
Review of Microwave Irradiation Assisted Transesterification of Vegetable Oil Using Calcium Oxide Derived from Renewable Sources as Heterogenous Catalyst

By

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ABSTRACT

Conventional transesterification for biodiesel production is well-established and becoming increasingly important, there remain considerable inefficiencies in existing transesterification processes. The application of microwave irradiation of vegetable oil for biodiesel production significantly reduces the reaction time. Although microwave technology has advanced in other food industries, pharmaceutical and polymer chemistry related research in industry; its potential large scale biodiesel is yet to be exploited. Recent laboratory scale microwave applications in biodiesel production have shown that this technology can achieve superior results over conventional techniques. This paper review the application of calcium oxide derived from renewable resources as heterogeneous catalyst for biodiesel production in a microwave irradiation assisted transesterification process. The review shows that calcium oxide derived from different renewable sources can be effectively used as heterogeneous catalyst for biodiesel production in microwave irradiation assisted transesterification process. It was further revealed that the process is characterized with short reaction time and reduced energy consumption when compared to conventional transesterification method. The biodiesel obtained from this process shows similar properties to biodiesel obtained from conventional process and petroleum diesel. The potential viability of waste derived calcium oxide as as a reusable heterogeneous catalyst in biodiesel production was established.

Key words: Biodiesel, calcium oxide, catalyst, heterogeneous, microwave, shell, vegetable oil

INTRODUCTION

Energy is a vital index for socio-economic and sustainable development of the most nations of the world (Basu *et al.*, 2014). Fossil fuels are presently the most dominant source of primary energy supply accounting for about 88% of global energy supply (Moriarty and Wang, 2015). Chalvatzis and Ioannidis (2017) predicted that the global demand for energy will increase by about 45% between

the year 2015 and 2030. The authors added that these increment will continue to over 300% at the end of this century. This rise is attributed to increase in human population, growing global economy and industrialization (Cabeza *et al.*, 2018). These has raised a lot of concerns over the economic and environmental consequences triggered by the accelerated rate of fossil fuel exploration from its natural reserves,

pessimism about future availability and global climatic change arising greenhouse gas emissions (Garba *et al.*, 2014). It is obvious from Table 1.0 that unconventional

fossil fuels can only substantially serve as a source of energy for a limited period with good political will.

Table 1: Proven world reserves of fossil fuels for 2013

Type of Fossil fuel	Estimated Global reserve	Approximate length of time
Coal (tonnes)	0.89×10^{12}	113
Petroleum (bbl)	1687.9×10^9	54
Natural gas (m ³)	185.7×10^{12}	53.3
*Nuclear (MTOE)	47,600	82

Source: Ozoegwu *et al.*, 2017; British Petroleum (2014)

In addition to the above, the combustion of fossil derived fuels accounts for approximately 66.67% of the total global anthropogenic CO₂ emissions to the atmosphere (Mohan *et al.*, 2006). Presently, there are several extensive research initiatives directed towards the development of renewable energy resources. Renewable energy sources have the potential capacity for global energy security. These energy resources are economically and environmentally beneficial and therefore capable of mitigating global warming and climate change (Melikoglu *et al.*, 2018). Different forms of renewable energy resources include geothermal, hydropower/hydroelectric, marine/wind ocean, and biomass. Biomass is presently the world's fourth most consumed energy source, after, petroleum crude oil, natural gas and coal (Oliveira *et al.* 2013). Biomass can be used for production of biofuels such as biogas, bioethanol, biomethanol and biodiesel.

Biodiesel is recognized as an alternative fuel to petroleum diesel due to their similarity in properties (Atabani *et al.*, 2012). It is a mono-alkyl esters of long chain fatty acids derived from transesterification of

vegetable oil with alcohol in the presence of different type (acidic, alkali and enzymatic) of catalysts (Kataria *et al.*, 2018; Hsiao *et al.*, 2017). It can be used directly as a substitute for diesel fuel or blended with it, without the need for diesel engine modification (Bello and Makanju, 2011; Bello *et al.*, 2016). Biodiesel possess higher flash point, higher cetane number, low viscosity, higher lubricity, excellent biodegradability and environmentally friendliness due to its lower carbon monoxide emissions compared to conventional diesel fuels (Refaat *et al.* 2008). The use of biodiesel has grown tremendously in the last few years (Bozbas, 2005). A major hurdle towards widespread commercialization is the high cost of edible oil which are most widely used as feedstock for its commercial production in developed countries of the world (Refaat *et al.*, 2008). The high prices of these oils in the global market have sharply increased the overall biodiesel production cost. According to Lim *et al* (2010) approximately 70 – 95 % of total cost of biodiesel production arises from the cost of these raw materials. One way of reducing the biodiesel production cost is to use less expensive feedstock such as non-edible oils, animal fats, waste food oil, and

by-products of the vegetable oil refining (Veljkovic *et al.*, 2006). Besides using inexpensive feedstock, researchers are focusing on minimizing the cost of production by improving on the production technology (Refaat *et al.*, 2008). This is because commonly used conventional, homogeneous alkaline (NaOH or KOH) and acid (H_2SO_4 or HCl) catalytic transesterification processes are characterized with a number of drawbacks such as catalyst consumption, corrosion of equipment, soap formation, waste water generation (Hsiao *et al.*, 2011) and slower reaction rate at room temperature (Vicente *et al.*, 2004).

More recently, research attention has been shifted towards the use of heterogeneous catalyst for the transesterification of vegetable oil. This is due to its significant advantages over homogeneous catalyst such as elimination of multiple purification steps, ease of catalyst recovery, higher catalytic activity, catalyst reusability, less toxicity and tolerance for high FFA content and consequently lowering of production cost (Lee *et al.*, 2009). Heterogeneous base catalysts of alkaline earth metal oxides have been more actively investigated for biodiesel production (Khemthong *et al.*, 2012). These catalysts include alkali-doped metal oxides such as CaO, MgO, SrO- Al_2O_3 , K_2CO_3/Al_2O_3 , and Ca(OH) $_2$ - Fe_3O_4 , other examples of alkaline catalyst include sodium aluminate and calcium ethoxide (Khemthong *et al.*, 2012; Chang *et al.*, 2017). Calcium oxide (CaO) is one of the most commonly used heterogeneous base catalysts for the transesterification of vegetable oil among all these catalyst due to its higher catalytic activity, mild reaction conditions,

