



DEVELOPMENT OF CATALYST FROM A LOCAL WASTE FOR BIODIESEL PRODUCTION FROM WASTE COOKING OIL



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Abstract: This study was aimed at investigating the production of biodiesel from waste cooking oil (WCO) using local catalyst developed from chicken egg shell. Egg shells were washed, pulverized and calcined at 700, 800 and 900°C for a time period of 4 h for the preparation of renewable catalyst. Then the calcined sample was refluxed in water at 60°C for 4 h and the solid particle was filtered and dried in hot air oven at 110°C for 5 h. The calcined eggshell catalyst was characterized using XRF, XRD, FTIR, SEM and surface analyzer. The WCO was first filtered to remove all solid particles before transesterification. Transesterification reaction was performed for the conversion of WCO to biodiesel using the developed catalyst. The effect of calcination temperature, deep eutectic solvent (DES) loading and catalysts loading on biodiesel yield were also investigated. XRF revealed CaO as the major constituent (90.86%) of catalyst. This was further confirmed by XRD and FTIR analyses. The maximum biodiesel yield was obtained at a DES loading of 12 g-wt%, catalyst loading of 14 g-wt% and calcination temperature of 900°C. The biodiesel produced was characterized as being composed mainly of saturated myristic acid (31.52%), lauric acid (18.12%), stearic acid (16.07%) and margaric acid (12.43%) with minor unsaturated components such as oleic acid.

Keywords: Biodiesel, catalyst, characterization, egg shell, waste cooking oil

Introduction

Biodiesel, mixture of fatty acid methyl esters (FAME), is generally produced from a varied range of edible and non-edible vegetable oils, animal fats, used frying oils and waste cooking oils by transesterification with methanol in presence of a catalyst (acid, base or biocatalyst). Due to benefits like renewable in nature, low cost and green house gas reduction potential, biodiesel is nowadays incorporated all over the world especially in developed countries like USA, France, Brazil in different proportions with diesel (Mohammed and Bhargavi, 2015). Biodiesel is quite similar to petroleum diesel fuel in its physical characteristics and can be used alone or mixed in any ratio with petroleum based diesel fuel in most existing modern four-stroke combustion ignition diesel engines with very few technical adjustments if any.

Currently, more than 95% of the biodiesel is made from edible oils or conventional sources like soybean, rapeseed, sunflower and palm (Basumatary, 2013). Continuous and large-scale production of biodiesel from edible oils may cause negative impact to the world such as depletion of food supply leading to economic imbalance. Taking these factors into consideration, non-conventional and non-edible oils definitely have the advantage over edible oils as biodiesel feedstocks. Therefore, exploring alternative biodiesel feedstocks like non-edible vegetable oils is an important objective for biodiesel industries (Sanjay, 2013).

Another solution proposed to the aforementioned drawbacks of biodiesel production is using alternative cheap feedstock such as WCO instead of fresh vegetable oil. WCO, which is much less expensive than edible vegetable oil, is a promising alternative to edible vegetable oil (Canakci and Van Gerpen, 2001). Several billions of gallons of waste vegetable oil are produced every year around the world, mainly from industrial deep fat fryers found in potato processing plants, factories manufacturing foods, and restaurants. Some of this wastage is already being re-used by other industries, such as in animal feed and cosmetics, but the amount that is still being wasted is alarming. The disposal of WCOs, if treated as waste, may cause blockage and odour problems while discharging into the drains and sewers, thus, using WCOs as a feedstock for biodiesel production would make commercial and environmental sense. Making biodiesel from WCO is much

the same as when using straight vegetable oil, except that the oil will need filtering first to remove debris, and because it has been used and most likely reheated several times, more FFAs. This high value of FFA will interfere with transesterification (in the presence of an alkali catalyst) resulting in the formation of unwanted soap by-product which requires expensive separations. Hence there is need to determine how much more sodium hydroxide (or potassium hydroxide) to add to neutralize these acids. Ease of separation and being cheaply available are among the other advantages of the heterogeneous catalyst. Moreover, the use of heterogeneous catalysts is reported to be the most economically viable process in a comparison of main four large scale continuous biodiesel production processes from WCO feedstock (Amir, 2010). The aim of this study therefore was to explore the potential application of a heterogeneous catalyst developed from egg shell for biodiesel production using WCO as feedstock.

