. Notari, F. Rivetti. *Fuel.* **86**, 690, (2007).
21. L. Wang, J. Yang. *Fuel.* **86**, 328, (2007).
22. G. Arzamendi, I. Campoa, E. Arguinarena, M. Sanchez, M. Montes et al. *Chem. Eng. J.* **134**, 123, (2007).
23. D. E. Lopez, D. A. Bruce Jr, J.G.E. Lotero. *Appl. Cat. A: General.***295**,105, (2005).
24. T. Tateno, T. Sasaki. Process for producing fatty acid fuels comprising fatty acids esters. Uni. State Patent 6818026, November 16, (2004).
25. M. Di. Serio, R. Tesser, M. Dimiccoli, F. Cammarota, M. Nasatasiet al. *J. Mol. Catal.* **239**, 111, (2005).
26. H. Mootabadi, B. Salamatinia, S. Bhatia, A.Z. Abdullah. *Fuel*. **89**, 1818, (2010).
27. B. Salamatinia, H. Mootabadi, S. Bhatia, A.Z. Abdullah. *Fuel Proc. Technol.* **91**, 441, (2010).
28. D.J. Vujicic, D. Comic, A. Zarubica, R. Micic, G. Boskovic. *Fuel.* **89**, 2054, (2010).
29. B. Yoosuk, P. Udomsap, P. Buppa, K. Pawnprapa. *Chem. Eng. J.* **162**, 135, (2010).
30. S.J. Yoo, H.S. Lee, V. Bambang, J. Kim, J.D. Kim et al. *Bioresour. Technol.* **101**, 8686, (2010) .
31. W.M. Antunes, C.O. Veloso, C.A. Henriques. *Catal. Today.* **133–135**, 548, (2008).
32. O. Ilgen. *Fuel Proc. Technol.* **92**, 452, (2011).
33. A. Alsalme, E.F. Kozhevnikova, I.V. Kozhevnikov. *Appl. Catal. A: General.* **349**, 170, (2008).
34. Y.M. Park, D. Lee, D.K. Kim, J. Lee, K.Y. Lee. *Catal. Today.* **131**, 238, (2008).
35. Y.M. Park, S. Chung, H.J. Eom, J. Lee, K. Lee. *Bioresour. Technol.* **101**, 6589, (2010).

36. A.C. Alba-Rubio, F. Vila, D.M. Alonso, M. Ojeda, R. Mariscalet al. *Appl. Catal. B: Environ.* **95**, 279, (2010).
37. A.M. Dehkhoda, A.H. West, N. Ellis. *Appl. Catal. A: General*. **382**, 204, (2010).
38. C. Guo, F. Baishan. *Bioresour. Technol.* **102**, 2635, (2011).
39. D.C. Deka, S. Basumatary, J.S. Lee. *Biomass and Bioenergy*. **305**, 1797, (2011).
40. R. Chakraborty, S. Bepari, A. Banerjee. *Bioresour. Technol.* **102**, 3610, (2011).
41. M. Agarwal, G. Chauhan, S.P. Chaurasia, K. Singh. *J. Taiwan Inst. Chem. Eng.* **43**, 94, (2012).
42. L. Wu, T.Y. Wei, Z.F. Tong, Y. Zou, Z.J. Lin et al. *Fuel Proc. Technol.* **144**, 340, (2016).
43. M. Menor, S. Sayas, A. Chica. *Fuel*. **193**, 358, (2017).
44. J. Shi, Y. Li, Q. Zhang, X. Ma, L. Duan et al. *Appl. Energy* **203**, 421, (2017).
45. C.H. Zhou, G.L. Li, X.Y. Zhuang, P.P. Wang, D.S. Tong et al. *Mol. Cat.* **434**, 231, (2017).
46. I. Reyero, A. Moral, F. Bimbela, J. Radosevic, O. Sanzet al. *Fuel*. **182**, 676, (2016).
47. S. Aslan, N. Aka, M.H. Karaoğlu. *Energy Sour. Part A*. **41**, 297, (2019).
48. W.N.N.W. Omar, N.A.S. Amin. *Fuel Proc. Technol.* **92**, 2405, (2011).
49. M. Cobas, L. Ferreira, M.A. Sanroman, M. Pazos. *EcologicalEngineering*.**40**,294,(2014).
50. E. Eren, O. Cubuk, H. Ciftci, B. Eren, B. Caglar. *Desalin*.**252**,96,(2010).
51. H. Shahraki, M.H. Entezari, E.K. Goharshadi. *UltrasonicsSonochemistry*. **23**,274,(2015).
52. M. Takase, Y. Chen, H. Liu, T. Zhao, L. Yang et al. *Ultrasonics Sonochemistry*. **21**, 1762, (2014).
53. H. Wu, J. Zhang, Q. Wei, J. Zheng, J. Zhang. *Fuel Proc. Technol.* **109**, 18, (2013).