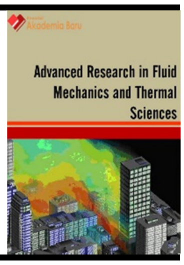
Penerbit Akademia Baru

Journal of Advanced Research in Fluid Mechanics and Thermal Sciences

Journal homepage: www.akademiabaru.com/arfmts.html
ISSN: 2289-7879



Thermally Produced Nano Catalyst for Biodiesel Production: A Review

Open Access

Nor Azyan Farrah Adila Zik[1], Sarina Sulaiman[1,*], Parveen Jamal[1]

[1] Department of Biotechnology Engineering, Faculty of Engineering, International Islamic University Malaysia, P.O BOX 10. 50728, Kuala Lumpur, Malaysia

ARTICLE INFO

Article history:
Received 13 August 2018
Received in revised form 5 December 2018
Accepted 10 December 2018
Available online 12 December 2018

Keywords:
Thermal decomposition, nano-catalyst, heterogeneous catalyst, biodiesel, Calcination, Calcium oxide

ABSTRACT

Catalyst is a substance that enables chemical reaction in faster rate. In biodiesel production, catalyst plays as an important role as it can increase the rate of the reaction. The type of catalyst that usually can be found are homogeneous and heterogeneous catalyst. However, homogenous catalyst is difficult to separate with the product (biodiesel) at the end of the reaction compared to heterogeneous catalyst. This will result in production of high waste water and creates issue in regeneration of the catalyst. In order to overcome the issue, many researchers have studied about heterogeneous catalyst and the use this type of catalyst in production of biodiesel. The heterogeneous catalyst can be developed from natural resources such as animal bone, waste and natural rock which is a type of alkali earth oxides. A way to improve the catalytic activity of the catalyst used is increase its surface area by preparing it in nano-sized of catalyst. Nano-catalyst has a high catalytic efficiency, large surface area, high resistance to saponification and good rigidity. However, the thermal condition during decomposition of catalyst could influence the activity of the catalyst during the reaction. Therefore, the reaction rate and the catalytic activity of the catalyst during transesterification reaction can be affected by the type of catalyst and the thermal condition involved during the preparation of the catalyst.

1. Introduction

In recent years, the rising of atmospheric greenhouse gas levels such as NOx, SOx, CO, CO_2 and the scarcity of conventional fossil fuels had caused problems associated with global warming [1]. Due to the limitation of the traditional fossil resources, the renewable energy have gain more attention [2,3]. Because of the consumption of fossil fuel is 10^5 faster than the natural production, the available fossil fuel is expected to be ran out in 2050 [4]. In order to overcome the issue caused by the traditional fossil fuel, biodiesel can be used. Biodiesel is made from renewable biological sources such as vegetable oils and animal fats [5]. Biodiesel also chemically known as fatty acid

* *Corresponding author.*
E-mail address: sarina@iium.edu.my (Sarina Sulaiman)

methyl ester (FAME) can be derived from transesterification of triglyceride in vegetable oils or animal fats which is as triglyceride source [5,6]. Figure 1 shows the transesterification for biodiesel synthesis. Besides, biodiesel also can be produced by esterification of free fatty acid [7]. In the production of biodiesel, various feedstock can be used such as soybean oil, rapeseed oil, sunflower oil, palm kernel oil, waste cooking oil, coconut oil, Jatropha oil, microalgae oil, rice bran oil, castor oil, Canola oil, and bombax ceiba oil [1,7–10].