Materials and Methods

Materials and chemical reagents

Chicken egg shells and WCO were obtained as wastes from a local restaurant in Benin City, Edo State. The reagents used include glycerol, methanol, sodium hydroxide, hydrochloric acid, choline chloride, benzene and ethanol. All reagents used were bought from a local chemical vendor in Benin City, Edo state and were of analytical grade.

Preparation of waste eggshells and waste vegetable oil

Eggshells were washed with water to remove sand and other unwanted particles. This was immediately followed by drying in an electric oven (vacutherm VT 6025) for 2 h. The dried shells were then crushed to smaller sizes and then calcined in a muffle furnace (Uniscope SM9080) for 4 h at 900, 800 and 700°C with a heating rate of 10°C/min. Then the calcined sample was refluxed in water at 60°C for 4 h and the solid particle was filtered and dried in hot air oven at 110°C for 5 h. The solid product was dehydrated by performing calcination at 600°C for 3 h to change the hydroxide form to oxide form. The developed catalyst was again crushed and the filtered with a mesh of size 200 micrometer. The waste cooking oil was filtered to remove all solid particles from it by passing it through a cotton cloth before transesterification.

Preparation of deep eutectic solvent

To prepare the deep eutectic solvent (DES), choline chloride (ChCl) was dried under vacuum at 100°C for 3 h because and then mixed with glycerol at 1:2 molar ratio of Choline Chloride to glycerol (Wei *et al.*, 2013). The mixture was stirred at 300 rpm at 70°C for 45 min until a homogeneous and transparent liquid was formed.

Preparation of catalyst

The prepared eggshell and DES were mixed at a various weights from 6 wt% to 16 wt% and 3 wt# to 18 wt%, respectively to the weight of oil in transesterification process. The calcined eggshell was weighed into 100 ml beaker and placed on a magnetic stirrer and then was added the prepared DES. The mixture was then stirred at 150 rpm for 20 min before the calcined eggshell was used as catalyst.

Transesterification process

The transesterification reactions were carried out in a 250 ml 3-necked round bottomed flask. The middle neck was used to insert a mechanical stirrer, one of the side necks was fitted with a water-cooled condenser, and the other neck was fitted with a temperature indicator. The speed of the mechanical stirrer was monitored using a digital tachometer.

The effects of WES calcination temperature (700 to 900°C), DES loading (3 to 18 wt.%), WES catalyst loading (6 to 16 wt.%) on the conversion to biodiesel were studied, based on preliminary studies.

The effect of calcination temperature on biodiesel production was investigated by varying the calcination temperature from 700 to 900°C, using a DES loading of 12 wt % and a WES catalyst loading of 14 wt %, the reaction was carried out. With a WES catalyst loading at 14 wt %, using the catalyst produced at calcination temperature of 900°C, the DES loading was varied from 3 to 18 wt %. The reaction was also carried out using catalyst produced at calcination temperature of 900°C, and at a DES loading of 12 wt % was varied from 6 to 16 wt %. The reaction were carried out at a temperature of 65°C, using 50 g of waste cooking oil, at a reaction time of 60 min and fixed 10:1 mol ratio of methanol to waste cooking oil. After the reaction was completed, the catalyst was separated by filtration and the transesterification products were allowed to settle overnight for the clear separation of biodiesel and glycerol.

Composition of the fatty acid methyl ester (FAME) was analyzed with gas chromatograph-mass spectrometry.

Catalyst and biodiesel characterization

The calcined samples were characterized by N₂ adsorption-desorption (Micromertics, Tristar 3000) for their BET surface area, pore volume and pore diameter. FTIR (FTIR 2000) and XRD (PAN analytical X'Pert PRO MPD, PW 3040/60) patterns were also obtained for the calcined samples. Scanning electron microscope (SEM) analysis was performed to confirm morphology of the samples. The biodiesel produced was characterized to determine its composition using a gas chromatograph- mass spectrometry (GC, SP-2100).

Results and Discussion

The SEM micrograph of the calcined egg shell at 900°C is shown in Fig. 1. The morphology of the calcined egg shell was investigated by SEM as shown in Fig. 1. From the SEM micrograph, the calcined egg shell had irregular shapes and sizes of micro morphology as previously observed in a related study (Khemthong *et al.*, 2012). The shape of calcined eggshell was formed by tiny crystals embedded on the large particles, probably due to the heterogeneous distribution in the mechanical properties of the eggshell used which can be regarded as an attribute of high catalytic activity (Jazie *et al.*, 2013). This characteristic heterogeneous morphology of CaO from calcined eggshell has been noted previously under

similar conditions (Jazie *et al.*, 2013; Tang *et al.*, 2013; Niju *et al.*, 2014).

