Materials Today: Proceedings xxx (xxxx) xxx

Contents lists available at ScienceDirect

Materials Today: Proceedings

journal homepage: www.elsevier.com/locate/matpr

Lithium silicate based catalysts prepared using arecanut husk ash for biodiesel production from used cooking oil

V. Vinu [a,b], N.N. Binitha [a,*]

[a] Department of Chemistry SreeNeelakanta Government Sanskrit College, Pattambi, Palakkad 679306, Kerala, India
[b] Department of Chemistry, Sree Krishna College, Guruvayur, Thrissur 680602, Kerala, India

ARTICLE INFO

Article history:
Received 4 December 2019
Received in revised form 4 January 2020
Accepted 8 January 2020
Available online xxxx

Keywords:
Arecanut husk ash
Lithium silicates
Greener catalyst
Waste management
Biodiesel

ABSTRACT

The proficient and cost-effective utilization of renewable waste materials for the solid catalyst development facilitates the commercial production of biodiesel through a green route. Here, arecanut husk ash, chemically modified with lithium compound is used as an efficient solid catalyst for the biodiesel production from used cooking oil. Lithium silicates are the major crystalline materials present in the lithium impregnated heterogeneous base catalyst. The activity of the arecanut husk ash derived catalyst in the transesterification of used cooking oil is excellent with a low catalyst loading under mild reaction conditions. Catalyst is best suited in the production of biodiesel from low cost feed stocks having high free fatty acid content and is found to be reusable.

Selection and peer-review under responsibility of the scientific committee of the International Conference on the Science and Technology of Advanced Materials.

1. Introduction

Arecanut husk is a widely available biomass in India, especially in the southern parts [1]. The husk of the arecanut fruit is removed and it has no traditional use, which is normally left in the land. India ranks first in the areca nut production in the world, having a contribution of 49.74% as per the 2013 statistics for food and agricultural organization (FAO) of United Nations, Rome [2].

The husk can be used as a fuel for the processing of the nut. This produces husk ash residue that has limited applications. Use of areca nut husk ash as a supplementary cementitious material has been evaluated [3]. The activated carbon from arecanut husk has been used for the adsorption of malachite green dye from aqueous solutions [4]. Mohammad et al investigated the ability of areca nut peel in the removal of Cr, Cd and Pb from aqueous solutions [5]. Sathish and co-workers produced biodiesel from arecanut shell oil by a two step reaction, pre-esterification followed by transesterification since the oil have high amount of free fatty acid (FFA) [6]. Activated carbon produced from arecanut husk by chemical activation method using phosphoric acid acts as an effective dye adsorbent [7]. Arecanut husk ash contains silica as the major compound. In addition, it also contains alumina, magnesium oxide and significant amount of alkali metal oxide (K_2O) [3,8].

Here, the use of areca nut husk ash for the development of a heterogeneous catalyst for biodiesel production is described. To the best of our knowledge, there are no reports mentioning the use of arecanut husk as a source of catalyst. Since the availability is plenty, its use as a heterogeneous catalyst is economical. So as to improve the alkali content in the ash, we have impregnated $LiNO_3$ to the areca nut husk ash in the presence of a suitable surfactant citric acid. The developed material was characterized and its performance as a catalyst for biodiesel production is investigated here in detail.

2. Experimental

2.1. Preparation of catalyst from arecanut husk

Cleaned and dried areca nut husk was burned in air, the char obtained was powdered and calcined at 750 °C for 3 h. Dirty white coloured hard ash obtained was powdered and lithium compound was incorporated by means of impregnation method with the aid of citric acid as a surfactant. Lithium nitrate (Nice Chemicals Pvt Ltd), arecanut husk ash and citric acid monohydrate (Nice Chemicals Pvt Ltd) were mixed thoroughly in a weight ratio of 2:1:1 respectively. In a typical procedure, citric acid was added to a

* Corresponding author.
E-mail address: binithann@sngscollege.org (N.N. Binitha).

https://doi.org/10.1016/j.matpr.2020.01.210
2214-7853/
Selection and peer-review under responsibility of the scientific committee of the International Conference on the Science and Technology of Advanced Materials.