Biodiesel has gain much attentions from researchers due to its capability as renewable energy because of its advantages. Biodiesel is environmental friendly because it is biodegradable, non-toxicity, free from sulfur and aromatics and containing oxygen in its structure that can cause in production of more tolerable exhaust gas emission than conventional fossil diesel despite providing similar levels of fuel efficiency [11]. In addition, biodiesel have many advantages that can solve the problems that created by the commercial diesel. For instance, no sulfur content in this type of biodiesel can provides a good lubricity than the conventional diesel fuel, thus can enhance the durability of the engine [12]. Besides, biodiesel is also low toxicity compared to diesel fuel and can degrades more rapidly which are can minimize the environmental consequences of biofuel spills [13]. Moreover, they also mentioned in their studies that biodiesel can reduce the emission of contaminant and can lower the health risk which is does have sulfur dioxide (SO_2) emissions.

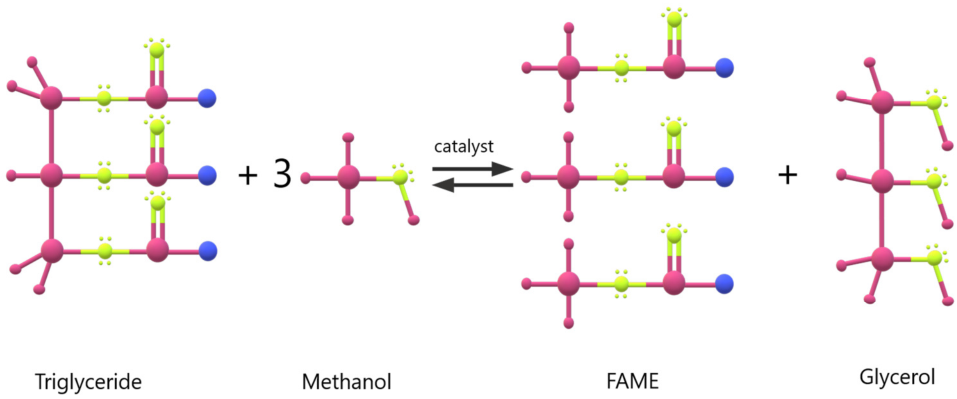


Fig. 1. Transesterification reaction of biodiesel synthesis

2. Catalyst

The transesterification reaction, a reversible process proceeds appreciably by the addition of catalysts, which can be acidic, basic or organic in nature, usually in molar excess of alcohol [14]. In the production process of biodiesel, a catalyst is necessarily used to initiate the reaction because the alcohol is sparingly soluble in the oil due to their polarity difference [15]. The type of catalyst then categorized into homogeneous and heterogeneous catalysts [16]. The economy of the production is depending on the catalyst used as compare as the other factors. Recently, a catalyst that derived from organic waste materials has gained much attention towards researcher as they are non-toxic, safe to handle and store, abundantly available, low cost and it comes from renewable sources [17].

2.1 Heterogeneous Catalyst

Recently, heterogeneous catalysts have received greater attention than homogeneous catalysts in the production of biodiesel [18,19]. Heterogeneous catalyst means that the reactants and the catalyst are in different forms; where in the heterogeneous catalytic biodiesel production, the reactants are in liquid form and the catalyst is in solid form [6]. The example of heterogeneous catalyst that can be used in biodiesel production have been reported such as mixed oxides, alkaline-earth metals oxides, alkali metals supported on zeolite, alumina and solid acid catalysts [1]. This type of catalyst has been found to be an efficient catalyst. This is because, it is easy to separate, low sensitivity towards free fatty acid, high catalytic activity, environmental friendly, reusable, non-corrosive, no soap formation and high stability and ability to produce FAME [1,18–22]. Calcium oxide (CaO) is one of the most used heterogeneous base catalyst for transesterification reaction of different oils and fats to biodiesel [2]. CaO also has been found to be one of the emerging and efficient heterogeneous base catalyst [23,24]. However, the most of the heterogeneous catalyst is quiet expensive or complicate to prepare, which limits their industrial application [10]. Therefore, many researchers derived heterogeneous catalyst from biomass in order to reduce the cost for the preparation of catalyst.

