



Production of Biodiesel from Soybean Oil in Less Time and at Low Temperature

RAJAN CHOUDHARY^{1,2,3,10}, ANUJ KUMAR⁴, VIJAY NAG ELLAPANI⁴, BARUAH TRINAYAN⁴, MURUGANANDAM LOGANATHAN^{4,10}, LAKSHMI RAVY⁵, VIJAYAKUMAR VIJAYAPARTHASARATHI⁶, AMIT MAHINDRAKAR BABURAO⁷, SUBRAMANIAM SHANTHAKUMAR^{7,10}, DEEPALEKSHMI PONNAMMA^{8,10}, KISHOR KUMAR SADASIVUNI^{9,10} and SASIKUMAR SWAMIAPPAN^{6,*,10}

¹Rudolfs Cimdins Riga Biomaterials Innovations and Development Centre of RTU, Institute of General Chemical Engineering, Faculty of Materials Science and Applied Chemistry, Riga Technical University, Pulka Street 3, LV-1007 Riga, Latvia

²Baltic Biomaterials Centre of Excellence, Headquarters at Riga Technical University, Kipsala Street 6A, LV-1048 Riga, Latvia

³Center for Biomedical Engineering, National University of Science and Technology "MISiS", Moscow, 119049, Leninskiy Prospect 4, Russia

⁴Department of Chemical Engineering, School of Chemical Engineering, Vellore Institute of Technology, Vellore, India

⁵Department of Chemistry, Auxilium College, Vellore-632006, India

⁶Department of Chemistry, School of Advanced Sciences, Vellore Institute of Technology, Vellore-632014, India

⁷Department of Environmental and Water Resources Engineering, School of Civil Engineering, Vellore Institute of Technology, Vellore-632014, India

⁸Materials Science and Technology Program, College of Arts and Sciences, Qatar University, P O Box 2713, Doha, Qatar

⁹Center for Advanced Materials, Qatar University, P O Box 2713, Doha, Qatar

*Corresponding author: E-mail: ssasikumar@vit.ac.in

Received: 21 February 2022;

Accepted: 27 June 2022;

Published online: 18 July 2022;

AJC-20905

The heterogeneous catalyst plays an important role in the production of biodiesel at industrial level. In present work, the utilization of wollastonite as a heterogeneous catalyst is attempted to explore its non-biomedical application. Wollastonite was synthesized by using the auto combustion method and L-alanine was used as a fuel for combustion. The X-ray diffraction pattern reveals the phase purity of wollastonite. The Fourier transform infrared spectra of the calcined precursor show the presence of characteristics functional groups in wollastonite. To evaluate the catalytic ability of the prepared wollastonite, transesterification reaction of soybean oil with methanol was performed. Following the reaction, the biodiesel, glycerol and the catalyst were separated by centrifugation. Optimization of the percentage of catalyst used in biodiesel production was done by using various quantities of catalyst during the transesterification reaction and subjecting the produced biodiesel to gas chromatography. It can be concluded that combined alkali metal oxide and silica in wollastonite has assisted in production of biodiesel (82.6%) in a less time and at a low temperature.

Keywords: Wollastonite, Heterogeneous catalyst, Biodiesel, Vegetable oil, Transesterification.

INTRODUCTION

There has been an exponential increase in the demand of energy sector and hence an over exploitation of diesel fuels is practiced. This has led to an alarming rate of increasing environmental problems and reduction in fossil fuel reserves [1]. Due to the depletion of major onshore oil fields and increase in oil prices, there is a huge demand for the human race to focus on the production of environmental friendly green fuels instead of the conventional fuels that would promise a safe and clean future [2]. Biodiesel is such an example of alternate renewable liquid fuel that can help to compensate for the increasing demand

of diesel fuels [3,4]. It is an ecological fuel and refers to a vegetable oil or animal fat-based diesel fuel consisting of long-chain alkyl esters. Biodiesels have several benefits over diesel fuel derived from petroleum deposits. It is safer, non-toxic, biodegradable and contains a minimal amount of sulfur and sulfur-based compounds. Biodiesel is more oxygenated than conventional mineral diesel, burning more efficiently in the engine, and thus resulting in less emission of hydrocarbons, CO₂ and particulates. The presence of oxygen also increases the lubricity of the fuel, extending the lifetime of a diesel engine. Furthermore, the biodiesel has high cetane number and flash point in comparison to diesel [5].