0.25 N solution of lithium nitrate to which, arecanut husk ash was added with stirring and the contents were evaporated to dryness. The lithium inserted ash was then dried in a hot air oven at 90 °C for 12 h and calcined at 650 °C for 3 h.The resultant material was powdered and refluxed with methanol at 65 °C for 1 h to separate the unbound components from the catalyst. The contents were filtered, dried and the catalyst was then activated at 650 °C for 1 h before its use for biodiesel preparation. The catalyst prepared without citric acid was not uniform and leaching of lithium species was observed in the reaction.

2.2. Material characterization

The lithium incorporated catalyst was characterized using FTIR spectroscopy (Thermo Nicolet Avtar 370), XRD (Bruker D8 Advance), temperature programmed desorption (TPD) of CO_2 (Micromeritics Chemisorb 2750) and SEM (Jeol 6390LA/ OXFORD XMX N).

2.3. Catalytic activity studies

In a typical reaction procedure, the degummed UCO (with FFA < 1) was mixed with the lithium impregnated catalyst and refluxed with methanol for the required time. The reaction parameters were also varied to attain better catalytic performance. After the reaction, the catalyst was separated, the purified biodiesel layer was collected and the biodiesel content was determined via gas chromatographic analysis. For the investigation of effect of FFA on the reaction, oleic acid was introduced into the reaction mixture. For the reusability studies, the catalyst was collected and repeatedly washed with water and methanol, and then activated at 650 °C for use in the further reactions.

3. Results and discussion

In the present study, arecanut husk ash after chemical modification with lithium is used as a catalyst for biodiesel production. Catalyst preparation was done by a simple method of impregnation with the aid of citric acid. To ensure the heterogeneity of the catalyst in the reaction, the unbound methanol soluble fraction is removed from the catalyst. The developed catalyst material was characterized using various techniques in order to investigate the active phase responsible for catalysis. The activity of the arecanut husk ash derived catalyst in the transesterification of used cooking oil (UCO) was studied by varying the reaction conditions.

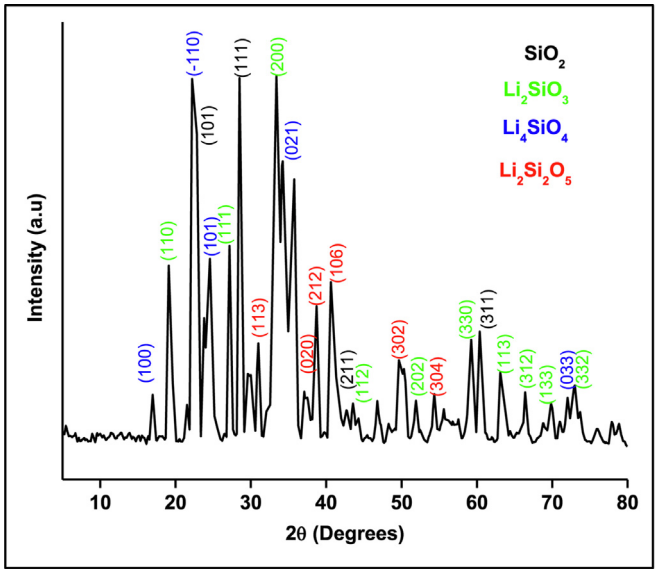

Fig. 2. XRD pattern of arecanut husk ash derived catalyst.

Fig. 1 shows the FTIR spectrum of the arecanut husk ash derived catalyst. In the spectrum, the broad band centered at 3433 cm^{-1} corresponds to the stretching vibration of –OH groups that may be mainly aroused from adsorbed water [9]. The stretching vibration of Si-O-Si is found at 1060 cm^{-1} and the band centered at 947 cm^{-1} is due to the Si-O-Li stretching vibration [10]. The peak at 866 cm^{-1} is attributed by the O-Si-O stretching vibration [11]. The absorption peak in the spectra at 741 cm^{-1} corresponds to the Si-O-Si symmetric stretching vibration [12]. The absorption band around 1450 cm^{-1} corresponds to the carbonate stretching mode [13]. The peak observed at 523 cm^{-1} is attributed to the Si-O-Li deformations and that at 423 cm^{-1} is attributed to the bending vibrations of Si-O-Si bond [12,14]. The spectral data indicates the formation of lithium silicate.