Catalyst efficiency depends on several factors such as specific surface area, pore size, pore volume and active site concentration. The pore size properties of the catalyst are given in Table 1.

The catalyst prepared was characterized by large pore diameter (34.12Å) and high surface area (59.0717 m²/g) which allow reactants to diffuse easily into the interior of the catalyst as postulated elsewhere (Wan *et al.*, 2014; Niju *et al.*, 2014). Sharma *et al.* (2011) reported that a high pore diameter is desirable for better diffusion of reactant and product molecules. The total surface area catalyst from egg shell compared well with what Niju *et al.* (2014) observed (30.7 m²/g) for CaO catalyst obtained from eggshell under a condition of calcination of 800°C. In contrast, Lee *et al.* (2011) and Jazie *et al.* (2013) obtained low surface areas of 9 m²/g and 3.41 m²/g respectively at calcination temperature of 800°C. Differences in these observations might be due to the initial particle size of the starting material.

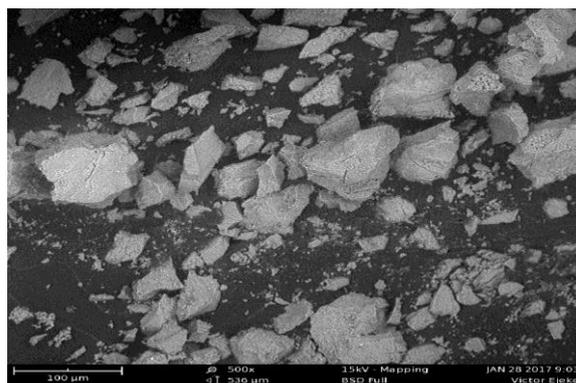


Fig. 1: Scanning electron micrographs of the catalyst

Table 1: Pore size characterization of catalyst

Physical property	Value
Surface area (m ² /g)	59.0717
Pore volume (cm ³ /g)	0.12
Mean pore diameter (Å)	34.12

Table 2: Chemical composition of catalyst

Major Oxides	(wt%)	Nature
CaO (Calcium Oxide)	90.86	Basic
Al ₂ O ₃ (Aluminum Oxide)	4.7	Amphoteric
Y ₂ O ₃ (Yttrium(III) Oxide)	2.6	Basic
Ag ₂ O (Silver(I) Oxide)	0.79	Basic
In ₂ O ₃ (Indium(III) Oxide)	0.49	Basic
SeO ₂ (Selenium(IV) Oxide)	0.15	Acidic
WO ₃ (Tungsten(VI) Oxide)	0.14	Acidic
Fe ₂ O ₃ (Iron(III) Oxide)	0.136	Basic
Lu ₂ O ₃ (Lutetium(III) Oxide)	0.041	Basic
BaO (Barium Oxide)	0.02	Basic
Cr ₂ O ₃ (Chromium(III) Oxide)	0.015	Amphoteric
TiO ₂ (Titanium(IV) Oxide)	0.009	Basic
V ₂ O ₅ (Vanadium(V) Oxide)	0.002	Amphoteric

X-ray fluorescence (XRF) was also used to determine the composition of catalyst. The composition is shown in Table 2. The result shows that the catalyst from eggshell mainly contained CaO (90.86%), considered a favourable base catalyst in biodiesel production with high basic strength, minor toxicity and easy reactions with water as shown in a

related study (Zhang *et al.*, 2010). The remaining 9.14% was composed of different metal oxides in trace amounts. These oxides have been reported to be active materials for transesterification (Birla *et al.*, 2012). The basic oxides (CaO, Y₂O₃, In₂O₃, and Ag₂O) will enhance the catalyst's basic strength (Boey *et al.*, 2011), while the acidic components (SiO₂, SeO₂, WO₃) have the potential to mediate esterification of the feedstock's free fatty acid (FFA) content as shown elsewhere (Boey *et al.*, 2011).