This is an open access journal, and articles are distributed under the terms of the Attribution 4.0 International (CC BY 4.0) License. This license lets others distribute, remix, tweak, and build upon your work, even commercially, as long as they credit the author for the original creation. You must give appropriate credit, provide a link to the license, and indicate if changes were made.

Biodiesel which consists of free acid methyl esters (FAME) is prepared by transesterification of vegetable oil with methanol as a solvent [6]. Transesterification reactions can also be performed using acid catalysts such as hydrochloric, phosphoric, sulfonic or sulfuric acids [7,8] such as metal hydroxides [9], metal alkoxides [10], alkaline earth oxides [11] or hydrotalcites [12]. Alternatively, if heterogeneous catalysts are used, the neutralization and the washing steps are reduced, which significantly reduces the downstream purification process [13]. Heterogeneous catalysts render non-polluting byproducts, can minimize corrosion and environmental problems and also it can be easily removed from the reaction medium due to their immiscibility with either reactants or products.

In US and Europe, the biodiesel is produced from edible oil such as sunflower oil, soybean oil whereas in India biodiesel is prepared from non-edible oil such as jatropha and karanja. Non-edible oils consist of high fatty acid contents, which lead to the loss of oil due to soap formation. Due to these problems, alternate methods such as supercritical process and enzymatic process have been reported. The supercritical process is fast and carried without a catalyst but due to the requirement of high temperature and pressure, this process need higher capital cost hence this limits its commercial utilization. In enzymatic process, the biodiesel is produced in high yield at moderate temperature, however the enzyme cost and its deactivation due to feeding impurities create obstruction for commercializing this process [14].

Most of the commercial biodiesel production is carried out using homogeneous catalyst through transesterification reaction where vegetable oil in the presence of sodium hydroxide and sodium methoxide reacts with methanol. The cost of production for the biodiesel produced using homogeneous catalyst is more compared to the petroleum-based fuel as the former requires lengthy purification and distillation process for separating glycerol from the biodiesel [15]. Homogeneous catalysts form soap during transesterification reaction which leads to the problem of product separation again [16].

Heterogeneous catalysts can remove saponification of biodiesel and can be easily separated from various products [17] as it remains in a different phase from that of the reactants and product phase [18,19]. In heterogeneous catalytic transesterification there is no need of washing the product due to the saponification reaction and so there will be very less wastage of water, leading to much easier separation of biodiesel from glycerol and the catalyst. Also, the catalyst can be easily recycled by calcining after separation in order to regain its catalytic activity. By all these advantages heterogeneous catalytic reaction comes under green technology [20,21]. The heterogeneous catalytic transesterification converts triglycerides into biodiesel in an economical way due to the reusability of catalyst both in batch as well as continuous processes [22-24].

A large number of heterogeneous catalysts such as acid heterogeneous catalysts [25-27], carbon based heterogeneous catalysts [28,29], alkali metal oxide and derivatives [30-32], alkaline earth metal and derivatives [33-35] are found to be used for the production of biodiesel.

The present work discusses the synthesis of wollastonite and its application as a heterogeneous catalyst for the production

of biodiesel through transesterification. The combustion method was employed to prepare the catalyst as it is expected to result in the smaller particles. The quantity of catalyst added in the process was optimized in order to achieve desirable transesterification reaction. The combination of wollastonite as a catalyst and soybean oil as the source is used here for the first time.

EXPERIMENTAL

Preparation of catalyst: Calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (S.D. Fine AR), tetraethyl orthosilicate (TEOS, $\text{SiC}_8\text{H}_{20}\text{O}_4$) (Acros organics 98%), L-alanine ($\text{C}_3\text{H}_7\text{NO}_2$), nitric acid and methanol were used. Commercial soybean oil were purchased from the local market.

