A Review of Biodiesel Production from Non-Edible Seed Oils using Calcium Oxide Derived from Renewable Sources

*Omale, F. D[1], Eterigho, E.J[1], Musa U[1]

[1]Chemical Engineering Department, Federal University of Technology, PMB 65 Minna Niger State, Nigeria

*Corresponding author email: omaledavid12@gmail.com, +2347038516421

ABSTRACT

This review is focused on the production of biodiesel from non-edible sources using calcium oxide derived from renewable sources. These sources are generally considered as waste products which are reported to be sustainable and cheap feedstock for biodiesel production. They are sourced from renewable materials and are cheap to obtain. The use of non-edible oils in biodiesel production will greatly reduce the problem of food shortage. Results reported showed that over 80 % yield of fatty acid alkyl esters could be achieved using some of these non-edible oils.

Keywords: Biodiesel, Free Fatty Acid, Non-edible oils, Transesterification.

1 INTRODUCTION

There is a great demand for energy globally to carry out daily activities especially in the transportation sector, industrial sector and for domestic needs. The conventional energy source that is, fossil fuels which are non-renewable poses a potential threat to energy supply due to rapid global population and industrial growth (Basumatary, 2013). Research is ongoing for new sources of energy which are renewable and are also environmentally friendly. Some of these sources of renewable energy include wind, solar, hydrothermal and biomass. Energy produced from these sources is free from pollutants such as CO, CO_2, SOx and NOx (Deng et al., 2011). Meher et al. (2004) and Highina et al. (2011) reported that any fuel that must serve as an alternative must be environmentally benign, technically viable and posseses economic competitiveness. Biodiesel is one of such alternatives owing to its conformity with these qualities.

Biodiesel is increasingly gaining preference over the fossil based fuels. As an attractive alternative to petroleum diesel, it has similar physical properties as that of petrol-diesel but on the other hand has better performance. Biodiesel unlike the conventional diesel is biodegradable, renewable, non-toxic and environmentally benign (Chopade et al., 2012; Sanjay, 2013; Abeke and Alex, 2015; Mahangani et al., 2015, Mohan, 2015). It is sourced from animal fats, plants and vegetable seed oils which are all renewable materials (Abeke and Alex, 2015).

There are a number of ways through which biodiesel can be produced some of which include pyrolysis, supercritical processes, ultrasonic methods and even microwave methods but the most common of them is transesterification (Chopade et al., 2012 and Sanjay, 2013). The process involves the reaction of a triglyceride with an alcohol (usually methanol) in the presence of a catalyst to produce an alkyl ester and glycerol which is a useful by-product as shown in Figure 1.
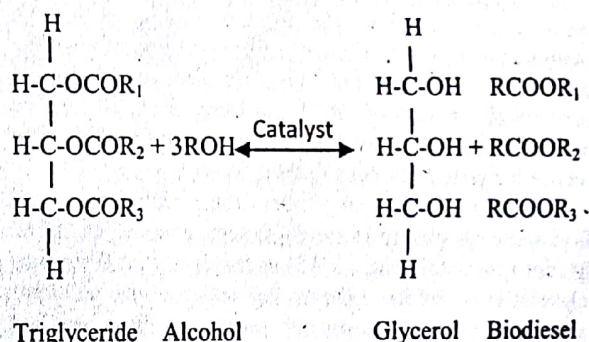

Figure 1: Transesterification of oil with methanol

The resulting fatty acid alkyl ester can be blended with petroleum diesel in a ratio mostly between B5 to B20 or used directly (B100) with little engine modification (Zaku et al., 2012; Sanjay, 2013; Istadi et al., 2014). Biodiesel has properties similar to those of the conventional diesel and can be a suitable replacement in most current uses. Table 1 compares some of the properties of petroleum diesel and biodiesel.