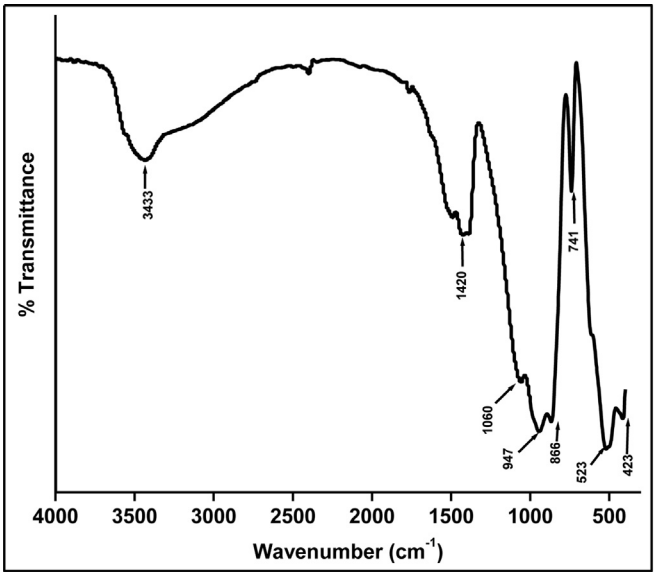

Fig. 1. FTIR of arecanut husk ash derived catalyst.

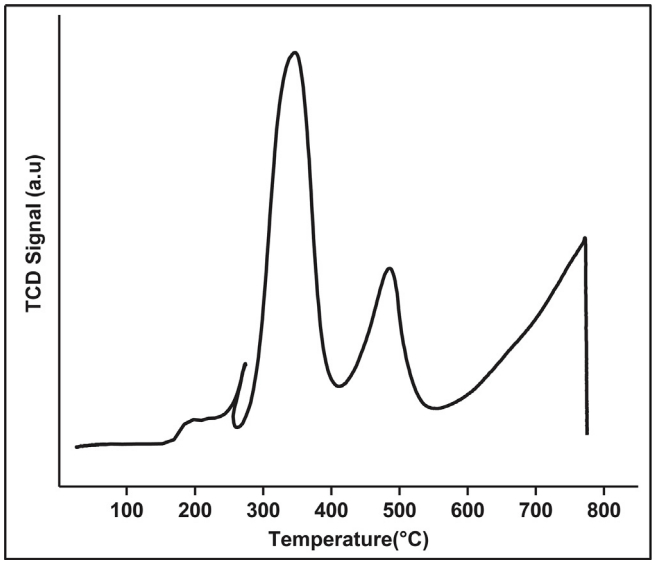

Fig. 3. TPD of CO_2 of arecanut husk ash derived catalyst.

Please cite this article as: V. Vinu and N. N. Binitha, Lithium silicate based catalysts prepared using arecanut husk ash for biodiesel production from used cooking oil, Materials Today: Proceedings, https://doi.org/10.1016/j.matpr.2020.01.210

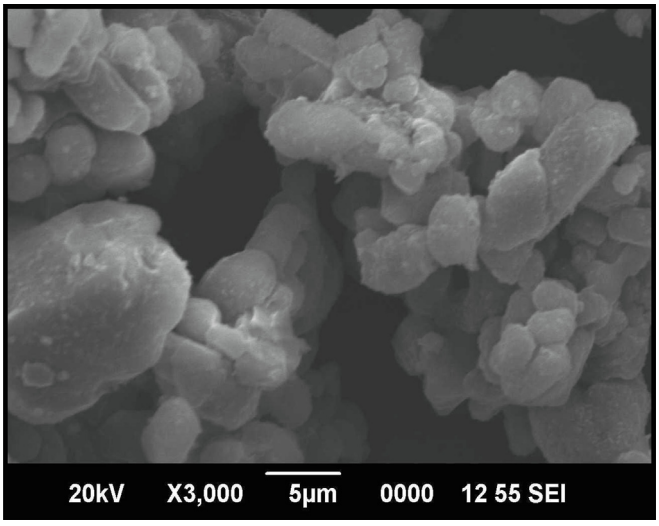

Fig. 4. SEM image of arecanut husk ash derived catalyst.