Calcium nitrate (23.6 g) was added in distilled water to make 100 mL of 1 M solution. Similarly, 8.909 g of L-alanine was added in distilled water to make 100 mL of 1M solution. Each of the prepared calcium nitrate and L-alanine solution (20 mL) were added to 4.5 mL TEOS and the pH of the solution was adjusted to 1 by adding nitric acid in order to increase the rate of the reaction. To disperse the solution properly and to form a gel phase, it was magnetically stirred for 40 h. The solution was further kept in a hot air oven for four consecutive days so that water and all other volatile components got evaporated and a dried gel was formed. The ignition temperature of L-alanine was reported as 314 °C [36]. In order to promote effective combustion reaction between fuel (reducing agent) and nitrates (oxidizing agent), an additional temperature of about 86 °C was maintained to the reaction mixture. Hence, the combustion of this dried gel was carried out by subjecting it to a temperature of 400 °C in a muffle furnace for 3 h. The precursor formed was light brown in colour and was finally calcined at 900 °C for 6 h and the resultant powder was analyzed by powder X-ray diffractometer to check for phase purity of the wollastonite.

Transesterification of soybean oil using wollastonite as heterogeneous catalyst: Wollastonite (200 mg) was added to 24 mL of methanol in a two-necked round bottomed flask and stirred for 20 min to disperse the wollastonite particles uniformly. Soybean oil (1.0 g) was then added to the prepared colloidal solution and stirred for 1 h while heating at 65 °C. Biodiesel formed and the catalyst were separated from the methanol by centrifugation.

The concentration of the analytes of the produced biodiesel was determined by using gas chromatography. The same procedure was carried out by varying the weight of the catalyst by 50 mg, 100 mg and 150 mg for transesterification of soybean oil.

Characterization: The functional groups present in the wollastonite were identified using FT-IR (JASCO 400) and the phase identification was done by Bruker D8 Advance X-ray diffractometer using, $\text{CuK}\alpha$ (1.5406Å), Ni-filtered radiation. The biodiesel produced was analyzed by means of gas chromatography (Clarus 680, Perkin-Elmer).

RESULTS AND DISCUSSION

Generally, either the alkali metal oxides or silica will be employed as a catalyst in the biodiesel preparation. But in present work, both elements were incorporated in one compound and

tried as a catalyst. The catalyst was prepared by auto combustion synthesis as it is a well-known method for the preparation of particles with smaller size and hence expected to have higher catalytic activity. L-alanine was used as a fuel as the heat evolution during combustion will be lesser than the carboxylic acids due to the presence of nitrogen atom in the molecule.

The mechanism of gel formation in the preparation of wollastonite involves three steps. The first step involves the mixing of metal ions, fuel and oxidizer uniformly throughout the solution in which the fuel plays a dual role as it prevents the precipitation of metal ions by means of complexation and also forms a polymeric network with the other constituents present in the solution. Nitric acid also plays a dual role as it acts as an oxidizer in the combustion reaction and in addition it acts as a catalyst in the hydrolysis of tetraethyl orthosilicate into silanol and ethanol. The second step involves the reaction between silanol and calcium ions whereas ethanol and L-alanine molecules undergo a polycondensation reaction and result in the formation of a thick gel. In the third step, the polymer network undergoes a vigorous combustion reaction in which the nitrate ions from nitric acid and calcium nitrate acts as oxidizers. The resultant product was white in color and the color of the precursor indicates the absence of carbonaceous and nitrate groups. Generally, the precursors of carboxylic acid fuels will be black in color due to the presence of carbonaceous product but L-alanine is an amino acid hence it didn't form any carbonaceous products in the precursor. The precursor was calcined at 900 °C for 6 h and the resultant product was found to be white in color.

FT-IR studies of wollastonite: The FT-IR spectrum of the wollastonite calcined at 900 °C shows the presence of bending modes of Si–O–Si and O–Si–O bonds at 460 cm⁻¹, stretching modes of O–Si–O bonds at 846 cm⁻¹, Si–O–Ca bonds containing non-bridging oxygen at 950 cm⁻¹ (Fig. 1). The symmetric stretching vibrations of Si–O–Si bonds were observed at 1078 cm⁻¹. However, the absorption bands present in the range of 1170–750 cm⁻¹ are due to O–Si–O vibration and absorption in the range 650–500 cm⁻¹ is due to Si–O vibration. A decrease of the band at 3419 cm⁻¹ with calcination temperature could be attributed to the release of water molecules trapped inside the solid matrix. These wavenumbers were found in agreement with the previous work [37].