2.2 Homogeneous Catalyst

Homogeneous catalyst is a type of catalyst that soluble in the middle of reaction and these type of catalyst are in a single phase either liquid or gaseous [25]. Currently, biodiesel is commercially produced using a homogeneous catalyst (NaOH, alkali catalysis; H2SO4, acid catalysis) for the transesterification process, because of its high reaction activity and low cost [21]. Conversion of vegetable oils to methyl esters using homogeneous catalysts can reach 99% within an hour due to high reaction rate of the catalyst [18]. However, it suffers from several drawbacks, such as equipment corrosion and have high waste water [10].

2.3 Enzymatic Catalyst

In biodiesel production, the enzyme that usually use as biocatalyst is lipase [13]. It has been receiving much attention in the production of biodiesel because of its high efficiency, selectivity and production of a highly purified product [26]. However, it leads to leads to very high production costs and consumes days to complete the process [15]. This is because, the low rate of reaction and deactivation of enzyme also limits its commercialization [27].

3. Nano-Catalyst

Nanocatalyst is a type of nanomaterials from nanotechnology with the range of size 100nm to 0.1nm [25]. Some researchers have been studied about the production of biodiesel by using nanocatalyst [23]. Recently, nanocatalyst has become the focus for an efficient biodiesel production because of high surface area, high catalytic efficiency and resistance to saponification along with good rigidity [28,29]. The particle size of the catalyst that used in biodiesel production is one of the most important factors for its catalytic activity [30]. Therefore, in order increase the catalytic activity of the catalyst, some studies have used nanocatalyst in biodiesel production because it has high surface area [2]. Many studies have confrimed that catalyst with a lower particle size and higher surface area accelerate reaction rates due to an increased number of molecules that have minimum required energy for the reaction to occur as illustrated in the Figure 2 [30].

(a) (b)

Fig. 2. Illustration image of comparison between (a) large particle with low surface area and (b) small particle with high surface area

However, according to Banković-Ilić *et al.,* the nanocatalyst also have some drawbacks which are difficult separation from the reaction mixture, difficult handling due to the formation of pulverulent materials, the high pressure drop and leaching of the solid phase [2]. Nevertheless, the yield of biodiesel can be optimised by controlling its parameters such as methanol to oil ratio, temperature, time and catalyst loading. Table 1 shows the comparison of conditions for various types of nanocatalyst. The highest yield of 98.54 % is obtained by using calcium oxide (CaO) as the heteogeneous base catalyst with 66±3 nm (diameter) [30]. However, Baskar *et al.,* reported that the yield of biodiesel increased with the increase in the concentration of catalyst [8]. However, the yield of biodiesel gradually decrease when the catalyst loading is more than 12 %. The reason for the decrease in biodiesel yield might be due to the diffusion limitation between oil and methanol it increased solid interfaces in the reaction mixture at high nanocatalyst concentration. Besides, the reaction time by using nanocatlyst with high surface area can reduce the reaction time.

3.1 Nano-Catalyst Based CaO

Calcium oxide (CaO) is one of the most used solid catalyst for transesterification reaction of different feedstocks in production of biodiesel [2]. Among the type of alkali earth oxides that available, CaO is widely used catalyst due to its availability in nature, low cost, long life time, highest activity under mild reaction conditions and high activity [35,36]. CaO has a white color, a spherical shape, high porosity and narrow particle size distribution [37]. This heterogeneous base catalyst was found to be effective in the catalysis of transeterification [24]. However, nano-sized CaO was found to have a 30 times higer conversion rate if compared to the meso CaO. This is because the catalytic activity of nano-sized CaO is better [23]. In addition, it is also reported that nano-sized CaO has many advantages compared to meso CaO such as higher conversion, large pore size, larger surface area to volume ratio which is can increase the availability of active sites, high catalystic activity, shorter reaction time, less amount of catalyst required, easy seperation, better recovery, recylability and reusability. The synthesis of nano-sized CaO is usually prepared through two main steps: preparation and activation of nano-particles which is the first step includes different methods such as thermal decomposition, impregnation, mixing and precipitation, while the second step is most frequently calcination of the produced nano-particles in order to achive the specific catalytic activity [2]. However, in producing CaO by calcination, reseachers found some drawbacks that can affected the efficiency of this type of catalyst in transeterification reaction. This is because its catalystic activity is sensitive towards moisture present which will decrease the reaction rate catalyzed by CaO [23]. Moreover, the calcination temperature also largely affects the catalytic properties of the resultant catalyst. A study that conducted by Pandit *et al.,* showed that calcium carbonate was decomposed to CaO and carbon dioxide above 800°C [29].