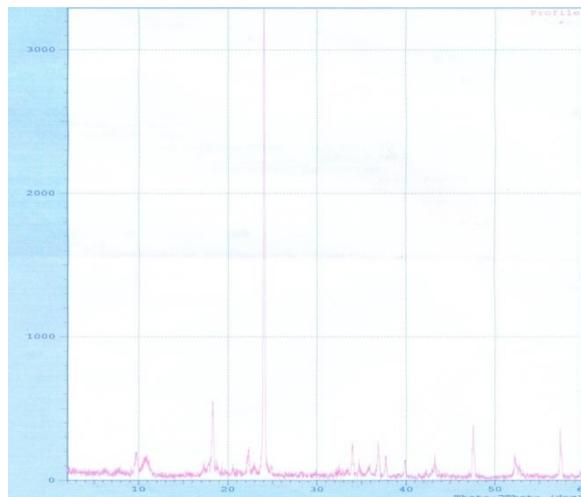


Fig. 2: XRD patterns of catalyst

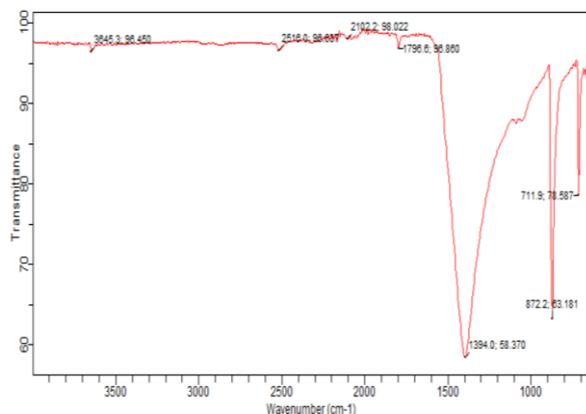


Fig. 3: FTIR pattern for catalyst

The major components of the catalyst were further confirmed by X-Ray diffractometer analysis. The X-ray diffractometer pattern is shown in Fig. 2. The XRD analysis of CaO shows a sharp peak of its separated metal oxide crystalline phases calcium and oxygen, which corroborated CaO as the dominant composition of the catalyst prepared. These peaks are similar with those reported by Sharma *et al.* (2011) and Wei *et al.* (2009) under similar conditions.

The FTIR spectrum of the catalyst derived from waste egg shell is shown in Fig. 3. The spectra band at 3645.96 cm⁻¹ is detected over the catalyst that can be assigned to the presence of O-H stretching vibrations of Ca(OH)₂ due to the moisture absorption on the surface of the catalyst (Tang *et al.*, 2013). While peak at 1394.0–1436 cm⁻¹ corresponds to the bending vibration of Ca-O stretching. The bands at 872.2 and 711.9 cm⁻¹ are assigned to the C-O asymmetric stretching, out-of-plane bending and in-plane bending vibration mode of the carbonate due to incomplete calcination of the eggshell.

To determine the composition of the biodiesel produced, GC-MS was used. The composition of the biodiesel is as shown in Table 3.

Table 3: Fatty acid compositions of biodiesel using GC-MS

Fame	Formula	Mol. Wt.	Composition (%)
Palmitic	C ₁₅ H ₃₁ CO ₂ CH ₃	256	7.56
Stearic	C ₁₇ H ₃₅ CO ₂ CH ₃	284	16.07
Oleic	C ₁₇ H ₃₃ CO ₂ CH ₃	282	5.04
Octadecenoic	C ₁₉ H ₃₆ O ₂	296	4.17
Lauric	C ₁₂ H ₂₄ O ₂	200	18.12
Myristic	C ₁₄ H ₂₈ O ₂	228	31.52
Tridecanoic	C ₁₄ H ₂₈ O ₂	228	1.04
Caprylic	C ₉ H ₁₈ O ₂	158	1.42
Capric	C ₉ H ₁₈ O ₂	158	1.32
Margaric	C ₁₇ H ₃₄ O ₂	270	12.43
Pentadecanoic	C ₁₇ H ₃₄ O ₂	270	1.31

The methyl ester produced was composed mainly of saturated myristic acid (31.52%), lauric acid (18.12%), stearic acid (16.07%) and margaric acid (12.43 %) with minor unsaturated components such as oleic acid.

The catalyst was tested by conducting transesterification reaction to determine the catalyst dosage, DES amount and calcinations temperature on biodiesel yield. Using a fixed amount of waste cooking oil of 50 g, constant reaction time (60 min) and fixed 10:1 mol ratio of methanol to waste cooking oil. The dosage of DES was varied and the biodiesel yield was investigated as shown in Fig. 4.