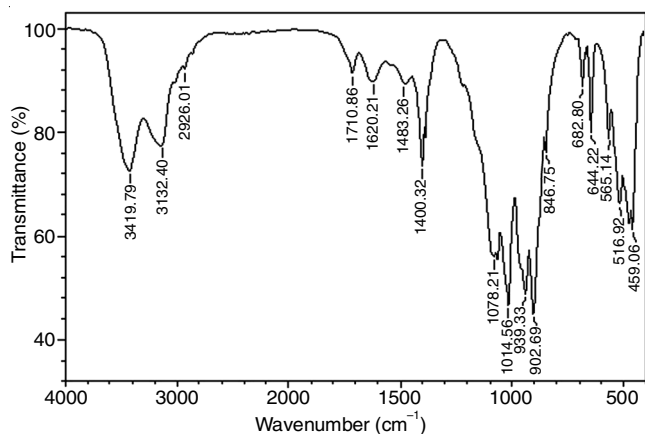


Fig. 1. FT-IR spectra of wollastonite calcined at 900 °C

XRD studies of wollastonite: The XRD pattern of wollastonite powder calcined at 900 °C for 6 h shows the formation of single phase wollastonite (Fig. 2) and matches with the standard JCPDS wollastonite pattern (043-1460). The absence of characteristic peaks of silica and calcium carbonate in FT-IR is confirmed by the XRD pattern, which shows the absence of any secondary phases. The background of XRD pattern indicates the slightly amorphous nature of the wollastonite particles.

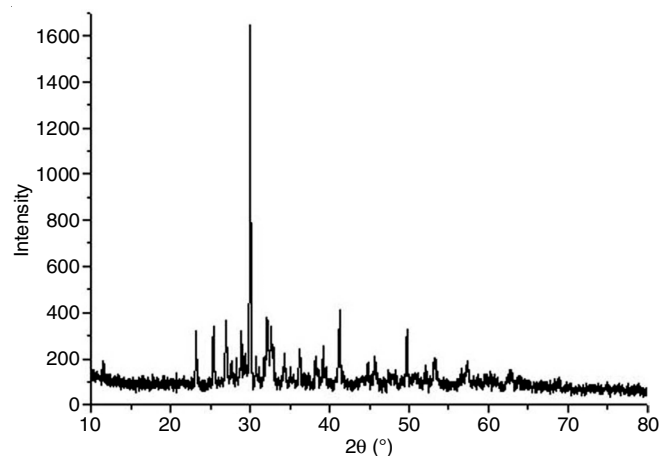


Fig. 2. XRD pattern of wollastonite prepared by sol-gel combustion method

Gas-chromatography of biodiesel: The well-characterized sample of wollastonite was subjected as a catalyst towards the transesterification of soybean oil in presence of methanol to produce biodiesel. The catalyst used was optimized by varying the amount of catalysts such as 50 mg, 100 mg, 150 mg and 200 mg and the transesterification reaction was carried out and the analysis of the product was done by gas chromatography.

GC-MS analysis of the biodiesel obtained by varying the amount of catalyst shows the presence of same constituents with different yield. The gas chromatogram (Fig. 3a) observed for 50 mg catalyst shows very less yield of FAMES when compared with the chromatograms obtained for the higher amount of catalysts. The mass spectra of the chromatogram peaks were matched with the standard library database and it shows the presence of 2,2-dimethoxybutane as a major constituent and the minor constituents present in the sample is found to be methyl 13,14-octadecadienoate and 1-pentatriacontanol. The yield of FAME was found to be 6.3%.

When the amount of catalyst added was increased from 50 mg to 100 mg, the percentage of FAMES present in the biodiesel is found to increase exponentially. The mass spectra of the chromatogram peaks (Fig. 3b) matched with the standard library database and shows the presence of 2-methoxy-3-methyl butyric acid and methyl 13,14-octadecadienoate as the major constituents and 1-pentatriacontanol, methyl 8-methyl-nonanoate and 25-methyl heptacosanoic acid as the minor phases. The yield of FAME was found to be 65.9 %.