The XRD pattern (Fig. 2) of lithium impregnated arecanut husk ash catalyst shows that the material is a combination of different lithium silicates. The diffraction peaks are in good agreement with the JCPDS data of Li_2SiO_3 (JCPDS-29-0829) [15], Li_4SiO_4 (JCPDS-37-1472) [16,17] and $Li_2Si_2O_5$ (JCPDS-04-0436) [18,19] accompanied with the diffraction patterns of α-cristobalite SiO_2 (JCPDS-39-1425) [20]. SiO_2 may increase the catalytic efficiency of various lithium silicates providing high activity as well as heterogeneity to the catalytic reaction.

Lithium impregnated arecanut husk ash catalyst showed three desorption peaks of CO_2 (Fig. 3), two of them centered at moderate basic sites in the temperature range of 300 °C to 500 °C, and one at strong basic sites in the range of 600 °C to 800 °C in the temperature programmed desorption profile. A total basicity of 0.8797 $mmolg^{-1}$ is aroused from the sum of both moderate (0.3216 $mmolg^{-1}$) and strong (0.5581 $mmolg^{-1}$) basic sites.

In the SEM image shown in Fig. 4, agglomeration of particles with macroporous morphology is observed. Macroporosity enhances the catalytic activity of the solid catalysts in the transesterification reactions [21,22].

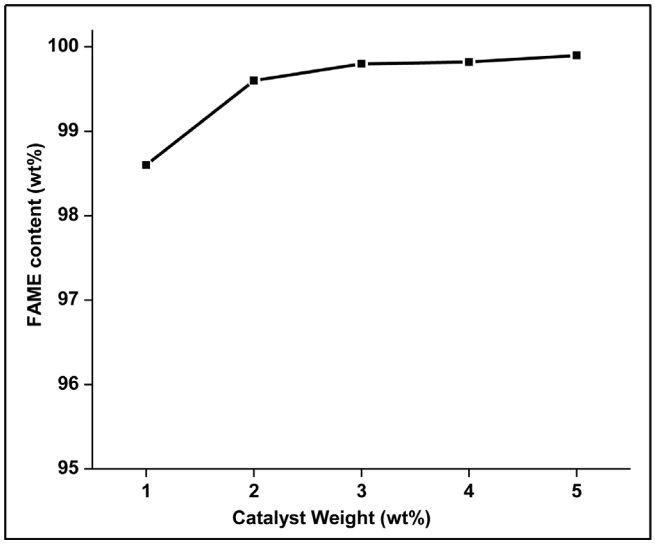

Fig. 5. Effect of catalyst dosage on FAME content under the reaction conditions of methanol to oil molar ratio of 15:1 at a reaction temperature of 65 °C for 120 min.

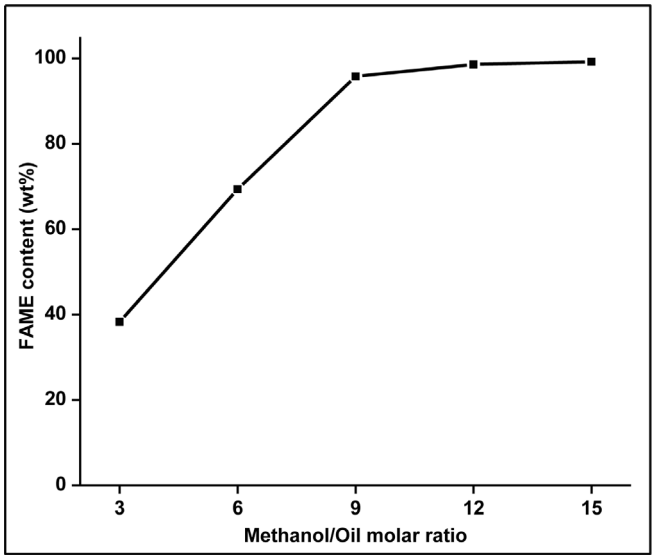

Fig. 6. Effect of methanol/oil molar ratio on FAME content under the reaction conditions of 1 wt% catalyst at a reaction temperature of 65 °C for 120 min.