TABLE 1: COMPARISON OF THE STANDARDS FOR PETROLEUM DIESEL AND BIODIESEL BASED ON THE AMERICAN STANDARD FOR TESTING AND MATERIALS (ASTM)

Property	Diesel	Biodiesel
Standard Number	ASTM D975	ASTM D6751
Composition	Hydrocarbon (C10-C12)	Fatty Acid Methyl Ester (C12-C22)
Specific Gravity	0.85	0.88
Flash point (K)	333 – 353	373 – 443
Cloud point (K)	258 – 278	270 – 285
Pour point (K)	243 – 258	258 – 289

Carbon (wt %)	87	77
Water (vol. %)	0.05	0.05
Cetene Number	40 – 55	48 – 60
Sulphur (wt. %)	0.05	0.05
Hydrogen (wt. %)	13	12
Oxygen (wt. %)	0	11

(Source: Chopade et al., 2012)

Transesterification process is brought about either by homogenous (acid or base) catalysis or heterogeneous (acid, base or enzymes) catalysis (Sanjay, 2013; Abeke and Alex, 2015). The type of catalyst used also has influence on the production of biodiesel which could range from cost to environmental problems. Biodiesel syntheses from homogeneous catalysts have shorter reaction time and lower temperature requirements. But these catalysts also have certain drawbacks. There is the problem of catalyst separation from the product since both are in the same phase, the formation of soap through saponification and the challenge of washing to remove the catalyst is also inherent which poses environmental concerns (Highina et al., 2011 and Deng et al., 2011). The presence of soap and water in the product tend to also reduce the yield of biodiesel.

Research is ongoing on the replacement of homogeneous catalysts with heterogeneous catalysts. Muthu and Viruthagiri, (2015) ascertained that these new class of catalysts have the ability to solve the problems associated with homogeneous catalysts. They are less expensive, can be used several times before they are spent, environmentally friendly, biodegradable and are also a channel of creating wealth from waste (Refaat, 2011). This is so because some of the raw materials are sourced from wastes such as waste egg shells, animal bones, snail shells and mollusc shells (Muthu and Viruthagiri, 2015).

Several journals have been published on the use of edible oils for biodiesel production. This paper therefore aims at reviewing several publications on the use of non edible oils with an approach that will promote its use in biodiesel production commercially thereby reducing the problem of food shortage associated with the use of edible oils and to also exploit cheap renewable sources of catalyst for transesterification reaction.

2 BIODIESEL FEEDSTOCK

Biodiesel feedstock today ranges from edible vegetable oils to non-edible vegetable oils, waste vegetable oils, animal fats and algae. Some examples of edible vegetable oils that have been exploited include but is not limited to soybean (Wei et al., 2009; Chakraborty et al., 2011), palm oil (Boey et al., 2009; Viriya-empikul et al., 2012), rapeseed (Yang et al., 2009) and waste frying oil (Birla et al., 2012; Nair et al 2012). Production of biodiesel from edible sources has its limitations as it can lead to food shortage. In other to avoid this problem, non-edible oils are suitably employed for biodiesel production especially in developing countries. These vegetable oils have certain compositions of free fatty acids (FFA) in them as shown in Table 2 below.

TABLE 2: COMPOSITIONS OF FREE FATTY ACIDS OF SOME VEGETABLE OILS

Fatty Acids	Acronym	Castor Oil (%)	Neem Oil (%)	Tallow
Palmitic	C16:0	1.3	18.1	25-37
Stearic	C18:0	1.2	18.1	9.5-34.5
Oleic	C18:1	3.6	44.5	14-50
Linoleic	C18:2	4.6	18.3	26-50
Linolenic	C18:3	0.4	0.2	
Ricinoleic	C18:1OH	88.9		
Arachidic	C20:0		0.8	

(Source: Nuria et al., 2015; Muthu et al., 2010; Thanh et al., 2012)

These oils are chemically characterized to have fatty acids which are expressed by the carbon number and also the degree of unsaturation. These characteristics affect the reactivity towards transesterification and as a result, the properties of the biodiesel produced. For example, biodiesel fuel properties such as cetene number, viscosity, melting point and heat of combustion increases with increase in carbon number and degree of unsaturation (Abeke and Alex, 2015).

