Biocatalysis and Agricultural Biotechnology 20 (2019) 101185

Contents lists available at ScienceDirect

Biocatalysis and Agricultural Biotechnology

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

An assessment study of using *Turel Kongreng* (river mussels) as a source of heterogeneous catalyst for biofuel production

Thokchom Subhaschandra Singh, Tikendra Nath Verma*

Department of Mechanical Engineering, National Institute of Technology Manipur, Langol, Imphal West, Manipur, India

ARTICLE INFO

Keywords:
Catalyst
Base catalyst
Heterogeneous
Mussels

ABSTRACT

The present study is an assessment of using *Turel Kongreng* (river mussels) as a source of heterogenous catalyst in biodiesel production. After the calcination is performed at 800 °C for 1 h, the calcinated samples were subjected to characterization techniques such as X-ray dispersive analysis, Fourier transform infra-red spectroscopy, Scanning electron microscopy and Energy dispersive x-ray analysis. The characterizations showed excellent formation of calcium oxide (CaO) and the same is compared with CaO synthesized from other sources. A confirmation test using the newly synthesized CaO is conducted using waste cooking oil with catalyst loading of 10% (wt.%), alcohol to oil ratio of 10:1, reaction temperature of 75 °C and a reaction time of 60 mins. The study showed a conversion rate of 91.04%, which is well within the high conversion band among all other catalyst materials.

1. Introduction

In the process of biodiesel production through transesterification, many researchers in the past have used both acid and base materials as catalyst. The presence of catalyst during the reaction helps in accelerating the conversion of esters from the oil sample. Although researchers have declared that acid transesterification has claimed more yield, this is hindered by the higher cost of the catalyst. The sudden boost in the biofuel research is primarily due to the ever-increasing requirement of diesel fuel and the inability to meet the demands. Also, researchers have shown that the pollution level has been increasing in the ecosystem due to accumulation of many commercial vehicles (Singh et al., 2018; Rajak and Verma, 2017; Toma et al., 2019; Zeng et al., 2019). Although researches have claimed to produce biodiesel from extensive sources including vegetable edible/non-edible oils, waste fats of animals and fish, tyre pyrolysis, alcohols, waste cooking oils, microalgae etc., commercialization of the same is still a distant dream (Hurdogan et al., 2017;Rajak and Verma, 2018a; Singh and Verma, 2019b; Moazeni et al., 2019; Devaraj et al., 2015; Rajak and Verma, 2019d; Rajak and Verma, 2018f; Garcia et al., 2013; Vassilev and Vassileva, 2016; Rajak et al., 2018c, 2019a, 2019b; Rajak et al., 2019c; Shrivastava and Verma, 2019). The production of biodiesel is normally initiated by sourcing the raw material, cleaning/filtering to remove any dirt and finally the transesterification process. The process of transesterification is normally carried out to reduce some of the properties such as density & viscosity of the raw material. A catalyst, which can either be acid or base, is normally used during the process for increasing the activity of separating the esters from the raw oil. Many researchers have already identified various kind of materials which has the potential to use as base heterogeneous catalyst, namely chicken egg shells, duck egg shells, ostrich eggs, river snail etc. (Tan et al., 2017; Latchubugata et al., 2018; Niju et al., 2014; Kaewdaeng et al., 2017). The choice of raw material for use as catalyst include ease in availability, cheap to produce and source, which can otherwise pollute the environment as waste material etc. The past researchers have claimed to produce more ester conversion yield using the heterogeneous catalyst, as compared to homogeneous ones (Vahabzadeh et al., 2010).

Scallop shells has been claimed to be a good source for use as heterogeneous catalyst during biodiesel production with a conversion rate of 95.44% in using palm oil as source oil (Buasri et al., 2014). Morphology of catalyst has been well defined by researchers and can be substantially used as reference for future works. Commonly sourced materials such as egg shells were proven by researchers as a promising source for heterogeneous catalyst (Zaki et al., 2006; Pandit and Fulekar, 2017). Oils such as third generation microalgae has been widely studied due to its increasing performance and capability to reduce emissions (Salam and Verma, 2019; Rajak et al., 2018d, 2018e). Therefore, transesterification of such third-generation biofuels using renewable catalyst will reduce cost and paves way for sustainable production. High density source oil such as waste cooking oil requires more amount