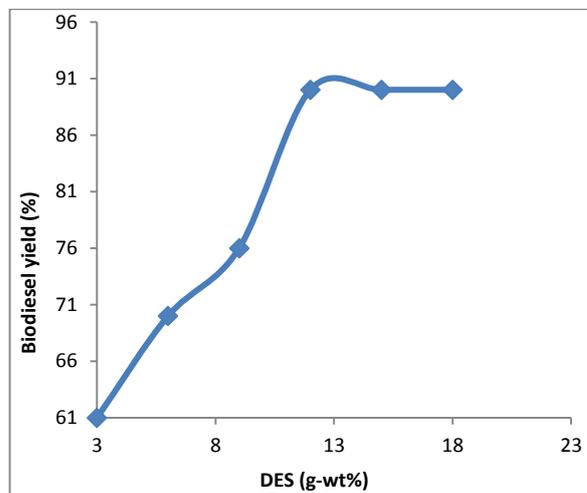


Fig. 4: Effect of DES amount on the biodiesel yield

From Fig. 4, it is observed that as the amount of DES increased, the biodiesel yield also increased with the maximum of 91 % occurring at DES of 12 g-wt%. Any further increase in the DES amount did not result in any further increase in the biodiesel yield. This may be due to the formation of more CaO and reduction in reversal of CaO to Ca(OH)₂. The effect of amount of catalyst on biodiesel yield was investigated as shown in Fig. 5.

Figure 5 shows the effect of catalyst amount on the biodiesel yield. From this plot, it is observed that as the amount of the catalyst is increased from 6 g-wt% to 14 g-wt%, there was a corresponding increase in the biodiesel yield from 67 to 91%. A further increase in catalyst amount led to a reduction in the biodiesel yield. This observation can be attributed to the availability of active sites on the catalyst for transesterification reaction (Birla *et al.*, 2012). Reaction rates increased as reactants occupied more catalytic sites until saturation was reached. The impact of mass transfer limitation

became more significant at higher catalyst loading, thus limiting reactants' accessibility to active sites (Tang *et al.*, 2013). The transesterification reaction is strongly dependent on the weight of catalyst which consequently affects the yield. An adequate increase in catalyst concentration results in an increase in the number of its active sites, thereby increasing the yield of methyl ester (Omar and Amin, 2011).

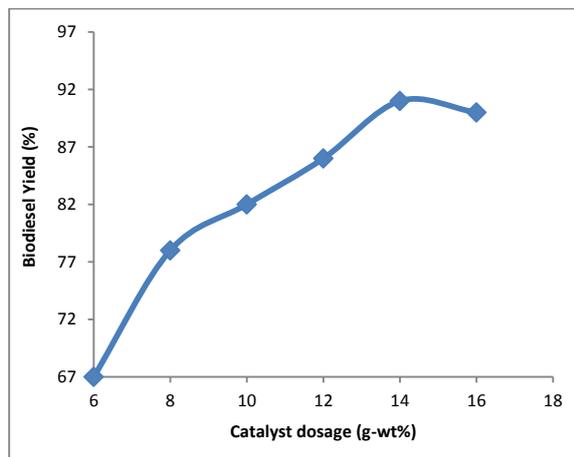


Fig. 5: Effect of catalyst dosage on the biodiesel yield

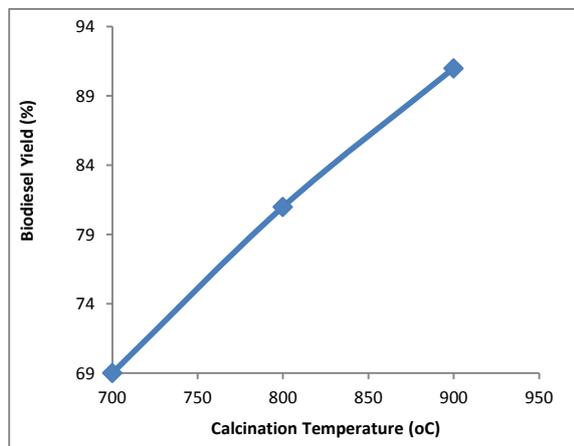


Fig. 6: Effect of calcination temperature on biodiesel yield

The effect of calcinations temperature on biodiesel yield was investigated as shown in Fig. 6. Fig. 6 shows the plot of biodiesel yield against the calcination temperatures (700, 800°C and 900°C) of the waste eggshell catalyst. It was observed that the biodiesel yield increased 61% as the calcinations temperature increased from 700 to 900°C. The possible reason for this observed trend is that the calcination at higher temperatures led to desorption of carbon dioxide from the egg shell catalysts, producing basic sites that catalyzed transesterification of the waste cooking oil with methanol as observed in a related study (Jazie *et al.*, 2013).