2.1 NON-EDIBLE OILS FOR BIODIESEL PRODUCTION

There are a wide variety of plant oils which are not suitable for consumption because they contain some form of toxins or chemical substance that are poisonous to the body. Ricin which is a highly toxic lectin is present in Castor oil. Castor oil having about 90% if its oil containing ricinoleic acid is not fit for consumption due to its laxative effects. Toxalbumine called curcine and the presence of various toxic phorbol esters found in Jatropha makes it unsuitable for cooking. Some of the non-edible oils that have been reported include Jatropha curcas (Topare et al., 2011), castor oil (Deshpande et al., 2012, neem oil (Aransiola et al., 2012). Other such oils include karanja (P.pinnata), tobacco seed (N. tabacum L.), rice bran, mahua (M. indica), rubber plant (H. brasiliensis), linseed, and microalgae seed oils (Demirbas, 2011). Some non-edible seeds oil that are yet to be reported are Therelia Peruviara, Crotalaria Spectabilis, Fatoua villosa, Afcola mellanni and Fumaria officinalis (Abeke and alex, 2015). According to Mittelbach and Rernschmidt (2004), some of these toxic substances can
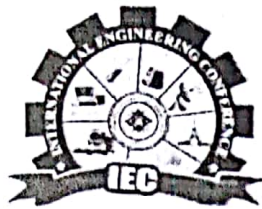
be removed through refining. Nevertheless, attempt has not been made on the removal of these toxic substances from these vegetable oils.

Most of these seeds which are produced annually and serve as a rich source of oil for biodiesel are found to litter the environment. It has become imperative therefore to utilize these rich sources by using them directly or through modifying them genetically.

2.2 FACTORS AFFECTING BIODIESEL PRODUCTION

There are a number of factors that affect the yield of biodiesel from transesterification reaction. They are reaction time, temperature, catalyst, molar ratio of alcohol and oil, mixing intensity, water content and free fatty acid content.

2.2.1 EFFECT OF PURITY OF RAW MATERIAL

Before tranesterification reaction is carried out, a number of pre-treatment steps are carried out on the feedstock so as to remove impurities such as free fatty acids, phosphatides, moisture or colorants which may interfere with the reaction. The removal of phosphatides is achieved through the process of degumming. These phosphatides are responsible for making the oil turbid during storage and increase the accumulation of water in the biodiesel (Dahlke and Buchold, 1995).

Excess amount of Free Fatty Acids (FFA) removal is also important; this is to prevent the formation of soap which impedes glycerol phase separation from the alkyl ester due to emulsifying effects of soaps. When the FFA is greater than 5 %, the oil might congeal after the base catalyst is added. Hence, alkali neutralization is employed to deacidify the oil (Magdalene, 2010).

2.2.2 EFFECT OF TEMPERATURE

Temperature is necessary in the collision and kinetics of a reaction. The Entropy of a substance is found to increase with increasing temperature, causing the frequency of effective collisions to also increase and thus shifting the equilibrium position towards the right. Transesterification can occur at different temperatures but high temperatures are liable to hasten the saponification of the triglycerides by the alkaline catalyst before completion of the transesterification reaction (Magdalene, 2010).

2.2.3 EFFECT OF MOLAR RATIO OF ALCOHOL TO OIL

The amount of product formed is dependent on the amount of substance involved in a reaction. For any reaction to take place, the reacting particles must first collide whether both particles are in solution, or whether one is in solution and the other a solid. Alcohol to oil

molar ratio is one important factor that can affect the yield of alkyl esters. From stoichiometry, 3 moles of triglycerides reacts with 1 mole of catalyst to yield 3 moles of ester and 1 mole of glycerol. Most researchers have found that to drive the reaction close to completion, excess alcohol was required (Magdalene, 2010). This is line with the works of Zhang et al. (2003) and Boocock et al. (1998) who observed higher ester yields at a molar ratio of 6:1 and decrease in ester yield with increase in the molar ratio beyond this point. The decrease can be attributed to the fact that the reverse reaction or saponification was favoured.

2.2.4 EFFECT OF STIRRING RATE

In the transesterification process, stirring (or the effect of agitation) is of precise importance because it guarantees homogeneity of the reacting mixture. The surface contact for the reaction between the oil and catalyst is increased by stirring which in turn aid in initiating the reaction. The reaction would only occur at the interface of the two layers and will be too low to be considered feasible if no agitation or mixing is performed (Magdalene, 2010).

2.2.5 EFFECT OF CATALYST CONCENTRATION

The use of catalyst in transesterification is to create a different pathway for the reaction to occur. An acid, alkaline or enzyme may be used as catalyst. The most commonly used catalyst for biodiesel production is the alkaline catalyst which has higher conversion in short time than the acid-catalyzed transesterification (Freedman et al., 1986). An increase in catalyst concentration was observed to decrease the production yield of biodiesel. The reaction of oil with an excessive amount of catalyst results in the formation of soap which will eventually cause the methyl ester to dissolve more in the glycerol (Caminiti et al., 2007). Boocock et al. (1998) reported that the alkyl ester concentration increases with increase in catalyst concentration at lower alcohol to oil mass ratio. This probably is due to the lag of methyl ester production because of the mass transfer limitation at the lower mass ratio of reactants.