When the amount of catalyst added is further increased to 150 mg, the percentage of smaller methyl esters came down drastically. The mass spectra of the chromatogram peaks (Fig. 3c) matched with the standard library database shows the

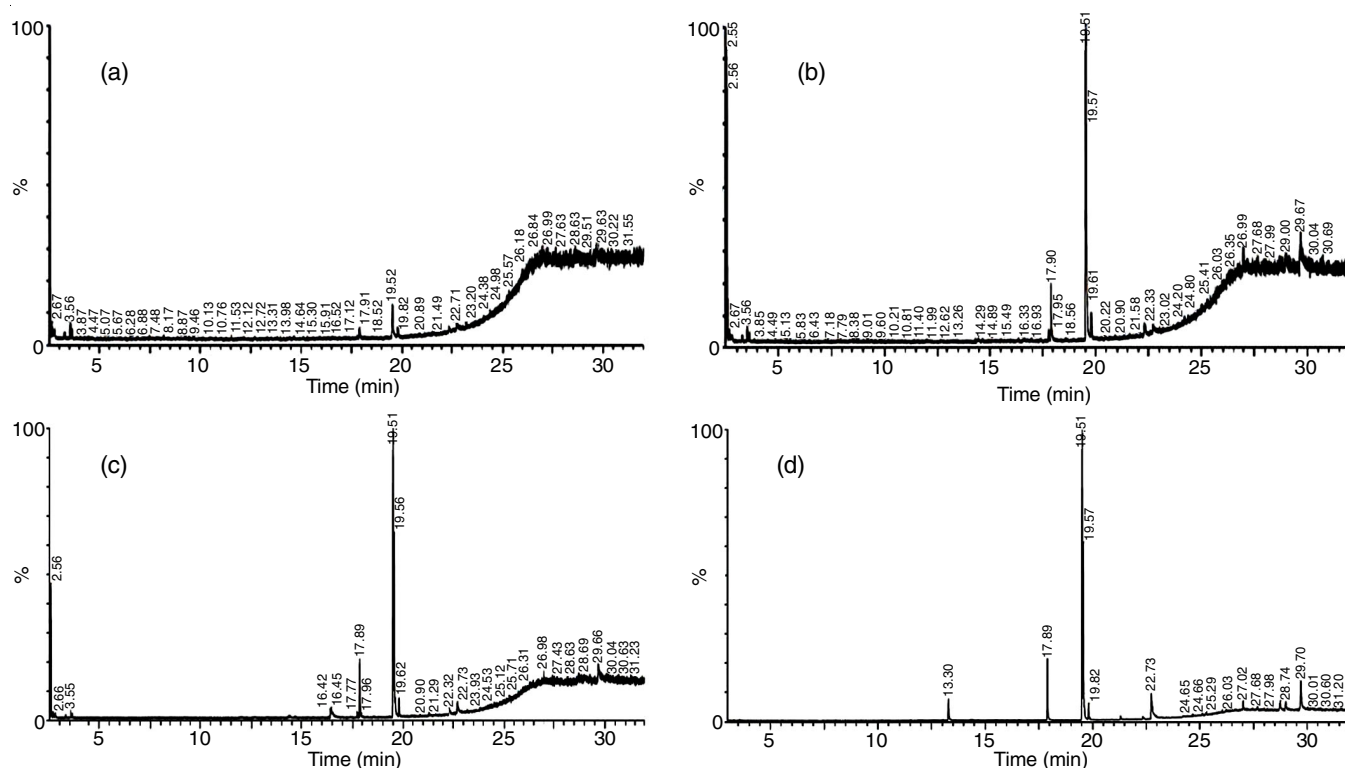


Fig. 3. Gas chromatograms of biodiesel obtained with (a) 50 mg wollastonite (b) 100 mg wollastonite (c) 150 mg wollastonite and (d) 200 mg wollastonite

presence of 4-hydroxy-2-butenic acid, methyl 11,14-octadecadienoate and methyl 13-octadecenoate as the major constituents and the minor phases identified were 10,13-dimethyl-tetradecanoic acid and 25-methyl heptacosanoic acid. Here the yield of FAME was about 72.1%.