reusability, and low cost, availability, non-corrosive, greater tolerance for water and high free fatty acids (FFAs) in oil, improve biodiesel yield and purity, ease of product purification process and separation (Hsiao *et al.*, 2011; Kesic *et al.*, 2016). Several literatures such as Boey *et al.* (2011); Sharma *et al.* 2011; Chouhan and Sarma, (2011); Motasemi, and Ani (2012); Kesić *et al.* (2016) have reported expository successful application of different inorganic calcium oxide based catalyst in heterogeneous transesterification for biodiesel production. According to Khemthong *et al.* (2012) calcium oxides derived from commercial inorganic precursor (compounds of carbonate, nitrate, hydroxide and acetate) are not economical for biodiesel production. The author further added that CaO from waste materials also exhibits excellent catalytic and are therefore potential alternative heterogeneous catalyst for biodiesel production (Adewuyi *et al.*, 2012; Tang *et al.*, 2013). These catalysts can be obtained from thermal decomposition of calcium carbonate ($CaCO_3$) present in calcite or animal products (Chakraborty *et al.*, 2010; Buasri *et al.*, 2015). These organic derived catalyst opens door for renewable catalyst development and simultaneous waste material recycling. A number of studies have been documented on the use of renewable CaO from different waste materials for vegetable oil transesterification using conventional heating system. Conventional transesterification is associated with inefficient heat transfer, higher energy consumption and longer reaction time (1 - 5h) for higher (>95%) biodiesel yield to be attained (Motasemi and Ani, 2012; Singh *et al.*, 2014). All these factors limit the commercial viability of biodiesel production. It is proposed that a continuous

transesterification process can help to lower the production costs and the recovery of high-quality by-products, such as glycerol, which is expected to compensate the feedstock costs (Ani and Elhameed, 2014).

Microwave irradiation is an alternative heating system that have gained a wide attention during the last decade as an efficient heat transfer medium (Motasemi and Ani, 2012; Singh *et al.*, 2014). Microwave irradiation is considered as green and environmental friendly heating process for biodiesel production due to its lower energy consumption, less reaction times and lower solvent requirements, excellent product selectivity and yield, less waste generation (Singh *et al.*, 2015; Joshi *et al.*, 2016). The process is characterized with low energy cost (two thirds far less than) in comparison with conventional heating approach. It has high reaction rate and tolerance for water presence (Buasri and Loryuenyong, 2017). According to Yakoob *et al.* (2008) microwave irradiation transesterification reactions can be completed in seconds or relatively few minutes. To the best of the authors' knowledge, there is no documented review on the use of organic derived calcium oxide in a microwave irradiation assisted system.

This study is therefore aimed at providing a review the application of calcium oxide derived from waste materials as potential catalyst for the synthesis of biodiesel from vegetable oil in a microwave irradiation transesterification process.

FEEDSTOCK FOR BIODIESEL

Oil and Fat

Globally, more than 350 oil-bearing crops have been identified as potential sources of vegetable oil for biodiesel production. The availability of feedstock depends on the regional climate, geographical locations, local soil conditions and agricultural practices. Among possible alternative biodiesel feedstocks are non-edible oil (Atabani *et al.*, 2012). Table 3 shows some different feedstock for biodiesel production. Non-edible oil plants are well adapted to arid, semi-arid conditions and require low fertility and moisture to grow. They are not suitable for human consumption due to the presence of toxins in the oils. For all these reasons, the use of non-edible oils as raw material for biodiesel production is promising for the biodiesel industry (Marinkovic *et al.*, 2016).

Table 3: Feedstock for biodiesel production

Edible oil	Non edible oil	Animal fat
Coconut	Jatropha oil	Beef tallow
Moringa	Used flying oil	Poultry fat
Fish oil	Neem oil	Sheep tallow
	Rubber oil	
Maize oil	Karanja oil	
Palm kernel oil	Pognominata	
Palm oil	micro algae oil	
Canola oil	Cotton seed oil	
Sesame seed oil	Camelina sativa	
Rice bran oil	Tobacco seed oil	

Source: Atabani *et al.*, (2012); Schenk *et al.*, (2008).

Alcohol

The alcohols used for transesterification are generally short chain alcohols such as methanol, ethanol, propanol, and butanol (Lucia *et al.*, 2006). Methanol and ethanol are the most commonly used alcohol due to their relative abundance and lower boiling point. Methanol is preferable due to low cost and the ease of recovery of downstream unreacted methanol is much easier. Methanol has a physical and chemical advantage (polar and short chain alcohol) over the other alcohol, react and easily dissolve the alkaline catalysts (Balat and Balat, 2010). Methanol is reported to be the most appropriate solvent for microwave transesterification reaction due to its higher potential for microwave absorption and low cost. It is also characterized with smaller molecular size that facilitates free localized rotations thereby leading to efficient localized superheating. This phenomenon is known to promote faster reaction completion since larger alcohol molecular size slowdown reaction by hindering localized rotation (Jain *et al.*, 2018).

Catalyst

Homogeneous and heterogeneous catalysts are used for transesterification. Homogeneous catalysts are more often used due to their superior performance in

transesterification reactions. These catalysts can be either acidic or basic in nature. The choice of catalyst depends on the free fatty acids (FFA) content in the raw oil (Stavarache *et al.*, 2005). Typical examples of catalysts employed for transesterification are homogeneous alkaline catalysts (NaOH or KOH) and acid catalysts (H₂SO₄ or HCl) (Hsiao *et al.*, 2011).

TRANSESTERIFICATION

Transesterification is the most viable process for biodiesel production. It is a process of exchanging the alkoxy group of an ester compound by another alcohol. Conventional transesterification is the most techniques for biodiesel production (Abdullah *et al.*, 2007). Stoichiometrically, a molar ratio of alcohol to oil of 3:1 is required (Stavarache *et al.*, 2005). Since the reaction is reversible, a higher molar of alcohol is required to shift the equilibrium to the product side (Vyas *et al.*, 2011). The production of biodiesel has been carried out using conventional heating systems. However, these systems are inefficient and usually require longer reaction times (Nezihe and Aysegul, 2007).