2.2.6 EFFECT OF REACTION TIME

The conversion rate of triglycerides to esters increases with time. The reaction at first seems to be very slow due to mixing and diffusion of the alcohol into the oil. Magdalene (2010) investigated the effect of reaction time from 10 minutes to 60 minutes on the yield of esters and found that the ester yield decreased slightly as the reaction time was increased beyond 45 minutes.

2.2.7 WATER CONTENT AND FREE FATTY ACID CONTENT

Free fatty acids (FFA) in the presence of a catalyst and alcohol are converted to fatty acid methyl esters. Water is formed from this reaction which must be removed to increase the yield. To carry out alkali catalyzed reaction to completion, the vegetable oil should contain less than 3 % of FFA. Ma et al., (2004) studied the transesterification of beef tallow catalyzed by NaOH. In the absence of FFA and water, the yield obtained was the highest. With 0.6 % of FFA, the apparent yield of beef tallow methyl ester was the lowest, less than 5 % with any amount of water added. With a feedstock of 20 % FFA, the two step acid-alkaline catalyzed transesterification reaction can be used to produce biodiesel. The process starts with an acid-catalyzed esterification of the FFA then an alkali-catalyzed transesterification.

3 HETEROGENOUS CATALYST FROM RENEWABLE NATURAL SOURCES

The search and development of inexpensively viable, eco-friendly, and renewable heterogeneous catalysts for biodiesel production has become very attractive. In recent times, some heterogeneous catalysts developed from renewable sources have been reported and demonstrated high potential for use as cost effective catalyst for biodiesel synthesis.

Viriya-empikul et al., (2012) produced calcium oxide catalysts (calcined at temperatures ranging from 700 – 1000 °C for 0.5 – 8 hours) from golden apple snail shell, meretrix venus shell and eggshell. Palm olein oil was transesterified using the solid catalyst of 10 % (wt. of oil) at optimum conditions of Methanol to oil ratios (12:1) at 60 °C for 2 hours producing yields of biodiesel to be more than 90 %. The biodiesel yield a well as the catalytic activity of the derived catalysts was observe to decrease and was reported in the following order: eggshell, 94.1 % FAME > golden apple snail shell, 93.2 % FAME > meretrix venus shell, 92.3 % FAME. The optimum temperature for calcination was observed at 800 °C for 2 hours. It was reported that there was incomplete formation of active Ca-based catalyst at lower temperature and shorter time, while at higher temperatures and longer time duration, there was severe sintering of catalyst particles, resulting in lower biodiesel yields.

Hu et al., (2011) developed a heterogeneous catalyst using waste freshwater mussel shell by a calcination-impregnation-activation method and utilized it for biodiesel production from Chinese tallow oil. The reaction was performed with catalyst 5 % (wt. of oil) at a temperature of 70 °C with a 12:1 methanol/oil molar ratio in 90 minutes. Under these conditions, the yield of biodiesel was 96 %. The catalyst was found to be active for 7 times of reuse before deactivation and the yield of biodiesel was more than 90 %. The high catalytic activity was also reported and explained by the BET. It indicated that the catalyst (calcined at 900 °C for 4 hours and completely impregnated in deionized water and then was activated at 600 °C for 3 hours) has a surface area of about 23.2 m²/g. This catalyst obtained from waste freshwater mussel shell can greatly reduce the cost of biodiesel production.

Wei et al., (2009) derived calcium oxide from waste eggshell and used as a catalyst for biodiesel production from soybean oil and showed high catalyst activity. The results showed that transesterification reaction of soybean oil with the shell-derived catalyst under optimum conditions exhibited high catalytic activity yielding more than 95 % biodiesel. These conditions are calcinations temperature of 1000 °C, 3 % wt. catalyst, methanol/oil molar ratio of 9:1 and temperature of 65 °C for 3 hours. Reusability of the catalyst was also investigated and reported that the eggshell-derived catalyst can be repeatedly used 13 different times with no significant loss of catalyst activity. It was reported that the catalyst gradually lost its activity after being used for more than 13 times. This low-cost waste eggshell catalyst could make the production of biodiesel inexpensively viable making it a suitable replacement for petroleum diesel.