Interestingly the smaller methyl esters vanished from the product when the amount of catalyst added was increased to 200 mg. The mass spectra of the chromatogram peaks (Fig. 3d) matched with the standard library database shows the presence of 10,13-dimethyl tetradecanoic acid, methyl 13-octadecenoate and methyl 11,14-octadecadienoate as the major constituents and N-propyl 11-octadecenoate and dihydrotachysterol were identified as minor phases. At this level, the yield of FAME was 82.6%.

The amount of catalyst added was not increased further as the product showed maximum heterogeneity in terms of its chemical constituents, which may affect the combustion process. From the observation, it is found that by adding 150 mg of catalyst

the biodiesel prepared will have maximum homogeneity and reasonable FAME. Several catalysts have been explored for the transesterification of soybean oil as shown in Table-1 [38-44]. It can be observed that combined alkali metal oxide and silica in same material *i.e.* wollastonite has assisted in production of biodiesel (82.6%) in a less time and at a low temperature when compared to these findings.

Conclusion

Single phasic wollastonite was synthesized by auto combustion using L-alanine as the fuel. By varying the amount of catalyst added in the preparation of biodiesel, the resultant chemical composition got varied. Percentage of the smaller methyl esters decreased with the increase in the quantity of the catalyst. Free acid methyl esters (FAMES) increased with the increase in the amount of catalyst added during the preparation of biodiesel in addition to the increase in heterogeneity of the constituents of biodiesel with the increase in catalyst

TABLE-1
TRANSESTERIFICATION OF SOYBEAN OIL UNDER DIFFERENT REACTION CONDITIONS FOR THE PRODUCTION OF BIODIESEL

Sample oil	Catalyst	Temperature (°C)	Time (h)	Yield (%)	Ref.
Soybean oil	CaO	65	3	95.0	[38]
Soybean oil	CaO	Reflux temperature	2	93.0	[39]
Soybean oil	K ₂ CO ₃ supported on MgO	70	2	99.0	[40]
Soybean oil	KI loaded mesoporous silica	70	8	90.0	[41]
Soybean oil	Tetramethylguanidine covalently bonded onto silica gel surface	80	3	86.0	[42]
Soybean oil	Potassium Methoxide	80	15 min	91.0	[43]
Soybean oil	Ca _{0.5} K _{0.5} TiCu _{0.25} O ₃	78	8	97.0	[44]
Soybean oil	Wollastonite (CaSiO ₃)	65	1	82.6	Present study

quantity. It is concluded that by varying the amount of catalyst percentage, FAME and heterogeneity of biodiesel can be balanced.

ACKNOWLEDGEMENTS

The authors present their sincere thanks to VIT Management for providing the necessary help to carry out this research. The authors gratefully acknowledge the financial support from the European Union's Horizon 2020 research and innovation program under the grant agreement No. 857287. The authors acknowledge the Ministry of Science and Higher Education of the Russian Federation in the framework of Increase Competitiveness Program of NUST "MISIS".