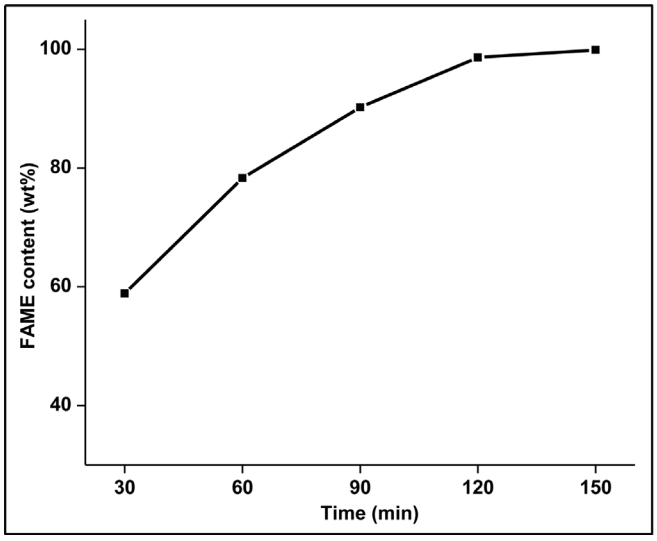

Fig. 7. Effect of reaction time on FAME content under the conditions of catalyst dosage of 1 wt%, temperature of 65 °C, methanol/oil molar ratio of 15:1.

Use of the catalyst in biodiesel production was investigated by varying the reaction conditions. The catalyst to oil weight percentage was varied from 1 wt% to 5 wt% by fixing the methanol/oil molar ratio at 15:1 at a temperature of 65 °C for 120 min reaction. Even with the use of 1 wt% of the catalyst, biodiesel meeting the international standard specifications (EN 14214) with FAME content above 96.5% is obtained. By increasing the catalyst dosage, more than 99% FAME content is resulted (Fig. 5).

The molar ratio of methanol to oil was varied from 3:1 to 15:1, keeping the reaction at a temperature of 65 °C for 120 min using 1 wt% of the catalyst. The FAME content met the EN14214 specifications at a higher methanol/oil molar ratio of 12:1 onwards (Fig. 6).

In order to study the time taken for the complete conversion of UCO into its corresponding methyl esters, the transesterification reactions were conducted at different time intervals (Fig. 7). It is found that 120 min is required for achieving the FAME content

Please cite this article as: V. Vinu and N. N. Binitha, Lithium silicate based catalysts prepared using arecanut husk ash for biodiesel production from used cooking oil, Materials Today: Proceedings, https://doi.org/10.1016/j.matpr.2020.01.210

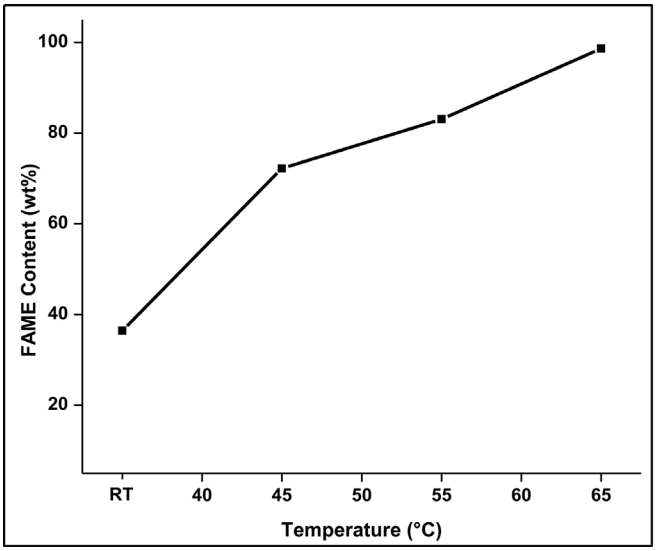

Fig. 8. Effect of reaction temperature on the FAME content under the conditions of catalyst weight 1 wt%, 15:1 methanol/oil molar ratio for 120 min reaction.

