

Nasopharyngeal Adenoid Cystic Carcinoma, a Rare Disease: a Case Report and Review of Literature Medical Oncology Department of Annaba University Hospital

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Abstract:

The current focus on renewable energy as a means of mitigating carbon footprint and emission of greenhouse gases has gathered momentum over the years. Biodiesel is one of the promising alternatives for the replacement of the conventional diesel. Currently about 36 billion liters of biodiesel has been produced globally by different countries using various feedstock such as edible oils, non-edible oils, algae oil, genetically modified microbes and waste sludge oils. Several techniques such as direct blending, microemulsion, thermal cracking and transesterification etc, have been used for production of biodiesel from various feedstock. The measure of the effectiveness of any technique depends on ease of operability and the percentage yield obtained at the end of the production process. Economic feasibility studies and life cycle assessment of biodiesel showed positive outcome indicating that biodiesel production and utilization is viable and sustainable.

Key words: biodiesel; transesterification; economic; feedstock; catalyst

Introduction

The rapid increase in the world population coupled with the advent of modern facilities has put much pressure on energy utilization. Record by Press (2015) indicated that the world total primary energy consumed (TPEC) as at 2015 was over 150,000,000 Gwh and it is estimated that by 2050 a rise of 57 % would be recorded. Over 80 % of this primary energy is from fossil fuel with crude oil leading with (35 %), coal (29%) and natural gas (24 %) (Baskar et al., 2017). According to report by Sieminski and Administrator (2016), 54 % of this, is utilized by transportation sector and is expected to increase by 1.1 % per year. The combustion of this fossil fuel has posed serious problem to the ecosystem. Report by Jamil et al. (2018) indicated that carbon dioxide emission would increase by 35 % between years 2000 and 2030 which is not a healthy development to the environment. To curtail these menaces a substitute energy source becomes imperative and one of such promising alternative is the

biodiesel. This is a biodegradable form of fuel derived from both plants and animals biomass. They are good source of energy and showed a promising potential of been a substitute for the conventional diesel. Gerpen (2005) described biodiesel as a renewable, eco-friendly, efficient energy source, replacement fuel which can provide fulfill energy security needs of the world without reducing engine's operational efficient. The properties of biodiesel in comparison with the conventional diesel are presented in Table 1. The high flash point of 423 K when compared to that of conventional diesel of 337 K makes it to exhibit non- flammable and non- explosive characteristics which makes it easy to be stored, handled and transported with little risk as compared to fossil fuel (Ling et al., 2014). Record from (OECD/FA, 2016) has it that about 36 billion litres of biodiesel was produced globally in 2017, by 2027 the figure is projected to increase by 9%.

Property	Unit	Diesel fuel (ASTM D975)	Biodiesel (ASTM 6751)
composition		C ₁₀ – C ₂₁	C ₁₂ – C ₂₂
Oxygen content	%	0	11
Hydrogen content	%	13	12
Density at 15 °C	g/cm ³	0.85	0.86 – 0.90

Kinematic viscosity at 40 °C	C.s t	2.5	1.9 - 6
Flash point	°C	60 - 80	100 - 170
Sulphur content	PPM	10	500
Calorific value	MJ/kg	45	37.3
Cetane number	-	40 -55	48 - 65

Table 1: Properties of biodiesel and conventional diesel (Adallah, et al. 2021)

2.0 Feedstock for biodiesel production

Oils for biodiesel production are categorized into two major group edible and non- edible oils. Though the current trend in raw materials demands that non-edible oil be used as feedstock for biodiesel production to reduce food crises occasioned by the use of edible oil (Balat, 2011). Edible oils are obtained from edible sources mainly seeds and vegetables food sources. Some common edible oil feedstock are peanut, coconut, soybean, palm, rapeseed, sunflower oils etc. These oils give high percentage yield when used for biodiesel production. Over 0.82 liter of biodiesel can be obtained from 1litre of palm oil (Riazi et al, 2017). According to Karmakar et al. (2010), 1.3 liter of Soybean oil is capable of producing 1litre of biodiesel under a good processing procedure. Demirbas (2007) reported that 1.1litre of rapeseed oil can produce a yield of 1litre biodiesel under good production conditions. Non-edible oils are not used as food by human; most of them are poisonous why others are not hygienic for human consumption. Non-edible oils are derived from animals and plants sources including rubber seed oil, linseed oil, jatropha seed oil, karaja oil, tallow oil, castor oil, waste-cooking oil (Rincon et al., 2014). Most of these sources have high percentage of oil and promising qualities when use in biodiesel production. Jatropha seed contained about 35 – 60 wt% of oil and is very good for biodiesel synthesis. According to Acquage et al. (2012) about 89 % of biodiesel produced in UK is from waste- cooking oil. Animal fat is another promising feedstock for biodiesel because it reduces the use of edible oils for processing of biodiesel (Thamsiriroj et al., 2011). Algae have about 20 % to 80 % oil content depending on the species (Akubude et al 2016). Sewage sludge including activated sludge is also a promising feedstock for biodiesel production due to their lipid deposit (Edeh, 2019; Edeh et al., 2019a; Edeh et al, 2019b; Matthew et al, 2021).