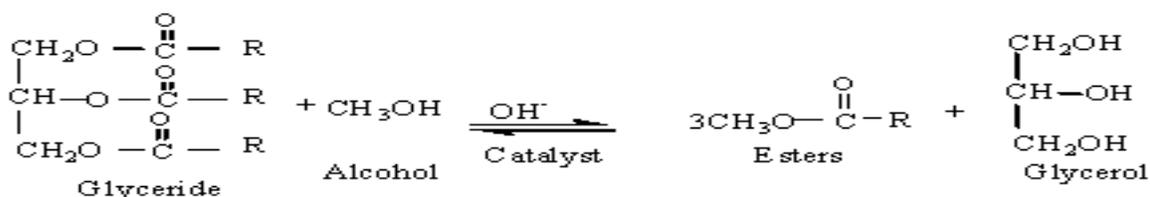


Figure 1: Transesterification reactions of triglycerides with alcohol (Abdullah *et al.*, 2007).

Acid-catalyzed transesterification is only effective when the oil has a high amount of free fatty acids. Acid catalyzed transesterification requires longer reaction time. Acid-catalyzed methods use acids such as H_2SO_4 and H_3PO_4 and are useful when a high amount of free acids (<3%) are present in the vegetable oil, but the reaction time is very long (48–96 h), and a high molar ratio of alcohol to oil (20:1) is needed.

Homogenous catalysts

The use of these homogenous catalysts in transesterification processes is characterized with high energy consumption, equipment corrosion problem, and non-reusability of catalyst, total catalyst consumption, formation of soaps, multiple process steps and the difficulty in transesterification of triglycerides with high free fatty acid (FFA) content. Moreover, the downstream processes such as the recovery of glycerol, the removal of inorganic salts and water from the product, catalyst removal and the treatment of alkaline waste water are complex and therefore incur additional cost (Hsiao *et al.*, 2011). In addition to the above challenges the reaction is known to be extremely slow under room temperature (Vicente *et al.*, 2004). The complicated post-treatment process deems the application of homogeneous catalysts as impractical and inefficient especially for industrial-scale applications (Tran *et al.*, 2016; Chang *et al.*, 2017).

Heterogeneous catalyst

Heterogeneous catalysts have emerged as an effective alternative catalyst for a more sustainable biodiesel production (Roschat *et al.*, 2016). Heterogeneous catalysts are characterized by a number of advantages in comparison to the

homogeneous catalysts. Several washing steps can be eliminated, the separation process is easy to handle, reaction is much faster, low cost, and environmentally friendly, catalyst can be reused, less toxicity, high catalytic activity, tolerance for high FFA content and consequent reduction in the production cost (Lee *et al.*, 2009). Heterogeneous base catalysts of alkaline earth metal oxides have been investigated for biodiesel production (Khemthong *et al.*, 2012). These catalysts include alkali-doped metal oxides such as CaO , MgO , $SrO-Al_2O_3$, K_2CO_3/Al_2O_3 , and $Ca(OH)_2-Fe_3O_4$. Other examples of alkaline catalyst are sodium aluminate and calcium ethoxide (Ken *et al.*, 2017). Among various reported heterogeneous acidic and basic catalysts, naturally derived CaO based basic catalysts has been used extensively due to its easy availability and low cost (Marinkovic *et al.*, 2016).

Calcium oxide (CaO) as heterogeneous catalyst

Calcium oxide (CaO) is a basic anhydride. CaO as a solid base catalyst is characterized by higher catalytic activity, reusability, cheapness, availability, non-corrosiveness, greater tolerance for water and free fatty acids (FFAs) (Hsiao *et al.*, 2011; Kesic *et al.*, 2016). According to Khemthong *et al.*, (2012) calcium oxides are primarily derived from the compounds of carbonate, nitrate, hydroxide and acetate which are known to be commercial inorganic precursor (feedstock). Wei *et al.*, (2016) reported the transesterification of palm oil under conventional heating system via the use of commercial grade CaO as heterogeneous catalyst. The optimum conditions were methanol/oil molar ratio of 9:1, catalyst of

5%, stirring speed of 450 r/min and reaction time of 180 min. According to Chakraborty *et al.* (2010) the use of heterogeneous catalyst from commercial precursors would lead to an increase in the cost of biodiesel synthesis. The author further reported that CaO derived from waste materials are potential alternative heterogeneous catalyst for biodiesel production. This recent development in biodiesel production is known to be very eco-friendly, environmentally friendly and cheap. Studies have been conducted on the use of ash from waste shell as heterogeneous catalyst for biodiesel production. CaO contained in ash from waste materials is a potential heterogeneous catalyst. This new orientation for biodiesel production is eco-friendly and economical (Khemthong *et al.*, 2012). CaO as heterogeneous catalyst can be produced from different sources such as chicken eggshell, mollusk shell, golden apple snail shell, mussel shell, oyster shell, and mud crab shell (Boey *et al.*, 2011; Jazie *et al.*, 2013). In Particular, eggshells constitute about 10-11% of the total weight of the whole eggshell are composed of approximately 85-95% of CaCO₃, weighing 5.5 grams of mass and the remaining 5% contains calcium phosphate (0.3%) and magnesium carbonate (0.3%). Calcium oxide (CaO) is a basic anhydride,

which enhances its catalytic activity (Chakraborty *et al.*, 2010; Krithiga and Sastry, 2011; Jazie *et al.*, 2013, Ngoya *et al.*, 2017). Calcium oxide (CaO) does not occur naturally, it is made from calcination of calcium carbonate at high temperatures. Calcination of CaCO₃ takes place at 500-600 °C but using higher temperature above 700 °C atmospheric pressure improves the performance of the catalyst and leads to a complete decomposition of CaCO₃ to produce CaO and CO₂ (Krithiga and Sastry, 2011; Sharma *et al.*, 2011; Navajas *et al.*, 2013). The BET analysis of the calcined eggshell and other sources is shown in Table 4. CaO obtained from these wastes possess excellent catalytic properties such as high basic strength and tolerance of high Free Fatty Acid (FFA) oil, less environmental hazard impacts due to its low solubility in methanol (Adewuyi *et al.*, 2012; Khemthong *et al.*, 2012; Rezaei *et al.*, 2013; Tang *et al.*, 2013). The CaO derived from eggshell are associated with large pore diameter and higher surface area shown in Table 2. The presence of these large pore diameter and high surface area are necessary for satisfactory diffusion of reacting substances and product formed in and out of the core of catalyst (Kawentar and Budiman, 2013; Sharma *et al.*, 2011).