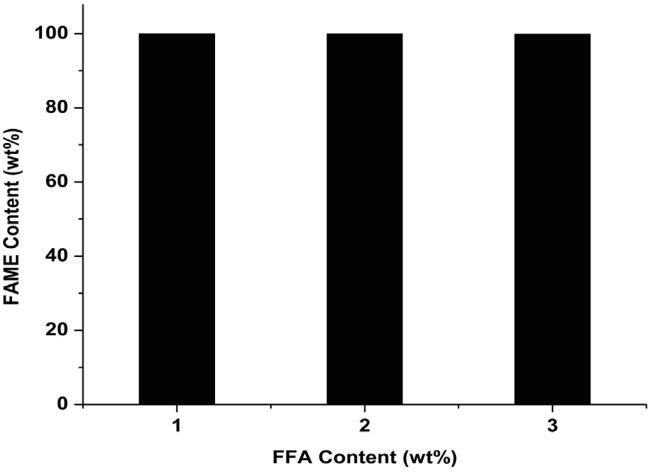

Fig. 9. Effect of FFA on the FAME content under the conditions of 3 wt% catalyst dosage/oil, at 65 °C with a methanol/oil molar ratio of 15:1 for 120 min reaction.

higher than 96.5% (fuel grade). Further increase in time to 150 min increased the conversion to 99.89%.

From the reactions carried out at different temperatures including room temperature (RT), it is found that high conversion of oil is obtained only at the reflux temperature of methanol (Fig. 8). The reaction is not so effective at lower reaction temperatures. The results are in agreement with many heterogeneous catalyzed processes [23,24].

A series of experiments were also conducted by adding oleic acid (as the free fatty acid (FFA)), into the reaction mixture in order to analyze the activity of the catalyst in the presence of FFA (Fig. 9). FAME content of above 99% was attained till 3 wt% of FFA in the oil. Thereafter, soap formation was the resultant of the reaction, creating loss of biodiesel yield. Usually a FFA content of more than 1 wt% in the feedstock will adversely affect the biodiesel production process, but some amount of FFA is inevitable in UCO feedstocks [25,26].

Water is added to the UCO before the transesterification reaction and it is seen that the catalyst was tolerant to a water content of 1 wt%. A water content of more than 0.5 wt% was tend to be

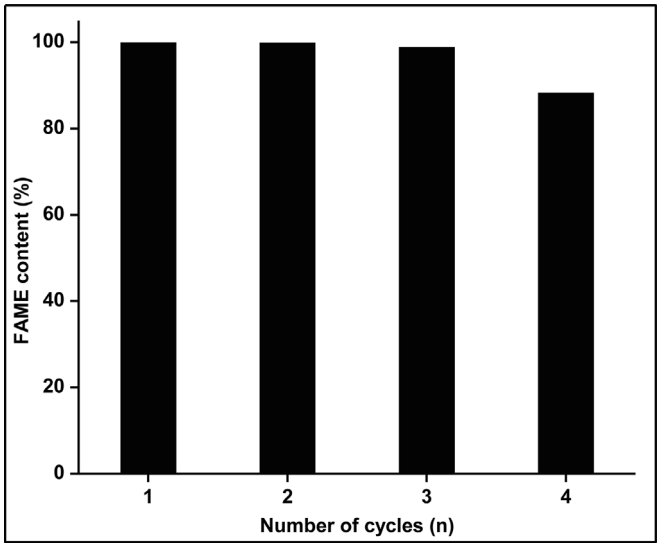

Fig. 10. Reusability result of the catalyst under the conditions of 5 wt% catalyst dosage/oil, at 65 °C with a methanol/oil molar ratio of 15:1 for 120 min reaction.