---

* Corresponding author.
E-mail addresses: tikendra.me@nitmanipur.ac.in, verma.tikks@gmail.com (T.N. Verma).

https://doi.org/10.1016/j.bcab.2019.101185
Received 2 May 2019; Received in revised form 27 May 2019; Accepted 29 May 2019

of catalyst for transesterification and therefore usage of commercial catalyst such as KOH/NaOH will promote higher cost of the final product (Singh and Verma, 2019a; Singh et al., 2019). Hence, it is very much essential to produce cheaper and environment friendly catalyst. Other researchers have also claimed usage of environmentally friendly biomass derived catalyst. Also, researchers have mentioned that catalyst must be environmentally friendly, cheap and easily to produce so as to reduce the final output biofuel (Hanis et al., 2016; Semwal et al., 2011; Beygmoradi and Homaei, 2017; Gupta et al., 2016; Mathimani and Pugazhendhi, 2018; Mumtaz et al., 2016; Melchias et al., 2018).

Therefore, in light of the above-mentioned facts, the source of material which has the potential to use as catalyst must be sourced from waste material and that it should not cause damage to the environment. Sourcing of cheap materials for catalyst production also results in lower cost of biofuel and therefore encouraging the end users to shift from fossil fuels to a more sustainable biofuel. A locally available source of waste material- *Turel Kongreng* (river mussels) is chosen for the present study due to its high-volume production and ease of availability of discarded shells. After characterization of the synthesized CaO, it is then used for transesterification of waste cooking oil. The result of the ester conversion is compared with other researchers.

2. Material and methods

2.1. Collection of material and preparation of catalyst

The *Turel Kongreng* (river mussels) were a local delicacy in the North-Eastern part of India. Therefore, in the state of Manipur also, they were harvested in local farms and in lakes. The same is also widely harvested from rivers of Manipur namely, Imphal river & Iril river. Fig. 1 shows the Waithou local market, Manipur, India (24.644 °N & 93.999 °E, 787 m above sea level) where the river mussels were purchased for the present study. 1 kg of *Turel Kongreng* yields about roughly 700–800 g m of discarded shells after complete removal of flesh from the body.

The collected samples were heated in an open bowl filled with water to facilitate opening of shells. The process lasted about 40–50 min. The meat is removed, and the shells were rinsed again with water to remove any dirt particles from the samples. The samples were dried inside an electric oven for about 120–180 min to ensure that the samples are fully dried, and no moisture is present on the samples (Singh and Verma, 2019a; Singh N. R. et al., 2019; Buasri et al., 2014). The presence of moisture in the sample will hinder the calcination process by agglomerating the carbon and hydrogen and therefore lowered the formation of CaO within the sample. The samples are loaded onto an electric weighing machine and a batch of 500 g m were taken into a muffle furnace for calcination process. Past researchers have claimed that 800 °C is suitable for calcination of samples (Singh and Verma, 2019a; Singh N. R. et al., 2019). Therefore, the samples were kept into the furnace at 800 °C for about an hour. The samples were then taken out and kept into an insulated electric oven for 4–5 h (Singh and Verma, 2019a; Singh N. R. et al., 2019; Buasri et al., 2014). They were then crushed into fine powder using a mortar.

Fig. 1. *Turel Kongreng* (river mussels) sourced from Waithou market, Manipur, India.

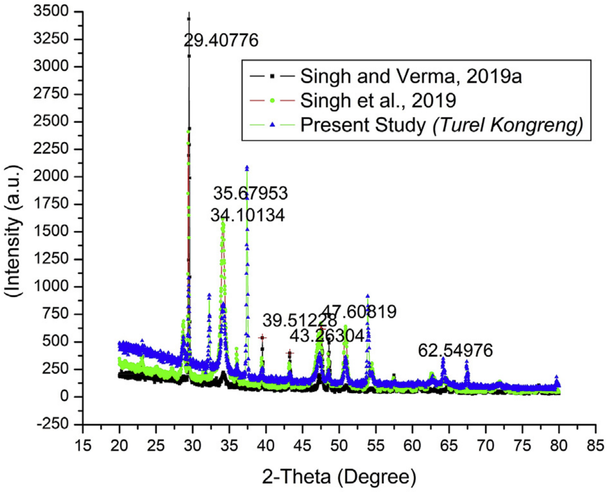

Fig. 2. XRD patterns of the present study and comparison with other researchers (Singh and Verma, 2019a; Singh et al., 2019).