Table 4: Surface area characteristics of calcium oxide from different sources

Feedstock	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size (Å)	Author
Eggshell	24	0.04	66.00	Buasri <i>et al.</i> (2014)
Eggshell	30.9	0.07	91.2	Ngoya <i>et al.</i> (2017)
Eggshell	59.07	0.1098	-	Jazie <i>et al.</i> (2012)
Eggshell	125.927	-	-	Asri <i>et al.</i> (2017)
Commercial grade CaO	9.2 - 68.57	-	-	Asri <i>et al.</i> (2017), Ismail <i>et al.</i> (2012); Kazi <i>et al.</i> (2014)
Limestone	13.2	-	-	Alonso <i>et al.</i> (2010)
Dolomite	14.6	-	-	Alonso <i>et al.</i> (2010)

Chemistry of CaO catalyzed transesterification

The mechanism of CaO catalytic transesterification is depicted by the scheme reported by Boey et al (2011) is shown in Figure 2. It is observed in this Figure 2, that at the beginning, reaction with the

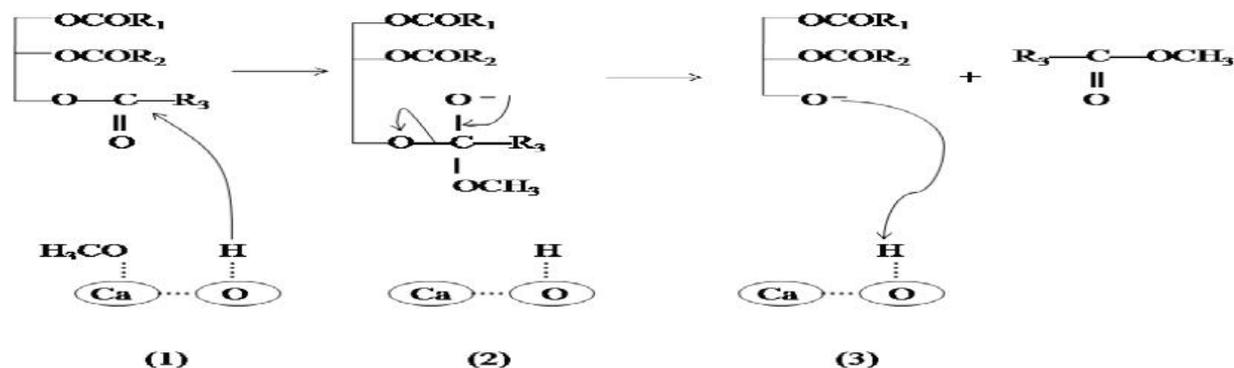


Figure 2: Mechanism of CaO catalyzed of triglycerides with methanol

This is followed by re-arrangement and disintegration of the intermediate into diglyceride anion and fatty methyl ester (biodiesel). The diglyceride anion is subsequently stabilized due to protonation from the catalyst surface reaction to produce a diglyceride molecule with simultaneous regeneration of the catalyst surface active site. The methoxide anion further attacks another carbonyl carbon atom in the diglyceride to produce another mole of biodiesel and a monoglyceride. These process is repeated all over again until all the three carbonyl centers of the triglyceride have been exhaustively attacked by the methoxide ions to produce three moles of biodiesel (methyl ester as the desired product and one mole of glycerol as a co-product (Boey *et al.*, 2011; Marinković *et al.*, 2016).

methoxide ion attached to the catalyst surface attacks the carbonyl carbon of the vegetable oil (triglyceride) molecule resulting into the formation of an unstable tetrahedral intermediate.

Table 5 shows the summary of reported literature on the use of waste derived calcium oxide for biodiesel synthesis. Nearly in all these studies conventional heating medium is employed. Conventional heating method is associated with inefficient heat transfer. Conventional heating of reactants during transesterification requires more energy and longer reaction time to obtain higher (>95%) biodiesel yields (Motasemi and Ani, 2012; Singh *et al.*, 2014). All these are factors that limit commercial viability of biodiesel production. Biodiesel production technology can also be improved via process intensification technologies that will ultimately increase the production process efficiency and further reduce operating costs (Ani and Elhameed, 2014).

Table 5: Conventional Heterogeneous Catalyst Transesterification of Vegetable Oil using Calcium oxide (CaO) derived from Waste Materials

Feedstock	Source	Catalyst conc (Wt%)	Time (hr)	Temp (°C)	Yield (%)	Molar ratio	Reference
Palm olein	Eggshell	5	2	65	95	5:1	Boey et al.,(2009)
Soybean Oil	Eggshell	3.0	8	65	85.6	10:1	Nakatani et al. (2009)
Palm oil	Eggshell	3.0	2	65	95	12:1	Viriya- Empikul <i>et al.</i> , 2010
Palm oil	Eggshell	3.0	4	65	95	8:1	Olutoye <i>et al.</i> (2011)
Karanja oil	Chicken eggshell		2		95	9:1	Sharma <i>et al.</i> (2011)
Soybean oil	Eggshell	2.5	-	65	98	9:1	Chouhan and Sarma, (2011)
Waste cooking oil	Eggshell	1.5	2	65	94	12:1	Tan <i>et al.</i> (2015)
Castor oil	Mussel shell	2.0	3	60	91.17		Nuridin <i>et al.</i> (2015)
Castor Oil	Mud clam shell	3.0	2	60	96.7	14:1	Ismail <i>et al.</i> (2016)
Used cooking oil	Snail eggshell	3.0	1	65	92.5	9:1	Kaewdang <i>et al.</i> (2017)
Palm oil	Chicken eggshell	25	2.5	65	92	8:1	Win, and Khine (2016)

MICROWAVE FUNDAMENTALS

Microwaves are electromagnetic spectrum whose wavelengths ranges from 1 mm to 1 m with corresponding frequencies between 300 MHz and 300 GHz. Several frequencies that are mostly used for radar, cellular phones and television satellite communications exists within this electromagnetic spectrum. In this case of microwave heating, 0.915 and 2.45 GHz are the two most usually employed frequencies (Datta and Anantheswaran, 2000; Lauf *et al.*, 1993). Microwave furnaces with the capacity for processing frequency within 0.9 to 18

GHz have been developed for material processing (Lauf *et al.*, 1993). Microwaves can be generated by different devices such as gyrotrons, klystrons, magnetrons, power grid tubes and traveling wave tubes. Magnetron is however most frequently used device due its reliability, efficiency, cheap availability in comparison to other sources (Chandrasekaran *et al.*, 2012).