Table 1
Comparisons of reactions conditions for various types of nanocatalysts

Catalyst	Feedstock	Calcination			Transesterification					Reusable	Reference
		Temp (°C)	*Time (h)*	*Size (nm)*	*Methanol : Oil*	*Catalyst loading*	*Temperature (°C)*	*Time (h)*	*FAME (%)*		
CaO	Jatropha oil	900	2.5	66±3	5.15:1	0.02:1 % (w/w)	65	2.22	98.54	6	[30]
Ni doped ZnO	Castor oil	800	3	35.1	8:1	11 %(w/w)	55	1	95.20	3	[8]
ZrO_2 loaded with $C_4H_4O_6HK$	Soybean oil	512	5	10-40	16:1	6.0 %	60	2	98.03	5	[10]
$TiO_2/PrSO_3H$	Waste cooking oil			23.1	15:1	4.5 wt%	60	9	98.3	4	[31]
Al/Sr	Sunflower oil	600	5	68	12:1		65	5	96.8		[32]
$MgO\text{-}La_2O_3$	Sunflower oil	550	4	20	18:1	60 wt%	65	5	97.7	4	[33]
CaO	Bombax Ceiba oil	900		18-30	10.37:1	1.5 wt%	65	1.10	96.2	5	[23]
CZO	Neem oil	500	2	40.62	10:1	10 %(w/w)	55	1	97.18	6	[34]

4. Thermal Decomposition of Cao

In the conversion of CaO, calcination temperature largely affects the catalytic properties of the resultant catalysts [10]. Calcination process is to convert calcium carbonate, $CaCO_3$ to CaO and carbon dioxide, CO_2 with heating above 800 °C as shown in equation 1. CaO is a type of metal oxide which can act as heterogeneous base catalyst for biodiesel production. This catalyst is closely resembled to an environmental-friendly material. Generally, calcium nitrate, $Ca(NO_3)_2$ or calcium hydroxide, $Ca(OH)_2$ is the raw material to produce CaO. Besides, CaO also can be derived from natural calcium sources from wastes, such as egg shell, mollusk shell, and bone [38]. The condition of calcination namely temperature and time have a significant effect upon the surface are, total pore volume, and mean pore diameter [39].

$$CaCO_3\ (solid) \xrightarrow{calcination} CaO\ (solid)\ +\ CO_2 \tag{1}$$

From some studies that have been conducted by some researchers in biodiesel production as shown in the Table 2, they were using nano-sized CaO as the catalyst. However, the condition of the calcination in the CaO synthesis was different. In the study conducted by Pandit *et al.,* hen eggs was utilized to synthesis CaO with the calcination condition of 900°C in 3h [29]. The study also reported the calcination conditions that were used in were attributed to the decomposition of $CaCO_3$ to CaO and CO_2. This is because, the release of carbon dioxide during the high heating process leads to the formation of nano-sized of CaO.