Table 1
Fuel properties of UCO biodiesel. Reaction conditions: 3 wt% catalyst dosage/oil, at 65 °C with a methanol/oil molar ratio of 15:1 for 120 min reaction.

Parameters	Unit	Limits	Standards	Biodiesel
Ester content	% m/m	96.5 min	EN 14214	99.92
Monoglyceride	% m/m	1.00 max	D 6751	0.00
Triglyceride	% m/m	0.25 max	D 6751	0.08
Free glycerol	% m/m	0.02 max	D 6751	0.00
Total glycerol	% m/m	0.38 max	D 6751	0.01
Acid value	mg KOH/g	0.80 max	D 6751	0.45
Water content	Vol.%	0.050 max	D 6751	0.00
Iodine value	mg I/100 g	120 max	D 6751	58
Viscosity	mm^2/s	1.96–6.0	D 6751	5.1
Density	kg/m^3	860–890	D 6751	868

detrimental to many homogeneous and heterogeneous catalyzed reaction processes [27,28]. Comparatively the lithium based present catalyst is water tolerant.

The reusability of the arecanut husk ash derived catalyst was investigated under the reaction conditions of 5 wt% of the catalyst at a temperature of 65 °C with a methanol to oil molar ratio of 15:1 for 120 min reaction. A FAME content of above 99% is retained till 3 consecutive cycles which decreased thereafter. The results are depicted in Fig. 10.

Fuel properties of UCO biodiesel produced over arecanut husk ash derived catalyst is determined and tabulated (Table1).

All the fuel properties are matching to the standard values as per EN 14,214 and ASTM D 6751 specifications [29,30].

4. Conclusions

In this study, arecanut husk ash is employed effectively in the preparation of a solid catalyst by lithium incorporation with the aid of a surfactant, citric acid. The active phase of the catalyst is found to be a mixture of lithium silicates as well as α-cristobalite SiO_2 and is evidently revealed from the XRD and FTIR spectral analyses. The catalyst is heterogeneous in nature and showed reusability till 3 repeated cycles of reactions. The catalyst showed tolerance towards low amount of FFA and water content in the oil feedstock. The major highlights of the present process are the first time use of arecanut husk for the solid catalyst preparation and the requirement of low amount of catalyst (1 wt%) in the transesterification reaction for biodiesel production.

Please cite this article as: V. Vinu and N. N. Binitha, Lithium silicate based catalysts prepared using arecanut husk ash for biodiesel production from used cooking oil, Materials Today: Proceedings, https://doi.org/10.1016/j.matpr.2020.01.210

CRediT authorship contribution statement

V. Vinu: Methodology, Investigation, Funding acquisition. **N.N. Binitha:** Conceptualization, Resources, Writing - original draft, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors thank Department of Science and Technology, New Delhi, India (No. DST/TSG/AF/2010/63) for the funding through a Technology System Development Programme on Alternate Fuels. SreeNeelakanta Govt. Sanskrit College Pattambi and the University of Calicut are acknowledged for providing the facilities for carrying out the research work. Vinu Vadery acknowledges higher education department, government of Kerala for providing the E-Grantz fellowship. SAIF KOCHI, India is acknowledged for XRD, FTIR spectra and SEM analysis.