Microwave irradiation is a well-known technique for acceleration of chemical reactions due to ability to deliver energy to the reactant species directly. It is a more effective and fast heat transfer process

since its reaction can reach completion in a much shorter time than the conventional process (Lidstrom *et al.*, 2001). The irradiation assisted reactions are enhanced due to the selective absorption of microwave energy by polar molecules, non-polar molecules being inert to the MW dielectric loss (Koopmans *et al.*, 2006). Microwave radiation is located between infrared radiation and radio waves. During microwave irradiation, the bonds are neither formed nor broken but the energy is rapidly transferred to the sample (Yakoob *et al.*, 2008). Microwave heating is associated with the ability of a materials to absorb microwave energy and convert it into heat (Chandrasekaran *et al.*, 2013). Yin *et al.*(2012)

state that this absorption potential depends on the ability of the material to be polarized by an electric field (dielectric constant) and the efficiency by which the electromagnetic radiation can be effectively transformed into heat (dielectric loss). Microwave irradiation process was first mentioned in 1986 when Gedye and Guigere reported a comparative assessment of conventional heating and microwave irradiation and reported a significant reduction in reaction time for microwave process (Lidstrom *et al.*, 2001). The obtained data from the studies revealed a significant reduction in reaction time for microwave process. Table 6 summarized the unique characteristic of microwave heating process as against conventional method.

Table 6: Comparison between microwave and conventional heating technique

Microwave dielectric heating	Conventional thermal heating
Energy conversion	Energy transfer
Uniform heating	Superficial heating
Very rapid and efficient	Slow and inefficient
Presence of hot spots	No hot spots
Dependent on the properties of material	Exhibit less dependent
Heating can be precisely controlled	Heating is less controllable

Source: (Yin *et al.*, 2012)

Microwave Assisted Transesterification for Biodiesel Production

The application of microwave irradiation in transesterification is a relatively new and still in the embryonic stage due to paucity of research and adequate knowledge in this area. Microwave assisted process operates primarily based on the polarization and the explicit contact of microwaves with the raw material and dielectric properties of solvent employed (Jain *et al.*, 2018). Microwave transesterification is more efficient due to lower reaction time and ease of products separation (Breccia, 1999). In microwave

assisted biodiesel production unit, the reactants such as vegetable oil, alcohol and catalyst are usually mixed using suitable stirring device and heated by the microwave heat source. The reactants are subjected to the microwave irradiation for the required reaction time of few min. The separation of the biodiesel and glycerin phase takes 30 to 60 min, after that the crude biodiesel is subjected to water washing to remove impurities and dried to remove the moisture content. The reaction time and setting time required for this method is low and hence the production cost is envisaged to be significantly reduced. (Yakoob *et al.*, 2008).

The yield and quality of biodiesel produced via microwave irradiation is comparable to yield from conventional transesterification and satisfy the international biodiesel standards as shown in Table 8 (Venkatesh *et al.*, 2011; Yakoob *et al.*, 2008). Table 6 shows reported studies on the application of microwave enhanced process for biodiesel

production using different homogenous catalyst. These studies revealed that reaction time for maximum biodiesel yield is within 2- 10 mins. This process however has an added advantage of significantly higher efficiency when compared to the conventional transesterification process.

Table 6: Microwave enhanced biodiesel production using different homogenous catalyst

Feedstock	Alcohol- feedstock	Catalyst	Temperature (°C)	Reaction time (mins)	Yield (%)	Micro- wave power (W)	Reference
Jatropha curcas oil	Methanol to oil ratio, 7.5:1	1.5 wt% KOH	65	2	97.4	-	Shakinaz <i>et al</i> (2010)
Pongamia pinnata	Methanol to oil, 8:1	1 wt% KOH 0.5 wt% NaOH	60	5 - 10	96- 97.5- 95.5-	300W	Kumar <i>et al.</i> (2011)
Sunflower oil	Methanol to oil, 6:1	1.5wt% KOH	60	1	98.10	-	Magidal <i>et al.</i> (2013)
Waste vegetable oil	Methanol to oil ratio, 15:1	1wt% NaOH	33	2	-	-	Lin and Hsiao (2013)
Castor oil	Ethanol to oil, 10:1	1.5wt% KOH	60	10	80.1	250	Hincapié <i>et al.</i> , (2014)
Safflower seed oil	Methanol to oil, 10:1	NaOH 1 wt%	60	6	98%	-----	Dai <i>et al</i>
Diary wastes scum oil	Methanol 6:1	KOH 1w% and NaOH 0.75w%	-	3	97.7	750	Murah and Ranji (2015)
Waste vegetable oil	Methanol to oil, 8:1	1 wt% KOH	-	6	>90	500W	Hong <i>et al</i> (2016)
Jatropha curcas oil	Methanol- oil ratio 7.5:1	1.5 wt% KOH	65°C	2mins	97.4	-	Shakinazetal 2016
Jatropha oil	Methanol to oil, 6:1	1 wt% KOH	65	20	-	-	Lin and Chen, (2017)

Heterogeneous Catalytic Microwave Assisted Transesterification using Renewable Calcium Oxide

Wei *et al.*, (2016) reported a comparative study of biodiesel production from palm oil using both conventional transesterification and microwave-assisted transesterification techniques in the presence of calcium oxide as heterogeneous catalyst. Investigations revealed that an optimum yield of 89.9% was obtained under a reaction time of 60 mins for microwave-assisted transesterification as against 240 mins for conventional transesterification under same conditions. This stated that microwave assisted process produced higher yield of FAME at a short reaction time. The

presence of microwave energy accelerates the transesterification reaction rate compared to conventional heat energy. Khemthong *et al.* (2012) investigated the use of (CaO) calcium oxide catalyst derived from waste eggshell by calcinations at 800°C in air atmosphere with heating rate of 10 °C/min for 4 h for the production of biodiesel from palm oil using microwave assisted transesterification techniques. The authors reported that the derived catalyst exhibited a high density of a strong base sites and also indicated good reusability (5 cycles) with approximately only 3% decrease in yield (i.e 96.7 - 93%). This indicates that the catalyst has high potential for biodiesel production.