Table 2
Preparation and characterization of nano-catalyst based CaO

Catalyst	Calcination condition	Morphology	Size (nm)	Reaction time	Yield (%)	Reusability	Reference
CaO from hen eggs	900 °C – 3h	Spherical shape, agglomerated due to high surface area	75	3.6 h	86.41	5	[29]
CaO from seashells	900 °C – 2.5 h	Rod and spherical shape, agglomerated due to high specific surface area	66.3	2.22 h	98.54	6	[40]
CaO	1000 °C – 2 h	Uniform spherical, bulk spherical, minor rod shape	< 100	80 min	89.89	3	[42]
CaO from calcium nitrate	900 °C	Irregular shape due to agglomerated of particles	8 -30	70.52 min	95.7	5	[23]
CaO – Al_2O_3	500 °C – 3 h	-	29.9		82.3		[41]
CaO from seashells	1100 °C – 3 h	A cluster of well-developed cubic crystal with obvious edges, agglomerates of spherical particle	66.2	2 h	93.5	5	[9]

The morphology structure of nano-sized CaO is in spherical shape with agglomerated due to the high surface area of the CaO particles. The active centers was well developed with the usage of the optimal calcination temperature, which is contributing to the favorable efficiency catalyst [2]. The highest yield of biodiesel achieved by Reddy *et al.,* was 98.54 % within 2.2h [40]. They reported that, at 850°C, the calcium carbonate of the shell powder decomposed to CaO and CO_2. The calcination temperature largely affects the catalytic properties of the catalyst produced. The morphology of the CaO particles that decomposed from the seashells showed a rod and spherical shape with agglomerated with relatively high surface area, small particle size and it was stated "highly active" of nano-catalyst. Besides, Hashmi *et al.,* reported the lowest yield of biodiesel, 82.3% was achieved because the calcination temperature (500 °C) was lower than the temperature needed to convert $CaCO_3$ to CaO [41].

4. Conclusions

Biodiesel which is also chemically known as fatty acid methyl ester (FAME) can be produced from transesterification of triglyceride in vegetable oils or animal fats. Due to the limitation of the traditional fossil resources, the biodiesel has gained more attention. Normally, biodiesel can be produced from a chemical reaction by transesterification process of a vegetable oil or animal fat with alcohol in the presence of catalyst to obtain methyl or ethyl esters (biodiesel) and glycerol (soap, side product). In order to produce high yield of biodiesel, catalyst with high catalytic activity will be used. Catalyst can be found in basic or acidic which are either in heterogeneous, homogeneous or enzymatic catalyst. In the industry, homogeneous catalysts had been used broadly in the production of biodiesel. However, this type of catalysts are toxic, highly flammable and corrosive in nature besides of producing soap and high waste of water. Therefore, to solve the problems, researchers have extensively focused on substituting homogenous catalyst with different types of heterogeneous catalysts which are can overcome the problems that caused by homogeneous catalyst.

CaO is one of highly efficient solid base catalyst for production of biodiesel and the one of the most used solid catalyst for transesterification reaction. CaO is cheap, easily available, non-corrosive, environmental friendly, easy to handle, high basicity that also can be regenerated and reused. However, the particle size of the catalyst is the one of the most important factors for the catalytic activity of the catalyst. Catalyst with the lower size of particle and higher surface area contribute to enhancing the reaction rate. Unlike many other solid catalyst, nano-sized CaO can be prepared without much effort.

The synthesis of CaO have two main steps which is preparation and activation of nano-sized of catalyst. Calcination was conducted for the activation of nano-sized catalyst to achieve the specific catalytic activity. The CaO was reported to start to synthesis when the heating temperature is more than 800 °C. Moreover, the calcination temperature has a significant effect upon the surface area, total pore volume, and mean pore diameter of the catalyst. Thus, with nano-sized solid base catalyst with the optimized calcination temperature, high catalytic activity of catalyst would be produced to have a high yield of biodiesel with a shorter reaction time.

Acknowledgement
The authors would like to express their gratitude to the International Islamic University Malaysia.