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

- M. Ghiaci, B. Aghabarari and A. Gil, *Fuel*, **90**, 3382 (2011); <https://doi.org/10.1016/j.fuel.2011.04.008>
- A. Ghaderi, *J. Petrol. Sci. Eng.*, **98-99**, 19 (2012); <https://doi.org/10.1016/j.petrol.2012.08.016>
- A.P.S. Chouhan and A.K. Sarma, *Renew. Sustain. Energy Rev.*, **15**, 4378 (2011); <https://doi.org/10.1016/j.rser.2011.07.112>
- N. Tippayawong, A. Promwungkwa and P. Rerkkriangkrai, *Iran. J. Sci. Technol. Tran. B*, **34**, 167 (2010).
- J.X. Wang, K.T. Chen, J.S. Wu, P.H. Wang, S.T. Huang and C.C. Chen, *Fuel Process. Technol.*, **104**, 167 (2012); <https://doi.org/10.1016/j.fuproc.2012.05.009>
- M. Kouzu and J. Hidaka, *Fuel*, **93**, 1 (2012); <https://doi.org/10.1016/j.fuel.2011.09.015>
- J. Otera, *Chem. Rev.*, **93**, 1449 (1993); <https://doi.org/10.1021/cr00020a004>
- J.M. Marchetti and A.F. Errazu, *Biomass Bioener.*, **32**, 892 (2008); <https://doi.org/10.1016/j.biombioe.2008.01.001>
- B. Freedman, R.O. Butterfield and E.H. Pryde, *J. Am. Oil Chem. Soc.*, **63**, 1375 (1986); <https://doi.org/10.1007/BF02679606>
- J. Schmidt, D. Reusch, K. Elgeti and R. Schomacker, *Chem. Ingen. Tech.*, **71**, 704 (1999); <https://doi.org/10.1002/cite.330710711>
- S. Gryglewicz, *Appl. Catal. A Gen.*, **192**, 23 (2000); [https://doi.org/10.1016/S0926-860X\(99\)00337-3](https://doi.org/10.1016/S0926-860X(99)00337-3)
- A. Corma, S. Iborra, S. Miquel and J. Primo, *J. Catal.*, **173**, 315 (1998); <https://doi.org/10.1006/jcat.1997.1930>
- K.G. Georgogianni, A.P. Katsoulidis, P.J. Pomonis and M.G. Kontominas, *Fuel Process. Technol.*, **90**, 671 (2009); <https://doi.org/10.1016/j.fuproc.2008.12.004>
- S. Semwal, A.K. Arora, R.P. Badoni and D.K. Tuli, *Bioresour. Technol.*, **102**, 2151 (2011); <https://doi.org/10.1016/j.biortech.2010.10.080>
- J. Ji, J. Wang, Y. Li, Y. Yu and Z. Xu, *Ultrasonics*, **44**, 411 (2006); <https://doi.org/10.1016/j.ultras.2006.05.020>
- S. Nakagaki, A. Bail, V.C. Santos, V.H.R. Souza, H. Vrabel, F.S. Nunes and L.P. Ramos, *Appl. Catal. A Gen.*, **351**, 267 (2008); <https://doi.org/10.1016/j.apcata.2008.09.026>
- Y.D. Long, F. Guo, Z. Fang, X.F. Tian, L.Q. Jiang and F. Zhang, *Bioresour. Technol.*, **102**, 6884 (2011); <https://doi.org/10.1016/j.biortech.2011.04.007>
- Z. Helwani, M.R. Othman, N. Aziz, J. Kim and W.J.N. Fernando, *Appl. Catal. A Gen.*, **363**, 1 (2009); <https://doi.org/10.1016/j.apcata.2009.05.021>
- M. Zabeti, W.M.A. Wan Daud and M.K. Aroua, *Fuel Process. Technol.*, **90**, 770 (2009); <https://doi.org/10.1016/j.fuproc.2009.03.010>
- J.S. Lee and S. Saka, *Bioresour. Technol.*, **101**, 7191 (2010); <https://doi.org/10.1016/j.biortech.2010.04.071>
- A.K. Sarma, J.K. Sarmah, L. Barbora, P. Kalita, S. Chatterjee, P. Mahanta and P. Goswami, *Recent Pat. Eng.*, **2**, 47 (2008); <https://doi.org/10.2174/187221208783478552>
- J.M. Marchetti and A.F. Errazu, *Fuel*, **87**, 3477 (2008); <https://doi.org/10.1016/j.fuel.2008.05.011>
- A. West, D. Posarac and N. Ellis, *Bioresour. Technol.*, **99**, 6587 (2008); <https://doi.org/10.1016/j.biortech.2007.11.046>