Table 7: Literature survey of optimum condition for microwave irradiation assisted transesterification

Feedstock		Optimum reaction conditions					Yield (%)	Ref.
Oil	Catalyst	Time (min)	Catalyst loading (wt%)	Methanol-to-oil molar ratio	Temp. (°C)	Microwave power (W)		
Palm	Chicken Eggshell	4	15	18:1	-	900	96.7	Khemthong <i>et al.</i> (2012)
<i>Jatropha</i>	Oyster & <i>Pyramidella</i> shell	6	4	15:1	-	800	95.12	Buasri <i>et al.</i> (2014)
<i>Jatropha</i>	Natural dolomite	4	4	18:1	-	800	95.88	Buasri <i>et al.</i> (2015)
Palm oil	<i>Cyrtopleura Costata</i> seashells	10	0.5	5:1	-	150/450	96.7	Marwan and Indarti (2016)
Palm oil	?????	-	5	9:1	65	-	89.9	Wei <i>et al.</i> (2016)
<i>Jatropha</i> & <i>Pongamia</i>	Waste chicken eggshells	6	3	6:1	-	-	78 & 74	Joshi <i>et al.</i> (2016)
<i>Jatropha</i>	Waste eggshell	5	4	18:1	-	800	94	Buasri and Loryuenyong (2017)
Custard apple seed	Guinea fowl bone	20	4	18:1	65	800	95.82	Singh and Sharma (2017)

Buasri *et al.* (2014) reported the use of solid oxide catalyst (CaO) derived from

waste shell of oyster and *pyramidella* via calcinations method at 900°C for 2 h for the

production of biodiesel from *Jatropha curcas* oil using microwave assisted transesterification. It was further reported that the catalyst exhibited good reusability up to 3 cycles while still maintaining a biodiesel yield of 78- 80%. Buasri *et al.* (2015) studied the synthesis of biodiesel from *Jatropha curcas* oil using CaO derived from natural dolomite rock at 900°C for 7 h. The optimum condition that yielded a conversion of oil to a nearly 95.88% of biodiesel from the derived catalyst. The catalyst was reused for 3 cycles and an apparent high yield of about 85% was observed after the third cycle. Table 7 summarizes the optimum condition reported in literature during the application of microwave irradiation assisted transesterification of vegetable oil. In another related investigation, Tan *et al.* (2015) produced biodiesel from used cooking oil using CaO derived from waste Ostrich and Chicken eggshells at a temperature of 1000°C as heterogeneous base catalyst in a microwave assisted transesterification system. The optimum yield of 96% and 94% was obtained. The catalyst was reused up to 5 cycles before the yield drop to 75%. According to Marwan and Indarti (2016), during the transesterification of palm oil with methanol using hydrated *Cyrtopleura Costata* seashells calcined at 900°C for 2 h. The maximum yield (96.7%) was obtained and the biodiesel produced compared favorably with relevant standards. In the transesterification of *Jatropha and Pongamia* oils reported by Joshi *et al.* (2016) investigating the effects of reaction time, waste chicken eggshells CaO concentration, methanol to oil. The biodiesel yields of *Jatropha curcas* and *pongamia* biodiesel attained maximum yield of 78.1 and 74.1% after 6 min. Buasri and Loryuenyong (2017)

reported the application of waste eggshell calcium oxide for production of biodiesel from *Jatropha curcas* oil and reported an optimum yield of 94% of biodiesel after 5mins.

Factors Affecting Microwave Assisted Transesterification of Vegetable Oil

The most important variables that influence biodiesel production and its quality are: reaction time, temperature, type of catalyst and concentration and methanol/oil molar ratio. It is important to optimize these variables in order to avoid either incomplete reactions or lower biodiesel yield (Manco *et al.*, 2012).

Effect of Reaction Time

In the transesterification reaction, reaction time is the key to the yield and quality of biodiesel obtained. Conventional transesterification requires a heating time of 60 to 75 min. The microwave irradiated technique is known to be time and cost saving (Saifuddin *et al.*, 2004). Microwave irradiation has been reported to reduce the reaction time by rapid heating that leads to a localized high temperature and pressure (Manco *et al.*, 2012). Khemthong *et al.* (2012) reported the effect of reaction time (1 - 4 min) during the microwave transesterification of palm oil with methanol in the presence of eggshell derived CaO. The biodiesel yield increased very fast up to 40.4% during the first 3 mins. The maximum biodiesel yield of 96.7% was obtained after 4 min. Ani and Elhameed (2014) reported the effects of reaction time (5-9 min) on the production of biodiesel from the transesterification of *Jatropha curcas* oil and methanol. The biodiesel yield was observed to increase with increase in

reaction time from 2 - 7 min. The optimum yield (96%) was obtained after a reaction time of 7 min. According to Buasri *et al.* (2015) the production of *Jatropha curcas* biodiesel was initially rapid and reached equilibrium after a reaction time of about 6 min. The maximum yields of 94.81 and 95.12% were obtained in 6 min at a methanol/oil molar ratio of 15:1 using a microwave power of 800 W for 4wt% oyster and *Pyramidella* shell derived CaO respectively. In another related study Buasri *et al.* (2015) studied the effect of reaction time (2 - 6 min) on the production of *Jatropha curcas* biodiesel using dolomite derived CaO and reported that the yield of biodiesel increased rapidly at the initial stage until a maximum yield was attained after a reaction time of about 4 min. The maximum yield of nearly 95.88% was obtained in 4 min. Marwan and Indarti (2016) observed that there was an increase biodiesel yield when the time was increased from 0 - 10 min during the transesterification of palm oil with methanol. Further increase in time beyond 10 mins was reported to result in to a decrease in biodiesel yield. The decrease in biodiesel yield could be attributed to the solubility of biodiesel in glycerol. The maximum yield (96.0%) was obtained after 10 min. Joshi *et al.* (2016) investigated the effects of reaction time (3 -8 min) on biodiesel yields from *Jatropha curcas* and *pongamia* oil. The yields of *Jatropha curcas* and *pongamia* biodiesel increased from 3 - 6 min until a maximum yield of 78.1 and 74.1% were obtained after 6 min. However, further increases in reaction time from 7 to 8 min resulted to a decrease in biodiesel yield. This signifies that longer reaction time result in greater glycerin solubility in the reaction mass consequently, lower the overall

biodiesel yield. In another related study Buasri and Loryuenyong (2017) stated that there is a noticeable increase in the biodiesel yield during the transesterification of *Jatropha curcas* as reaction time increase from 2 to 5 min. The maximum yields of 92.78% and 92.11% were obtained in 5 min using 4 wt% calcined quail eggshell and crab shell, respectively. The author further added that increase in reaction time beyond 5 min did not have any significant effect on biodiesel yield.