References

[1] Alsharifi, Mariam, Hussein Znad, Sufia Hena, and Ming Ang. "Biodiesel production from canola oil using novel Li/TiO2 as a heterogeneous catalyst prepared via impregnation method." *Renewable Energy* 114 (2017): 1077-1089.
[2] Banković–Ilić, Ivana B., Marija R. Miladinović, Olivera S. Stamenković, and Vlada B. Veljković. "Application of nano CaO–based catalysts in biodiesel synthesis." *Renewable and Sustainable Energy Reviews* 72 (2017): 746-760.

[3] Zabeti, Masoud, Wan Mohd Ashri Wan Daud, and Mohamed Kheireddine Aroua. "Activity of solid catalysts for biodiesel production: a review." *Fuel Processing Technology* 90, no. 6 (2009): 770-777.
[4] Demirbas, Ayhan. "Progress and recent trends in biodiesel fuels." *Energy conversion and management* 50, no. 1 (2009): 14-34.
[5] Berrios, M., M. A. Martín, A. F. Chica, and A. Martín. "Study of esterification and transesterification in biodiesel production from used frying oils in a closed system." *Chemical Engineering Journal* 160, no. 2 (2010): 473-479.
[6] Tan, Yie Hua, Mohammad Omar Abdullah, and Cirilo Nolasco-Hipolito. "The potential of waste cooking oil-based biodiesel using heterogeneous catalyst derived from various calcined eggshells coupled with an emulsification technique: A review on the emission reduction and engine performance." *Renewable and Sustainable Energy Reviews* 47 (2015): 589-603.
[7] Srivastava, Richa, Amrik Singh, and Kumar Gaurav. "Advancement in Catalysts for Transesterification in the Production of Biodiesel: A Review." *Journal of Biochemical Technology* 7, no. 3 (2018): 1148-1158.
[8] Baskar, G., I. Aberna Ebenezer Selvakumari, and R. Aiswarya. "Biodiesel production from castor oil using heterogeneous Ni doped ZnO nanocatalyst." *Bioresource technology* 250 (2018): 793-798.
[9] Mazaheri, Hoora, Hwai Chyuan Ong, H. H. Masjuki, Zeynab Amini, Mark D. Harrison, Chin-Tsan Wang, Fitranto Kusumo, and Azham Alwi. "Rice bran oil based biodiesel production using calcium oxide catalyst derived from Chicoreus brunneus shell." *Energy* 144 (2018): 10-19.
[10] Qiu, Fengxian, Yihuai Li, Dongya Yang, Xiaohua Li, and Ping Sun. "Heterogeneous solid base nanocatalyst: preparation, characterization and application in biodiesel production." *Bioresource technology* 102, no. 5 (2011): 4150-4156.
[11] Thanh, Le Tu, Kenji Okitsu, Luu Van Boi, and Yasuaki Maeda. "Catalytic technologies for biodiesel fuel production and utilization of glycerol: a review." *Catalysts* 2, no. 1 (2012): 191-222.
[12] Gerhard, Knothe, Van Gerpen Jon, and Krahl Jürgen. "The biodiesel handbook." (2005).
[13] Romano, Silvia Daniela, and Patricio Aníbal Sorichetti. *Dielectric spectroscopy in biodiesel production and characterization*. Springer Science & Business Media, 2010.