Boey et al., (2009) investigated the use of waste mud crab shell calcined at 900 °C for 2 hours as another highly efficient heterogeneous catalyst for transesterification of palm oil into Fatty Acid Alkyl Esters. The major composition of the shell is calcium carbonate which decomposed into calcium oxide when calcined above 700 °C for 2 hour. The optimal conditions reported were 0.5:1 methanol/oil molar ratio, catalyst amount 5 % (wt. of oil), reaction temperature of 65 °C and a stirring speed of 500 rpm. Under the optimized conditions, the reusability of the developed catalyst was studied and established to be active for 11 times producing yields above 96.5 %. The BET surface area for calcined catalyst was found to be 13 m²/g and that for uncalcined catalyst was only 4 m²/g which indicated the higher activity of the synthesized catalyst. These waste mud crab shells therefore introduces another low-cost catalyst source for producing biodiesel.

Sharma et al., (2010) applied chicken eggshell as heterogeneous catalyst used for biodiesel production from P. pinnata oil. The CaO catalyst was derived from the shells by calcination in a furnace at 900 °C for 2 hours. The studies show that optimized conditions of 8:1 methanol/oil molar ratio, 2.5 % (wt. of oil) catalyst, and 2.5 hours reaction time at 65 °C produced 95 % yield of biodiesel.

Busari et al., (2013) studied the effects of catalyst loading from duck eggshell and chicken eggshell. Under the optimum conditions of 4 hours reaction time, temperature of 65 °C, methanol/oil molar ratio of 9:1 and

catalyst loading of 20 wt. %, the FAME yield from palm oil was 92 % and 94 % for duck and chicken eggshells respectively. It was observed that the rate of reaction increased with increase in mass of catalyst u to a maximum of 20 wt. % and then decreased with higher loadings. The decrease resulted from catalyst accumulation on the walls of the reacting vessel. CaO reuseability was studied and showed high stability (80 % after the fourth time) for transesterification with little loss of catalytic activity. Although, leaching of the active phase was attributed to the breaking and formation of Ca^{2+} and CH_3O^- bond.

Boey et al., (2011) investigated transesterification of palm oil to biodiesel using calcium oxide derived from waste cockle shell (*Anadara granosa*) as heterogeneous catalyst and reported a high yield. At optimum reaction conditions; 4.9 % (wt. of oil) catalyst (activated at 900 °C for 2 hours) and 0.54:1 methanol/oil molar ratio and reaction time of 3 hours, more than 97 % yield of biodiesel was attained. The report showed that the synthesized catalyst was highly active, thereby making it a low-cost catalyst source for biodiesel production. The catalyst showed good reusability and could be reused for at least three times under the optimized conditions.

Investigations by Chakraborty et al., (2011) showed a high-performance, reusable, low-cost heterogeneous catalyst from waste *Labeo rohita* scale (calcined at 600-1000 °C for 2 hours). This catalyst was employed for the synthesis of biodiesel from soybean oil. Under optimal conditions; methanol/oil molar ratio of 6.27:1, calcination temperature at 997.42 °C and catalyst amount 1.01 % (wt. of oil), a maximum biodiesel yield of 97.73 % was reported. The BET surface area of catalyst obtained was measured at 39 m^2/g and found to have a basicity of 16.23 mmol of HCl/g of catalyst. The reusability of the waste fish scale heterogeneous catalyst was found to be six times under optimized conditions indicating a low-cost catalyst for production of biodiesel.