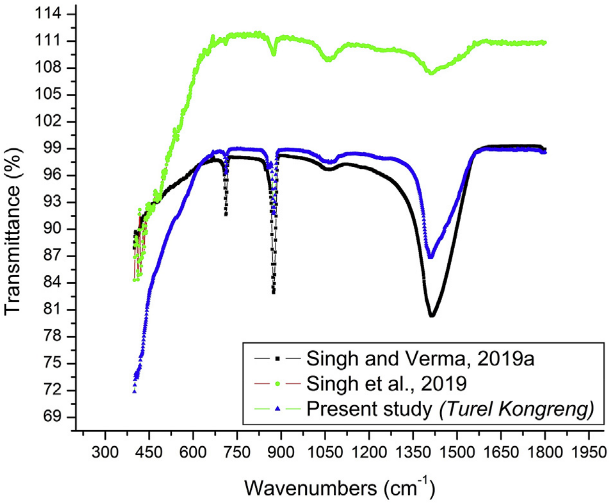

Fig. 3. FTIR peaks of the present study and comparison with other researchers (Singh and Verma, 2019a; Singh et al., 2019).

2.2. Characterization of catalyst

The finely crushed samples were subjected into an XRD for recording the diffraction patterns using a Bruker AXS (D8-Advanced) with 1.5406 Å of Cu-Kα radiation in a 2θ range of 20°–80°. PerkinElmer (Spectrum Two) FT-IR spectrometer is used for determining the infrared spectrum of the samples. The corresponding data were recorded using instrument-equipped Spectrum 10™ software with $LiTaO_3$ detector. Nova NanoSEM (1.0nm@30 kV resolution, 5x to 1,000,000x magnification) with Bruker SDD-EDS detector attached with EDX analyzer is used for studying the chemical morphology of the samples. The techniques and methodology placed by AOAC (AOAC, 1998) is followed for determining the properties of the chicken and duck egg shells.

2.3. Transesterification

Transesterification is a process by which an organic alkyl group R″ of an ester is exchanged by an organic group R' of an alcohol in the presence of a catalyst thereby forming fatty acid alkyl ester and

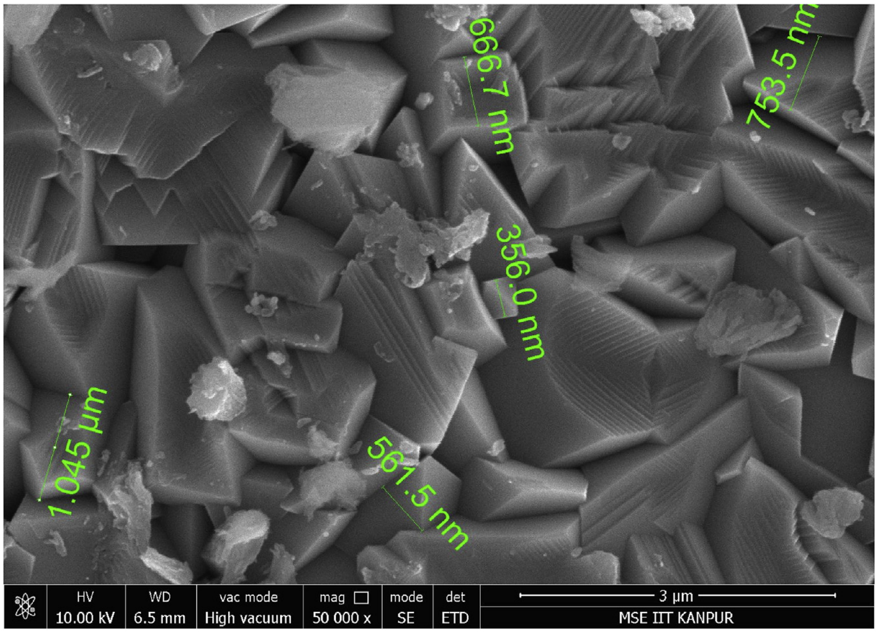

Fig. 4. Morphology of CaO synthesized from *Turel Kongreng* (river mussels) at 800 °C using SEM.