[14] Ejikeme, P. M., I. D. Anyaogu, C. L. Ejikeme, N. P. Nwafor, C. A. C. Egbuonu, K. Ukogu, and J. A. Ibemesi. "Catalysis in biodiesel production by transesterification processes-An insight." *Journal of Chemistry* 7, no. 4 (2010): 1120-1132.
[15] Kamel, Dena A., Hassan A. Farag, Nevine K. Amin, Ahmed A. Zatout, and Rehab M. Ali. "Smart utilization of jatropha (Jatropha curcas Linnaeus) seeds for biodiesel production: Optimization and mechanism." *Industrial Crops and Products* 111 (2018): 407-413.
[16] Talha, Nur Syakirah, and Sarina Sulaiman. "Overview of catalysts in biodiesel production." *ARPN Journal of Engineering and Applied Sciences* 11, no. 1 (2016): 439-448.
[17] Smith, Siwaporn Meejoo, Chutima Oopathum, Vararut Weeramongkhonlert, Christopher B. Smith, Suwilai Chaveanghong, Pradudnet Ketwong, and Supakorn Boonyuen. "Transesterification of soybean oil using bovine bone waste as new catalyst." *Bioresource technology* 143 (2013): 686-690.
[18] Gohain, Minakshi, Anuchaya Devi, and Dhanapati Deka. "Musa balbisiana Colla peel as highly effective renewable heterogeneous base catalyst for biodiesel production." *Industrial Crops and Products* 109 (2017): 8-18.
[19] Abdullah, Sharifah Hanis Yasmin Sayid, Nur Hanis Mohamad Hanapi, Azman Azid, Roslan Umar, Hafizan Juahir, Helena Khatoon, and Azizah Endut. "A review of biomass-derived heterogeneous catalyst for a sustainable biodiesel production." *Renewable and Sustainable Energy Reviews* 70 (2017): 1040-1051.
[20] Feyzi, Mostafa, Asadollah Hassankhani, and Hamid Reza Rafiee. "Preparation and characterization of Cs/Al/Fe3O4 nanocatalysts for biodiesel production." *Energy conversion and management* 71 (2013): 62-68.
[21] Ma, Yingqun, Qunhui Wang, Xiaohong Sun, Chuanfu Wu, and Zhen Gao. "Kinetics studies of biodiesel production from waste cooking oil using FeCl3-modified resin as heterogeneous catalyst." *Renewable Energy* 107 (2017): 522-530.
[22] Suwannasom, Pirom, Panadda Tansupo, and Chalerm Ruangviriyachai. "A bone-based catalyst for biodiesel production from waste cooking oil." *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects* 38, no. 21 (2016): 3167-3173.
[23] Hebbar, HR Harsha, M. C. Math, and K. V. Yatish. "Optimization and kinetic study of CaO nano-particles catalyzed biodiesel production from Bombax ceiba oil." *Energy* 143 (2018): 25-34.
[24] Degirmenbasi, Nebahat, Samet Coskun, Nezahat Boz, and Dilhan M. Kalyon. "Biodiesel synthesis from canola oil via heterogeneous catalysis using functionalized CaO nanoparticles." *Fuel* 153 (2015): 620-627.
[25] Leo, Vincent Vineeth, and Bhim Pratap Singh. "Prospectus of Nanotechnology in Bioethanol Productions." In *Green Nanotechnology for Biofuel Production*, pp. 129-139. Springer, Cham, 2018.
[26] Kareem, S. O., E. I. Falokun, S. A. Balogun, O. A. Akinloye, and S. O. Omeike. "Enzymatic biodiesel production from palm oil and palm kernel oil using free lipase." *Egyptian Journal of Petroleum* 26, no. 3 (2017): 635-642.