Effect of Catalyst Concentration

The transesterification reaction can be catalyzed by alkali, acid or enzyme catalysts. Enzymes-catalyzed methods use lipase as catalyst and do not produce side reactions, but lipases are very expensive for industrial scale production. Khemthong *et al.* (2012) reported the effect of CaO catalysts (0 - 15 wt%) derived from eggshells on the production of biodiesel from palm oil in a microwave assisted transesterification. The increase in CaO concentration from 0 - 15 wt% led to an increase biodiesel yield of 96.7%. According to this study, 15wt% of catalyst is the most suitable catalyst loading. According to Ani and Elhameed (2014) higher CaO catalyst concentration of 8%wt gave highest biodiesel yields during the transesterification of *Jatropha curcas* oil and methanol. Buasri *et al.* (2015) studied the effect of CaO catalyst concentration (2 - 6wt %) on *Jatropha* biodiesel production reported that an increase in biodiesel yield as the catalyst concentration gradually increased from 2 - 4wt%. The biodiesel yield was observed to decrease when the catalyst concentration was increased from 5-6wt%. The authors attributed the decrease to slurries formation which hinders satisfactory

mixing between the reacting phases. Marwan and Indarti (2016) investigated the variation of CaO catalyst loadings (0-5wt %) during the transesterification of palm oil with methanol. The authors stated that biodiesel rapidly increased as the catalyst concentration increases from 0 - 4wt% to give a biodiesel yield of 59.2%, using 4wt% catalyst. Increasing the catalyst loading from 4.0 to 5.0wt% led to a reduction in biodiesel yields. This is due to the lack of mass transfer at higher catalyst loadings. Joshi *et al.* (2016) studied the effect of CaO (0 - 5 wt %) for the transesterification of *Jatropha* and *Pongamia* oils. The maximum biodiesel yield was at 3.0 wt% CaO. Increasing the catalyst concentration from 3.0 to 5.0 wt% resulted into a reduction in biodiesel yield. This is due to excess amount of the CaO which led to the formation of emulsion thereby making the products separation difficult. Buasria and Loryuenyonga (2017) studied the effect of catalyst range from 2 - 6wt% during the transesterification of *Jatropha curcas* oil. It was reported that 4wt% was the most appropriate CaO concentration resulting into a yield of 92.78 and 92.11% for calcined quail eggshell and crab shell, respectively.

Effect of Methanol to Oil Ratio

The methanol to oil molar ratio is a very important parameter for the production of methyl ester both in catalytic and non-catalytic reaction. Normally, transesterification requires 3 moles of alcohol for one mole of triglyceride to form three moles of fatty acid esters and one mole of glycerol (Mathiyazhagan *et al.*, 2011). In alkaline catalyzed process, the yield of methyl ester increases with an increase in alcohol to oil molar ratio as the equilibrium

shift towards the product side and resulting in higher yield of methyl esters (Lokman *et al.*, 2014). Methanol to oil molar ratio is also associated with the type of catalyst used. In general acid catalyzed process requires high molar ratio than base catalyzed process (Nakarmi and Joshi, 2014). Large amount of methanol will compensate the reaction due to high dispersibility of catalyst in presence of methanol (Lokman *et al.*, 2014). Hsiao *et al.* (2011) reported the methanolysis of soy beans at different methanol to oil molar ratios (6:1- 10:1) on biodiesel yield. The biodiesel yield increases as the molar ratio of methanol to oil increases from 6:1 to 7:1. Further increase in methanol to oil ratio above 7:1 resulted to a decrease in biodiesel yield. The yield decreases as the mole ratio increases beyond 7:1. This is due to the solubility of the glycerol which favours the reverse reaction. The optimum yield (96.6%) was obtained at methanol/oil molar ratio of 7:1. Khemthong *et al.* (2012) studied the effect of methanol to oil ratio of palm olein oil from 12:1 to 24:1. It was reported that the highest molar ratio (24:1) had less significant effect on the conversion of palm olein oil. This is because excessive methanol resulted in the dilution of the reaction of catalyst. On the other hand, the lowest molar ratio (12:1) could not generate a practical production due to the limited formulation of methoxy species on CaO surface, resulting in the low reaction rate. However, the separation between biodiesel and glycerol was very difficult at the high methanol to oil molar ratio. Thus, the most suitable molar ratio was found to be in a range of 15:1-18:1. Buasri *et al.* (2014) reported the variation of methanol to oil molar ratio (9:1 - 21:1) with the 4wt% oyster and *Pyramidella* shell derived CaO catalysts.

It was observed that the biodiesel yield increased significantly when the methanol/oil molar ratio was changed from 9 to 21. The high amount of methanol promoted the formation of methoxy species on the CaO surface, leading to a shift in the equilibrium in the forward direction, thus increasing the rate of conversion up to 93.92 and 94.81% for oyster and *Pyramidella* shell, respectively. Lower methanol/oil ratios resulted in poor suspension of the slurry in the reacting solution, which possibly induced mass transfer problems thus resulting in lower activity. In another study, Buasri *et al.* (2015) reported the variation of methanol to oil molar ratio (9:1 - 21:1) with the 4wt% dolomite derived CaO catalysts. It was reported that the biodiesel yield increased significantly when the methanol/oil molar ratio was increased from 9:1 to 18:1 giving a biodiesel yield of 95%. According to these authors lower yield was obtained at lower molar ratio was due to mass transfer limitations arising from the suspension of the reacting system slurry while the higher yield at higher molar ratio were associated with the formation methoxy species on the surface of calcium oxide. Joshi *et al.* (2016) reported the effect of methanol to oil ratios on algae oil, *Jatropha* oil and *pongamia* oil transesterification from 6:1 - 12:1 with 3wt% CaO catalyst. It was observed that there was an increase in biodiesel from 68.1% - 70.1% for algae, 61.1%-65.5% for *Jatropha* biodiesel and 60.0 - 64.1% for *pongamia* biodiesel as the molar ratio increased from 6:1 - 10:1. Buasria and Loryuenyong (2017) in the study of effect of methanol to oil molar ratios (9:1- 21:1) on the yield of biodiesel from transesterification of *Jatropha* using 4wt% of CaO catalyst. The authors reported that there was a rapid

increase in yield as the molar ratio increases from 9:1 - 18:1 with a corresponding yield of 64 - 94%, respectively. The yield was observed to decrease to 90% when the methanol to oil ratio increased to 21:1. This means that further increase in the methanol to oil molar ratio (21:1), did not promote the reaction. The author stated that the reduction in yield is due to the dissolution of glycerol in the excessive methanol which subsequently inhibit of the reaction rate negatively. The optimum biodiesel yield of 94% was obtained at a methanol to oil molar ratio of 18:1. Tan *et al.* (2016) studied the synthesis of biodiesel from used cooking oil using CaO derived from waste Ostrich and chicken eggshells in a microwave assisted transesterification system. The authors observed that as ratio increased from 6:1 to 10:1 and reach optimum at 12:1. The optimum yield of 96% and 94% was obtained at this ratio.