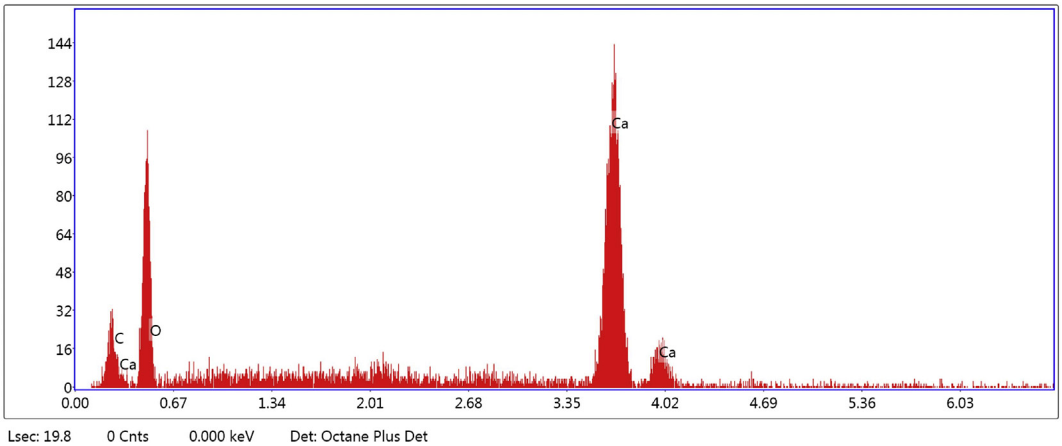

Fig. 5. Elemental composition of CaO synthesized from *Turel Kongreng* (river mussels) calcinated at 800 °C for 1 h

Table 1
Comparison of percentage conversion of present study with past researchers.

Ref. No.	Catalyst used	Feed stock	Percentage conversion
Present Study	Turel kongreng (river mussels)- CaO	Waste cooking oil	91.04%
Singh and Verma (2019a)	Chicken egg shells - CaO	Waste cooking oil	96.6%
Singh et al. (2019)	Duck egg shells - CaO	Ineffectual soybean oil	94.55%
Kaewdaeng et al. (2017)	River snail- CaO	Used cooking oil	92.5%
Buasri et al. (2014)	Scallop- CaO	Palm oil	95.44%

glycerol. In order to confirm the usability of the synthesized CaO from *Turel Kongreng* (river mussels), transesterification reaction is performed using optimal conditions (Singh and Verma, 2019a). Waste cooking oil is taken as source material for the confirmation test (Singh and Verma, 2019a). Catalyst loading of 10% (wt.%), alcohol to oil ratio of 10:1, reaction temperature of 75 °C and a reaction time of 60 min were taken for the confirmation study. The prescribed percentage of mixing is performed in a lab scale 1000 ml flask. Evaporator and centrifugation were used for removing excess alcohol and catalyst from the sample. The rate of ester conversion is calculated using equation (1). The findings were compared to the findings of other researchers. The experiment was conducted for three times to confirm the result.

$$WCOFAMEyield = \frac{WeightofWCOFAMEproduced}{WeightofWCOprocured}x100 \tag{1}$$

3. Results and discussion

3.1. X-ray diffraction pattern

The X-ray diffraction patterns of the present study along with the corresponding comparison between the findings of Singh and Verma (2019a) and Singh et al. (2019) are shown in Fig. 2. As observed from Fig. 2, the diffraction patterns of the *Turel Kongreng* (river mussels) CaO calcinated at 800 °C for 1 h, showed similar characteristics to that of CaO prepared from chicken and duck egg shells as cited in the figure itself. Diffraction peaks corresponding to (111), (222) and (220) of the face centered cubic phase were observed at 20.40776°, 34.10134° and 47.50571°. The present findings were analogous to that of other researchers (Singh and Verma, 2019a, 2019b; Kaewdaeng et al., 2017; Buasri et al., 2014). Therefore, the XRD shows the diffraction of CaO within the sample.