[27] Liu, Yingying, Houfang Lu, Kwesi Ampong-Nyarko, Tanya MacDonald, Lawrence L. Tavlarides, Shijie Liu, and Bin Liang. "Kinetic studies on biodiesel production using a trace acid catalyst." *Catalysis today* 264 (2016): 55-62.
[28] Hu, Shengyang, Yanping Guan, Yun Wang, and Heyou Han. "Nano-magnetic catalyst KF/CaO–Fe3O4 for biodiesel production." *Applied Energy* 88, no. 8 (2011): 2685-2690.
[29] Pandit, Priti R., and M. H. Fulekar. "Egg shell waste as heterogeneous nanocatalyst for biodiesel production: optimized by response surface methodology." *Journal of environmental management* 198 (2017): 319-329.
[30] ANR, Reddy, Abu Ahmed Saleh, Md Saiful Islam, Sinin Hamdan, and Md Abdul Maleque. "Biodiesel production from crude Jatropha oil using a highly active heterogeneous nanocatalyst by optimizing transesterification reaction parameters." *Energy & Fuels* 30, no. 1 (2015): 334-343.
[31] Gupta, Jharna, and Madhu Agarwal. "Preparation and characterizaton of CaO nanoparticle for biodiesel production." In *AIP conference proceedings*, vol. 1724, no. 1, p. 020066. AIP Publishing, 2016.
[32] Marques Correia, Leandro, Juan Antonio Cecilia, Enrique Rodríguez-Castellón, Célio Loureiro Cavalcante, and Rodrigo Silveira Vieira. "Relevance of the physicochemical properties of calcined quail eggshell (CaO) as a catalyst for biodiesel production." *Journal of Chemistry* 2017 (2017).
[33] Tangboriboon, N., R. Kunanuruksapong, and A. Sirivat. "Preparation and properties of calcium oxide from eggshells via calcination." *Materials Science-Poland* 30, no. 4 (2012): 313-322.
[34] Viriya-Empikul, N., Puttasawat Krasae, B. Puttasawat, B. Yoosuk, N. Chollacoop, and K. Faungnawakij. "Waste shells of mollusk and egg as biodiesel production catalysts." *Bioresource technology* 101, no. 10 (2010): 3765-3767.
[35] Mazaheri, Hoora, Hwai Chyuan Ong, H. H. Masjuki, Zeynab Amini, Mark D. Harrison, Chin-Tsan Wang, Fitranto Kusumo, and Azham Alwi. "Rice bran oil based biodiesel production using calcium oxide catalyst derived from Chicoreus brunneus shell." *Energy* 144 (2018): 10-19.
[36] ANR, Reddy, Abu Ahmed Saleh, Md Saiful Islam, Sinin Hamdan, and Md Abdul Maleque. "Biodiesel production from crude Jatropha oil using a highly active heterogeneous nanocatalyst by optimizing transesterification reaction parameters." *Energy & Fuels* 30, no. 1 (2015): 334-343.
[37] Hashmi, Sidra, Sumbal Gohar, Tariq Mahmood, Umar Nawaz, and Hadayatullah Farooqi. "Biodiesel production by using CaO-Al2O3 Nano catalyst." *International Journal of Engineering Research & Science (IJOER)* 2 (2016).
[38] Gardy, Jabbar, Ali Hassanpour, Xiaojun Lai, Mukhtar H. Ahmed, and Mohammad Rehan. "Biodiesel production from used cooking oil using a novel surface functionalised TiO2 nano-catalyst." *Applied Catalysis B: Environmental* 207 (2017): 297-310.
[39] Feyzi, Mostafa, and Zahra Shahbazi. "Preparation, kinetic and thermodynamic studies of Al–Sr nanocatalysts for biodiesel production." *Journal of the Taiwan Institute of Chemical Engineers* 71 (2017): 145-155.
[40] Feyzi, Mostafa, Nahid Hosseini, Nakisa Yaghobi, and Rohollah Ezzati. "Preparation, characterization, kinetic and thermodynamic studies of MgO-La 2 O 3 nanocatalysts for biodiesel production from sunflower oil." *Chemical Physics Letters* 677 (2017): 19-29.
[41] Gurunathan, Baskar, and Aiswarya Ravi. "Process optimization and kinetics of biodiesel production from neem oil using copper doped zinc oxide heterogeneous nanocatalyst." *Bioresource technology* 190 (2015): 424-428.
[42] Badnore, Amruta Udaykumar, Nilesh Lakshaman Jadhav, Dipak Vitthal Pinjari, and Aniruddha Bhalchandra Pandit. "Efficacy of newly developed nano-crystalline calcium oxide catalyst for biodiesel production." *Chemical Engineering and Processing-Process Intensification* 133 (2018): 312-319.