References

[1] P. Rethinam, K. Sivaraman, J. Indian, Arecanut, Species Med. Plants 3 (2001) 35–50.
[2] T.V. Ramachandra, G. Kamakshi, B.V. Shruthi, Renewable Sustainable Energy Rev. 8 (2004) 1–47.
[3] N. Das, S. Singh, Concr. Res. Lett. 6 (2015) 126–135.
[4] A. Basker, P.S.S. Shabudeen, S. Daniel, P.V. Kumar, RASAYAN J. Chem. 7 (2014) 1–15.
[5] M.A. Rahman, M.A. Hasan, M.A. Salam, A. Salam, N. Siddique, A.M.S. Alam, Pak. J. Anal. Environ. Chem. 13 (2012) 137–147.
[6] B.Y.S. Kumar, IJESC 6 (2016) 2242–2247.
[7] A.S. Jadhav, G.T. Mohanraj, Carbon Sci. Tech. 8 (2016) 32–39.
[8] N. Das, S.K. Singh, AJET 4 (2016) 149–151.
[9] W.J. Xun, C.K. Tung, W.J. Syuan, W.P. Hsiang, H.S. Tsuena, C.C. Chang, Fuel Process. Technol. 104 (2012) 167–173.
[10] N. Hindryawati, G.P. Maniam, M.R. Karim, K.F. Chong, Eng. Sci. Technol. 17 (2014) 1–9.
[11] A.N. Lazarev, Vibration Spectra and Structure of Silicates, Consultants Bureau, New York, 1972.
[12] B. Zhang, M. Nieuwoudt, A.J. Easteal, J. Am. Ceram. Soc. 91 (2008) 1927–1932.
[13] J.O. Landerosa, L.M. Cruz, C.G. Yanez, H. Pfeiffer, Thermochim. Acta 515 (2011) 73–78.
[14] B. Zhang, A.J. Easteal, N.R. Edmonds, J. Am. Ceram. Soc. 90 (2007) 1592–1596.
[15] K.F. Hesse, Acta. Cryst. 33 (1977) 901–902.
[16] H. Peiffer, P. Bosch, S. Bulbulian, J. Nucl. Mater. 257 (1998) 309–317.
[17] P.V. Subha, B.N. Nair, A.P. Mohamed, G.M. Anilkumar, K.G.K. Warrier, T. Yamaguchi, U.S. Hareesh, J. Mater. Chem. A 4 (2016) 16928–16935.
[18] T. Fuss, A.M. Milankovic, C.S. Ray, C.E. Lesher, R. Youngman, D.E. Day, J. Non-Cryst. Solids 352 (2006) 4101–4111.
[19] X. Li, H. Yang, Cryst. Eng. Comm. 16 (2014) 4501–4523.
[20] A. Honglin, Y. Tang, M. Pam, S. Fleming, Opt. Express 12 (2004) 1055–1060.
[21] N.G. Ortega, E.R. Ramírez, A.S. Muñoz, A.Z. Molina, J.M. Vallejo, Catalysts 9 (2019) 403.
[22] T. Witoon, S. Bumrungsalee, P. Vathavanichkul, S. Palitsakun, M. Saisriyoot, K. Faungnawakij, Bioresour. Technol. 156 (2014) 329–334.
[23] I. Sreedhar, Y.K. Kishan, Int. J. Ind. Chem. 7 (2016) 121–129.
[24] V. Mahdavi, A. Monajemi, J. Taiwan Inst. Chem. Eng. 45 (2014) 2286–2292.
[25] V. Vadery, S.K. Cherikkallinmel, R.M. Ramakrishnan, S. Sugunan, B.N. Narayanan, Renewable Energy 141 (2019) 1042–1053.
[26] V. Vadery, B.N. Narayanan, R.M. Ramakrishnan, S.K. Cherikkallinmel, S. Sugunan, D.P. Narayanan, S. Sasidharan, Energy 70 (2014) 558–594.
[27] B. Thangaraj, P.R. Solomon, B. Muniyandi, S. Ranganathan, L. Lin, Clean Energy 3 (2019) 2–23.
[28] L. Du, S. Ding, Z. Li, Energy Convers Manage. 173 (2018) 728–734.
[29] S.P. Singh, D. Singh, Renewable Sustainable Energy Rev. 14 (2010) 200–216.
[30] G. Knothe, Fuel Process. Technol. 86 (2005) 1059–1070.

Please cite this article as: V. Vinu and N. N. Binitha, Lithium silicate based catalysts prepared using arecanut husk ash for biodiesel production from used cooking oil, Materials Today: Proceedings, https://doi.org/10.1016/j.matpr.2020.01.210