3.2. Fourier transform infrared spectroscopy

In order to reconfirm the findings of the XRD, a Fourier transform infrared spectroscopy (FTIR) is conducted. The spectra bands were shown in Fig. 3 in which black line denotes the spectroscopy of Singh and Verma, 2019a, green line denotes the spectral line of Singh et al. (2019) and blue line depicts the present study. A comparison is also being made with past researchers (Singh and Verma, 2019a; Singh et al., 2019) to check the peaks between the present study with that of past works. The findings of the present study are coherent to other researchers' findings. The asymmetric stretching at 1414 cm^{-1} and 875 cm^{-1} defines the presence of carbonaceous C=O group, which is due to chemisorption of atmospheric CO_2 during the synthesis. The formation of Ca–O is displayed in the extra stretching of 406 cm^{-1}. Similar findings were also reported in past research works (Singh and Verma, 2019a; Singh et al., 2019; Zaki et al., 2006; Pandit and Fulekar, 2017).

3.3. Scanning electron microscopy and energy dispersive x-ray analysis

The morphology of the synthesized CaO calcinated at 800 °C for 1 h, at 50,000 x magnification and its composition in its elemental state is shown in Figs. 4 and 5. From Fig. 4, it can be seen that the grains are of asymmetrical nature and of varying size. This may be due to the non-uniform exposure of time and temperature of the samples. Therefore, the grains were agglomerated with tremendous porosity and therefore arises the requirements of EDX (Singh and Verma, 2019a, 2019b; Singh et al., 2019; Buasri et al., 2014). The elemental composition using EDX shows high concentration of Ca and O ions, depicting greater formation of CaO in the sample. The sample contains 78.35 wt% of Ca and 18.15 wt % of O. Other elements such as C are also present with 3.49 wt %.

3.4. Transesterification and confirmation study

After performing the reaction at a laboratory scale set up, the glycerol was removed and equation (1) is used for calculating the percentage conversion. The average methyl ester conversion rate was obtained to be 91.04 ± 0.56%. Table 1 shows the conversion percentage of the present study to that of past researchers. The comparison shows that *Turel Kongreng* (river mussels) can be effectively used as a source of heterogeneous base catalyst.

The catalyst can be reused for about five (5) times after which the catalytic ability reduces after the 5th time, showing lower conversion rate between 70 and 50% in the next few sessions and later, less than 30% in consecutive sessions. Therefore, the ability in showing catalytic activity for a duration of five times shows the sustainability of the material for use as catalyst.

4. Conclusion

An attempt has been made in checking the locally available mussels' shells (*Turel Kongreng*) for use as a source material in synthesizing CaO and application of the same as heterogeneous base catalyst.

XRD shows that the diffraction patterns of the synthesized CaO were close to that of other sources such as chicken, duck egg shells. FTIR spectroscopy showed extra stretching of Ca–O at 406 cm^{-1}, which is also coherent to other researcher's findings. SEM morphology and EDX result confirms the high formation of CaO from the calcinated samples of *Turel Kongreng* at 800 °C. The confirmation transesterification test showed 91.04% methyl ester conversion rate, which is higher than other homogeneous catalyst such as KOH/NaOH.

It can be concluded that the locally sourced mussel shells (*Turel Kongreng*) which are normally discarded and left as waste, be sourced and treated to form valuable CaO, which is one among the valuable sources of heterogenous catalyst.

Acknowledgement

The authors sincerely thank Department of Chemistry, NIT Manipur, Imphal, India for extensive support in providing XRD & FTIR analysis along with other facility for measuring various properties. The authors also acknowledge IIT Kanpur for providing SEM with EDX facility. The authors acknowledge Central Analytical Instrumentation Facility, IIT Guwahati for their extensive support in providing GC-MS facility.

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.bcab.2019.101185.