Marinkovic et al. (2016) investigated the production of biodiesel from various non-edible oils. Calcium oxide catalyst sourced from boiler ash was used to transesterify waste cooking oil giving an optimum yield of 99.5 %. The optimum reaction conditions were methanol-to-oil molar ration of 15:1, reaction time of 32 minutes, catalyst loading of 3.39 wt% and temperature at the boiling point of methanol. Also, Jatropha oil was transesterified using KOH/CaO catalyst under a temperature of 60 °C, reaction time of 67.9 minutes, methanol-to-oil molar ration of 8.42:1 and catalyst concentration of 3.17 wt% to give an optimum yield of 97.6 %. Furthermore, the transesterification of Karanja oil having an FFA of 5.75 % was also investigated. The catalyst used for the reaction was Na/CaO prepared via wet impregnation. The optimum FAME yield of 90.3 % was obtained under the optimum conditions; temperature of 65 °C, reaction time of 8 hours, methanol/oil molar ratio of 12:1 and catalyst concentration of 2 wt%. The author also reported a yield of over 91 % for non-edible oils such as Pinnai, Pungai, Karingatta and Neem with the exception of Castor oil and Marotti oil having yields of 70 % and 62 % respectively. The optimal condition under which the transesterification was carried out are temperature of 65 °C, reaction time of 5 hours, methanol/oil molar ratio of 5.6:1 and catalyst loading of 5 wt%.

Paulo et al. (2017) studied the synthesis of bi-functional CaO/Al_2O_3 catalyst for production of biodiesel from crambe oil. The reaction was carried out in a closed reactor at a temperature of 150 °C. At ethanol/oil molar ratio of 10:1, catalyst loading of 10 wt% and reaction time of 6 hours, the average yield of fatty acid ethyl ester obtained was 84 %. Results showed that the catalyst has strong acidic sites and the catalyst showed an excellent performance in the biodiesel reaction.

Farooq et al. (2015) showed that the heterogeneous catalyst (CaO) derived from chicken bones calcined at 900 °C exhibited good catalytic activity in the transesterification of waste cooking oil (WCO). A maximum biodiesel yield of 89.33% was obtained at 5.0 g of catalyst loading, methanol/oil molar ratio of 5:1, reaction temperature of 65 °C and reaction time of 4 h. The catalyst showed better activity in the transesterification reaction. This could be ascribed to the presence of high active basic sites.

Marinkovic et al. (2016) studied the synthesis of biodiesel from karanja oil having a high FFA. The oil was esterified using H_2SO_4 to reduce the FFA. The catalyst used was sourced from chicken eggshells calcined at 764 °C. The optimal reaction conditions are stirring rate of 600 rpm, methanol:oil molar ratio of 8:1, catalyst loading of 2.5 wt%, temperature of 65 °C and reaction time of 2.5 hours. The optimum yield obtained was 95 %

Aziz et al. (2016) reported the transesterification of moringa oleifera oil to biodiesel over potassium fluoride loaded on eggshell catalyst. The catalyst was prepared by impregnation method followed by calcinations at 873k for 3 hours. The transesterification reaction was carried out in a batch reactor with 1 wt% KF loading on eggshell, 6:1 methanol/oil molar ratio, catalyst concentration of 5 wt%, temperature of 50 °C and reaction time of 1 hour, giving an optimum yield of 90 %.

4 ADVANTAGES AND DISADVANTAGES OF BIODIESEL

Table 3 below shows some of the advantages and disadvantages of biodiesel.

TABLE 3: SOME OF THE ADVANTAGES AND DISADVANTAGES OF BIODIESEL

Description	Advantages	Disadvantages
Cost	It is made from renewable resources	Currently more expensive that fossil diesel fuel
Energy Availability	Fossil diesel fuel is a limited resource, but biofuels can be manufactured from a wide range of materials	Mainly produced from edible oil, which could cause shortages of food supply and increased prices
GHG Emission	Significantly less harmful carbon (CO_2^*, CO, THC) emission	Reduction of fuel economy
Usage	Reduction of fuel economy	Less suitable for use in low Temperatures
	Significantly better lubricating Properties	It can only be used in diesel powered Engines
	Significantly less harmful carbon emission compared to standard diesel	More likely than fossil diesel to attract moisture
Air pollution	Significant reduction of particulate matter emissions	Caused increases in NOx

(Source: Dainis and Ligita, 2014)

5 CONCLUSION

This work reviews the production of biodiesel from non-edible oils. The results obtained from various studies shows that these non-edible oils can be used as cheap feedstock for biodiesel production. Under optimum reaction conditions, the yield of FAME is usually above 80 % and has the properties that are similar to that of petroleum diesel. This therefore, creates an avenue for the use of non-edible oils for biodiesel to avoid food crisis; in terms of competition between food and biofuel.

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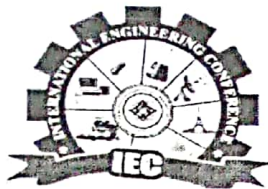
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