Effects of Microwave Power

Khemthong *et al.* (2012) studied the effect of power from 450 to 900W. It was observed that higher microwave power gave rise to a higher biodiesel yield. The optimum yield of fatty acid methyl esters reached 96.7% under the optimal condition of reaction time of 4 min with 900 W microwave power. Ani and Elhameed (2014) investigated the effect of power within the range of 100 - 300W on the biodiesel yield. It was reported that yields of biodiesel increased with higher microwave exit power for all three catalyst concentration. The maximum yield (96%) was obtained using 300 W microwave power. Buasri *et al.* (2014) reported the effect of power during the transesterification of *Jatropha* oil between 180 - 800W. It was observed that the higher

microwave power gave rise to higher biodiesel yield. The optimum microwave power of 800 W gave a conversion of nearly 93% for both waste shell-derived catalysts. Buasri and Loryuenyong (2017) reported that there was an increase in biodiesel yield from 28.5 - 98.5%, as the power increased from 150-800 W. Thus the microwave power of 800 W was reported as optimum. Joshi *et al.* (2016) found that the biodiesel yields initially increased as microwave power increased from 300 to 700 W. With further increase in power to 800 and 900W respectively a decrease in biodiesel yields was observed. According to the authors very high power may degrade the triglycerides to free fatty acid which adversely affect biodiesel yields. Therefore, 700 W was reported as the optimum microwave power.

Effect of Reaction Temperature

The rate of transesterification is strongly affected by the reaction temperature. However, the reaction can be carried out at room temperature if given longer reaction time. The reaction temperature is always kept close to the boiling point of methanol, if methanol is used as the alcohol at atmospheric pressure (Srivastava and Prasad, 2000). In transesterification of biodiesel, higher reaction temperature helps to decrease the time and increase the reaction yield

(Saifuddin *et al.*, 2004). Dai *et al.* (2014) found out that the decreasing rate of dielectric constant declines as the temperature rises. Therefore the response to the changing electric field is faster, which increases the realignment process, enhancing the dipolar rotation of molecules and the dielectric constant of the material compared to lower temperature.

Effect of Mixing

The mixing intensity is an important parameter which enhances the contact rate between methanol and feedstock (two different phases) during the reaction. It is known that without mixing, the catalysis reaction occurs slowly between the phases which results in incomplete reaction (Soltani *et al.*, 2016). Sufficient mixing is therefore required to permit appropriate dispersion of the reactant.

PROPERTIES OF BIODIESEL FROM MICROWAVE IRRADIATION ASSISTED TRANSESTERIFICATION

The quality of biodiesel produced via microwave irradiation satisfy the international biodiesel standards as shown in Table 8. The yield and quality of biodiesel produced via microwave irradiation is comparable to conventional transesterification (Venkatesh *et al.*, 2011; Yakoob *et al.*, 2008).

Table 8: Fuel properties of biodiesel Microwave process in comparison with standard and conventional process

Properties	Diesel	AST M	EN	*Castor Biodiese l	**Soya biodiese l	*Jatroph a biodiesel	**Waste Vegetabl e biodiesel	*Custard apple biodiese l
Specific gravity	0.82- 0.86	0.88	860	0.889	0.88	0.88	0.87	0.86
Flash point (°C)	> 55	93 min	120 min	178.8	93	163	-	140
Pour point (°C)	- 33 to -15	12 max	-	-	- 6	8	10	6
Cloud point (°C)	-15 to -5	-	-	-	-	11	-	3
Kinematic viscosity (mm ² /s)@40° C	2.5 - 3.5	1.9- 6.0	3.5- 5.0	6.3	4.63	4.75	4.5	3.04
Water & sediments (%)	-15-5	0.50	0.2	-	0.006	0.01	-	0.08
Cetane number	49 - 55	47 min	51.0	61.05	48	51	48	48
Acid value (mgKOH/g)	-	0.8	0.5	0.11	1.072	0.37	0.2	1.91
Calorific value (MJ/kg)	42			-	-	-	-	39.01
	Enweremadu & Alamu, (2010)			Nurdin <i>et al.</i> (2015)	Ayodeji <i>et al.</i> (2018)	Buasri <i>et al.</i> (2015),	Ngoya <i>et al.</i> (2017)	Singh and Sharma (2017)

*Biodiesel from Microwave irradiation process, ** Biodiesel from Conventional process

CONCLUSION

The review has shown that calcium oxide from waste organic sources like shells are viable potential heterogeneous catalyst for microwave irradiation assisted transesterification of vegetable oil to biodiesel. The microwave irradiation process enhances the reaction conversion rate of vegetable oil to biodiesel is characterized effective heat transfer, shorter reaction time and improves product recovery compared to

conventional transesterification. It has tolerance for high FFA feedstocks such as animal fats and used cooking oils. It is also evident that higher biodiesel yield can be obtained when fundamental variables such as reaction temperature, time microwave power, catalyst concentration and molar ratio of alcohol to oil affecting the reaction are optimized. The following research gap has been indentified: (1) The application of statistical design of experiment for

optimization of effect of process variables in the microwave irradiation assisted transesterification of different non-edible oils such as castor, neem, cotton, tobacco, hemp, desert date, yellow oleander, *allamanda*, *karanja* e.t.c using waste eggshell CaO for biodiesel production via response surface methodology, artificial neural network and genetic algorithms requires research attention. (2) Kinetic studies of microwave irradiation assisted transesterification of non-edible oil require investigation, as this will serve as a spring board for the design and development of a pilot plant. (3) Techno-economic analysis of microwave irradiation assisted transesterification of non-edible oil need to be studied to determine the economic viability of the process. (4) The catalyst was observed to lose its activity after a number of cycles. There is the need to develop advanced porous carbon (activated carbon) material from biomass waste which will serve as a catalyst support for anchoring CaO in order to ensure sustainability and economic of the biodiesel production process. Anchoring CaO on support will increase the dispersion of catalyst active site and ensure stability.

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