References

AOAC, 1998. Official Methods of Analysis, sixteenth ed. Association of official analytical chemists, Gaithersburg, MD.
Beygmoradi, A., Homaei, A., 2017. Marine microbes as a valuable resource for brand new industrial biocatalysts. Biocatalysis Agric. Biotechnol. 11, 131–152.
Buasri, A., Worawanitchaphong, P., Trongyong, S., 2014. Utilization of scallop waste shell for biodiesel production from palm oil - optimization using Taguchi method. Procedia Soc. Behav. Sci. 8, 216–221.
Devaraj, J., Robinson, Y., Ganapathi, P., 2015. Experimental investigation of performance, emission and combustion characteristics of waste plastic pyrolysis oil blended with diethyl ether used as fuel for diesel engine. Energy 85, 304–309.
Garcia, M.C.C., Sanchez, M.D.M., Miron, A.S., Camacho, F.G., Grima, E.M., 2013. A process for biodiesel production involving the heterotrophic fermentation of Chlorella protothecoides with glycerol as the carbon source. Appl. Energy 103, 341–349.
Gupta, J., Agarwal, M., Dalai, A.K., 2016. Optimization of biodiesel production from mixture of edible and nonedible vegetable oils. Biocatalysis Agric. Biotechnol. 8, 112–120.
Hanis, S., Sayid, Y., Hanis, N., Hanapi, M., Azid, A., 2016. A review of biomass-derived heterogeneous catalyst for a sustainable biodiesel production. Renew. Sustain. Energy Rev. 70, 1040–1051.
Hurdogan, E., Ozalp, C., Kara, O., Ozcanli, M., 2017. Experimental investigation on performance and emission characteristics of waste tire pyrolysis oil-diesel blends in a diesel engine. Int. J. Hydrogen Energy 2 (36), 23373–23378.
Kaewdaeng, S., Sintuya, P., Nirunsin, R., 2017. Biodiesel production using calcium oxide from river snail shell ash as catalyst. Energy Procedia 138, 937–942.
Latchubugata, C.S., Kondapaneni, R.V., Patluri, K.K., Virendra, U., Vedantam, S., 2018. Kinetics and optimization studies using response surface methodology in biodiesel production using heterogeneous catalyst. Chem. Eng. Res. Des. 135, 129–139.
Mathimani, T., Pugazhendhi, A., 2018. Utilization of algae for biofuel, bio-products and bio-remediation. Biocatalysis Agric. Biotechnol. 17, 326–330.
Melchias, G., et al., 2018. A comparative analysis of biodiesel production and its properties from Leptolyngbya sp. BI-107 and Chlorella vulgaris under heat shock stress. Biocatalysis Agric. Biotechnol. 16, 502–516.
Moazeni, F., Chen, Y., Zhang, G., 2019. Enzymatic transesterification for biodiesel production from used cooking oil, a review. J. Clean. Prod. 216, 117–128.
Mumtaz, M.W., Mukhtar, H., Dilawer, U.A., Hussain, S.M., Hussain, M., Iqbal, M., 2016. Biocatalytic transesterification of Eruca sativa oil for the production of biodiesel. Biocatalysis Agric. Biotechnol. 5, 162–167.
Niju, S., Begum, K.M.M.S., Anantharaman, N., 2014. Modification of egg shell and its application in biodiesel production. J. Saudi Chem. Soc. 18 (5), 702–706.
Pandit, P.R., Fulekar, M.H., 2017. Egg shell waste as heterogeneous nanocatalyst for biodiesel production: optimized by response surface methodology. J. Environ. Manag. 198, 319–329.
Rajak, U., Verma, T.N., 2017. Numerical investigation on cylindrical combustion chamber for methane-air fuel. Int. J. Theo. App. Res. Mech. Eng. 6 (1).
Rajak, U., Verma, T.N., 2018a. Effect of emission from ethylic biodiesel of edible and non-edible vegetable oil, animal fats, waste oil and alcohol in CI engine. Energy Convers. Manag. 166, 704–718.
Rajak, U., Verma, T.N., 2019d. Spirulina microalgae biodiesel – a novel renewable alternative energy source for compression ignition engine. J. Clean. Prod. 201, 343–347.
Rajak, U., Nashine, P., Verma, T.N., 2018c. Assessment of diesel engine performance

using spirulina microalgae biodiesel. Energy 166, 1025–1036.

Rajak, U., Nashine, P., Singh, T.S., Verma, T.N., 2018d. Numerical Investigation of combustion, performance and emission characteristics of various biofuels. Energy Convers. Manag. 156, 235–252.

Rajak, U., Nashine, P., Verma, T.N., 2018e. Comparative assessment of the emission characteristics of first, second and third generation biodiesel as fuel in a diesel engine. J. Therm. Eng (Accepted Manuscript).