Conclusion

The present study investigated the use of a cost-effective and environment-friendly catalyst and waste cooking oil for the production of biodiesel. Waste eggshells were used to develop the catalyst for this process. It can be concluded that:

1. The experimental results revealed that catalyst obtained from eggshell calcined at 900°C had excellent activity and stability during transesterification reaction.
2. The conditions, which yielded a maximum conversion of waste vegetable oil of 91% for developed

catalyst were, deep eutectic solvent loading of 12 g-wt.% and catalyst loading 14 g-wt.%

3. The catalyst developed from chicken eggshell showed potential for industrial application as catalyst in the transesterification of waste vegetable oil to biodiesel.

References

- Amir MD 2010. Developing Biochar-Based Catalyst for Biodiesel Production. M.Sc Thesis, The University Of British Columbia, Vancouver
- Basumatary S 2013. Non-conventional seed oils as potential feedstocks for future biodiesel industries: A brief review. *Res. J. Chem. Sci.*, 3(5): 99-103.
- Birla A, Singh B, Upadhyay SN & Sharma YC 2012. Kinetics studies of synthesis of biodiesel from waste frying oil using heterogeneous catalyst derived from snail shell. *Bioresour Techn.*, 106:95-100.
- Boey P, Maniam G, Hamid S & Ali DMH 2011. Crab and cockle shells as catalyst for the preparation of methyl esters from low free fatty acid chicken fat. *Chem. Eng. J.*, 88: 283-288.
- Canakci M & Van Gerpen J 2001. Biodiesel production from oils and fats with high free fatty acids. *Trans. Am. Soc. Agric. Eng.*, 44(6): 1429-1436.
- Jazie A, Pramanik H & Sinha SSK 2013. Eggshell as eco-friendly catalyst for transesterification of rapeseed oil: Optimization for biodiesel production. *Int. J. Sust. Develop. Green Econ.*, 2: 2315-4721.
- Khemthong P, Luadthong C, Nualpaeng W, Changsuwan P, Tongprem P, Viriya-empikul N, Faungnawakij K 2012. Industrial eggshell wastes as the heterogeneous catalysts for microwave assisted biodiesel production. *Catal. Today*, 190: 112-116.
- Lee HV, Yunus R, Juan JC & Taufiq-yap YH 2011. Process optimization design for jatropha-based biodiesel production using response surface methodology. *Fuel Process*, 92: 2420-2428.
- Mohammed AR & Bhargavi R 2015. Biodiesel production from waste cooking oil. *J. Chem. Pharm. Res.*, 7(12): 670-681.
- Niju S, Meera KM, Begum S & Anantharaman N 2014. Modification of egg shell and its in biodiesel production. *J. Saudi Chem. Soc.*, 18 (5): 702-706.
- Omar WNN & Amin NAS 2011. Optimization of heterogeneous biodiesel production from waste cooking palm oil via response surface methodology. *Biomass Bioenergy*, 35: 1329-1338.
- Sanjay B 2013. Non-conventional seed oils as potential feedstocks for future biodiesel industries: A brief review. *Res. J. Chem. Sci.*, 3(5): 99-103.
- Sharma YC, Singh B & Korstad J 2011. Latest developments on application of heterogeneous basis catalysts for an efficient and eco-friendly synthesis of biodiesel. *Fuel*, 90: 1309-1324.
- Tang Y, Xu J, Zhang J & Lu Y 2013. Biodiesel production from vegetable oil by using modified Cao as solid basic catalysts. *J. Clean. Prod.*, 42(0): 198-203.
- Wan L, Liu H & Skala D 2014. Biodiesel production from soybean oil in subcritical methanol using MnCO₃/ZnO as catalyst. *Appl. Catal. B: Environ.*, 152-153: 352-359.
- Wei H, Shaokun T, Hua Z & Songjiang T 2013. Activation of commercial CaO for biodiesel production from rapeseed oil using a novel deep eutectic solvent. *Ind. Eng. Chem. Res.*, 52: 11943-11947.
- Zhang J, Chen S, Yang R & Yan Y 2010. Biodiesel production from vegetable oil using heterogeneous acid and alkali catalyst. *Fuel*, 89: 2939-2944.