- T. Sakai, A. Kawashima and T. Koshikawa, *Bioresour. Technol.*, **100**, 3268 (2009); <https://doi.org/10.1016/j.biortech.2009.02.010>
- Y.M. Park, S. Chung, H.J. Eom, K. Lee and K.-Y. Lee, *Bioresour. Technol.*, **101**, 6589 (2010); <https://doi.org/10.1016/j.biortech.2010.03.109>
- G. Perin, G. Alvaro, E. Westphal, L.H. Viana, R.G. Jacob, E.J. Lenardao and M.G.M. D'Oca, *Fuel*, **87**, 2838 (2008); <https://doi.org/10.1016/j.fuel.2008.01.018>
- R.A. Holser, K.M. Doll and S.Z. Erhan, *Fuel*, **85**, 393 (2006); <https://doi.org/10.1016/j.fuel.2005.07.018>
- S. Baroutian, M.K. Aroua, A.A.A. Raman and N.M.N. Sulaiman, *Fuel Process. Technol.*, **91**, 1378 (2010); <https://doi.org/10.1016/j.fuproc.2010.05.009>
- Q. Shu, J. Gao, Z. Nawaz, Y. Liao, D. Wang and J. Wang, *Appl. Energy*, **87**, 2589 (2010); <https://doi.org/10.1016/j.apenergy.2010.03.024>
- W. Xie, H. Peng and L. Chen, *J. Mol. Catal. Chem.*, **246**, 24 (2006); <https://doi.org/10.1016/j.molcata.2005.10.008>
- D. Fabbri, V. Bevon, M. Notari and F. Rivetti, *Fuel*, **86**, 690 (2007); <https://doi.org/10.1016/j.fuel.2006.09.003>
- G. Arzamendi, I. Campo, E. Arguñeira, M. Sánchez, M. Montes and L.M. Gandía, *Chem. Eng. J.*, **134**, 123 (2007); <https://doi.org/10.1016/j.cej.2007.03.049>
- H. Mootabadi, B. Salamatina, S. Bhatia and A.Z. Abdullah, *Fuel*, **89**, 1818 (2010); <https://doi.org/10.1016/j.fuel.2009.12.023>
- D.J. Vujicic, D. Comic, A. Zarubica, R. Micic and G. Boskovic, *Fuel*, **89**, 2054 (2010); <https://doi.org/10.1016/j.fuel.2009.11.043>
- S.J. Yoo, H. Lee, B. Veriansyah, J. Kim, J.-D. Kim and Y.-W. Lee, *Bioresour. Technol.*, **101**, 8686 (2010); <https://doi.org/10.1016/j.biortech.2010.06.073>
- A. Sutka and G. Mezinskas, *Front. Mater. Sci.*, **6**, 128 (2012); <https://doi.org/10.1007/s11706-012-0167-3>
- R. Choudhary, S.K. Venkatraman, I. Bulygina, F. Senatov, S. Kaloshkin, N. Anisimova, M. Kiselevskiy, M. Knyazeva, D. Kukui, F. Walther and S. Swamiappan, *Mater. Sci. Eng. C*, **118**, 111456 (2021); <https://doi.org/10.1016/j.msec.2020.111456>
- X. Liu, H. He, Y. Wang, S. Zhu and X. Piao, *Fuel*, **87**, 216 (2008); <https://doi.org/10.1016/j.fuel.2007.04.013>
- M. Kouzu, T. Kasuno, M. Tajika, S. Yamanaka and J. Hidaka, *Appl. Catal. A Gen.*, **334**, 357 (2008); <https://doi.org/10.1016/j.apcata.2007.10.023>
- X. Liang, S. Gao, H. Wu and J. Yang, *Fuel Process. Technol.*, **90**, 701 (2009); <https://doi.org/10.1016/j.fuproc.2008.12.012>
- C. Samart, P. Sreetongkittikul and C. Sookman, *Fuel Process. Technol.*, **90**, 922 (2009); <https://doi.org/10.1016/j.fuproc.2009.03.017>
- E.A. Faria, H.F. Ramalho, J.S. Marques, P.A.Z. Suarez and A.G.S. Prado, *Appl. Catal. A Gen.*, **338**, 72 (2008); <https://doi.org/10.1016/j.apcata.2007.12.021>
- D. Celante, J.V.D. Schenkel and F. de Castilhos, *Fuel*, **212**, 101 (2018); <https://doi.org/10.1016/j.fuel.2017.10.040>
- F. Storti, M.A.L. Nobre and S. Lanfredi, *Mater. Sci. Forum*, **912**, 207 (2018); <https://doi.org/10.4028/www.scientific.net/MSF.912.207>