Rajak, U., Verma, T.N., 2018f. Influence of Emission Characteristics Using Microalgae Biodiesel in Diesel Engine. Computer Application in Education and Research for Science and Technology. International Research Publication House, 978-93-87388-21-5pp. 221–230.

Rajak, U., Nashine, P., Verma, T.N., 2019a. Effect of fuel injection pressure in a diesel engine using Microalgae-diesel emulsion. Int. J. Eng. Adv. Technol. 8 (3), 225–232.

Rajak, U., Nashine, P., Verma, T.N., 2019b. Performance analysis and exhaust emissions of Aegle methyl ester operated compression ignition engine. Therm. Sci. Eng. Prog. https://doi.org/10.1016/j.tsep.2019.05.004. (Accepted).

Rajak, U., Nashine, P., Verma, T.N., 2019c. A comparative analysis of engine characteristics from various biodiesels: numerical Study. Energy Convers. Manag. 180, 904–923.

Salam, S., Verma, T.N., 2019. Appending empirical modelling to numerical solution for behaviour characterisation of microalgae biodiesel. Energy Convers. Manag. 180, 496–510.

Semwal, S., Arora, A.K., Badoni, R.P., Tuli, D.K., 2011. Biodiesel production using heterogeneous catalysts. Bioresour. Technol. 102 (3), 2151–2161.

Shrivastava, P., Verma, T.N., 2019. An experimental investigation into engine characteristics fueled with Lal ambari biodiesel and its blends. Therm. Sci. Eng. Prog. https://doi.org/10.1016/j.tsep.2019.100356. (Accepted).

Singh, N.R., Singh, R.N., Singh, L.D., Singh, T.S., Verma, T.N., 2019. Base transesterification of ineffectual soybean oil using lab scale synthesized catalyst. In: Proceedings of the International Conference on Advances in Mechanical Engineering Research. NIT Warangal, India.

Singh, T.S., Verma, T.N., Nashine, P., Shijagurumayum, C., 2018. BS-III diesel vehicles in imphal, India: an emission perspective. In: Sharma, N., Agarwal, A., Eastwood, P., Gupta, T., Singh, A. (Eds.), Air Pollution and Control. Energy, Environment, and Sustainability. Springer, Singapore. https://doi.org/10.1007/978-981-10-7185-0_5.

Singh, T.S., Verma, T.N., 2019a. Taguchi design approach for extraction of methyl ester from waste cooking oil using synthesized CaO as heterogeneous catalyst: response surface methodology optimization. Energy Convers. Manag. 182, 383–397.

Singh, T.S., Verma, T.N., 2019b. Impact of Tri-fuel on compression ignition engine emissions: blends of waste frying oil–alcohol–diesel. In: Agarwal, A., Gautam, A., Sharma, N., Singh, A. (Eds.), Methanol and the Alternate Fuel Economy. Energy, Environment, and Sustainability. Springer, Singapore.

Tan, Y.H., Abdullah, M.O., Nolasco-hipolito, C., Zauzi, N.A., 2017. Application of RSM and Taguchi methods for optimizing the transesterification of waste cooking oil catalyzed by solid ostrich and chicken-eggshell derived CaO. Renew. Energy 114, 437–447.

Toma, M., Micu, D., Andreescu, C., 2019. Influences of engine faults on pollutant emission. Procedia Manuf 32, 529–536.

Vahabzadeh, F., Hajar, M., Shokrollahzadeh, S., 2010. Empirical modeling of the enzymatic methanolysis of canola. Oil. Sci. Iran. 17 (1), 97–105.

Vassilev, S.V., Vassileva, C.G., 2016. Composition, properties and challenges of algae biomass for biofuel application: an overview. Fuel 181, 1–33.

Zaki, M.I., Knözinger, H., Tesche, B., Mekhemer, G.A.H., 2006. Influence of phosphonation and phosphation on surface acid – base and morphological properties of CaO as investigated by in situ FTIR spectroscopy and electron microscopy. J. Colloid Interface Sci. 303, 9–17.

Zeng, Y., Cao, Y., Qiao, X., Seyler, B.C., Tang, Y., 2019. Air pollution reduction in China: recent success but great challenge for the future. Sci. Total Environ. 663, 329–337.