3.0 Classifications of biodiesel

Biodiesel are classified based on era in which the particular feedstock was massively used. Three different generations are identified by Zulqarnain et al. (2021). These are first generation, second generation and third generation. The first generation feedstocks are from edible sources. The

second generation biodiesel are produced from non-edible oils, and the third generations are made from micro-and macro-species like algae. The fatty acid compositions of the generations of biodiesel are presented in Table 2. Apart from the three common generations of biodiesel mentioned, the fourth generation has also been identified to be made from genetically modified algae (Edeh, 2020). This modified algae also promotes carbon dioxide capturing and utilization for algae production.

4.0 Reduction of Free Fatty Acid from Oil (Pretreatment)

Obviously, most of the oils for biodiesel production come with some percentage impurity. Some oils have high percentage of free fatty acid which can form soap during biodiesel synthesis, thereby reducing the yield of the product, thus the need for pretreatment. The two methods used to pretreat oils are the use of acid and glycerolysis. Acids such as H₂SO₄, H₃PO₄, HCl etc. are used to reduce free fatty content in oils. Hayyan et al. (2011) investigated the use of H₂SO₄ to reduce the free fatty acid and recorded reduction from 24 wt% to 2 wt%. Chai et al. (2014) using 10 wt% of H₂SO₄ reduced free fatty acid in waste-cooking oil from 5 wt% to 0.5 wt%. Three different acids (H₂SO₄, H₃PO₄ and HCl) were examined to ascertain their effectiveness in reducing free fatty acid content of waste-cooking oil by Sadaf et al. (2018). The result showed that H₂SO₄ was the most effective with reduction from 2.75 wt% to 0.33 wt% under the following reaction conditions, methanol to oil ratio of 2.5:1 and reaction temperature of 60 °C. Bolonio et al. (2019) established that the used of acid for the reduction of free fatty acid corrode the equipment and also consumed large amount of alcohol, thus it becomes imperative to find new methods in which free fatty acid reduction can be achieved. Glycerolysis reduced free fatty acid without causing corrosion to the reacting system. Glycerolysis has the advantage of increasing the quantity of glyceride in the feedstock while reducing the quantity of free fatty acid (Dias et al. 2017). Two different catalysts sodium sulfate (Na₂SO₄) and Zinc-aluminum oxide (Zn-Al₂O₃) were studied by Anderson et al. (2016) to ascertain their efficiency in reducing free fatty acid content of scum derive oil. The result showed that Zinc-Aluminum oxide was more effective by reducing free fatty acid from 86 wt% to 1 wt%.

Classification	Type of feedstock	Palmitic acid (C ₁₆ H ₃₂ O ₂)	Stearic acid (C ₁₈ H ₃₆ O ₂)	Oleic acid (C ₁₈ H ₃₄ O ₂)	Linoleic acid (C ₁₈ H ₃₂ O ₂)	Linolenic acid (C ₁₈ H ₃₀ O ₂)
First generation feedstocks	Soybean oil	10.4–24.8	2.6–4.7	16.5–24.8	51.8–53.0	6.5–7.0
	Palm oil	37.80–43.79	2.7–4.76	39.90–42.6	9.59–12.20	0.17–0.53
	Olive oil	9.7	1.74	82.3	-	-
	Rapeseed oil	3.49–4.0	0.55–2.3	62–77.8	1.8–8.23	1.8–8.23
	Sunflower oil	10.58	4.76	22.52	8.19	8.19
Second generation feedstocks	Tallow oil	29.0	24.5	44.5	-	-
	Jatropha. C oil	14.2	7.0	44.7	32.8	-
	P. pinnata oil	10.2	7.0	51.8	17.7	0.2
	M. indica oil	24.5	22.7	37.0	14.3	3.6
	Neem oil	13.8	18.2	52.6	13.6	-
	Rubber seed oil	9.1	5.6	24.0	46.2	14.2
	Linseed oil	5.61	4.04	19.34	17.15	48.79
	Castor oil	0.92	0.16	3.53	4.21	0.91
Third generation feedstocks	Mustard oil	2.80	1.09	24.98	11.64	8.61
	Crude castor oil	1.06	1.15	3.71	5.41	0.58
	WCO	4.1–26.5	4–10.9	38.6–44.7	32.8–36	0.2

Chicken fat oil	19.82	-	37.62	-	1.45
Yellow grease	23.24	-	44.32	2.43	0.80
Waste frying oil	6.90	2.35	61.58	20.01	20.01
Waste animal fat,	22.31	17.02	43.26	9.76	1.71

Table 2: Compositions of various feedstock (%)

5.0 Oil Extraction

There are several methods that are applied for oil extraction. These methods are based on the source in which the oil is to be extracted.

Summary of some important methods of extraction are highlighted in Table 3.

Technique	Merit	Demerit
Steam distillation	It is good for non- temperature sensitive plant	Continuous wetting is needed to supply the cold temperature feed Into the system.
	Thermal degradation is minimized	It is capital intensive
Solvent extraction	Small amount of solvent is needed to extract a large quantity of oil	Some of the solvent used are highly flammable, thus not environment friendly.
	The process is easier to handle	
Mechanical extraction	Oil extraction efficient using this method is better than manual	This method is limited to few oil sources.
Enzymatic extraction	It does not have negative effect on the environment	Enzymes used for this process are very expensive
Microwave-assisted extraction	CO ₂ is not released during this process	It can only be applied for non-polar compound
Supercritical fluids extraction	Due to high solubility of solvent with oil, good percentage of oil is obtained.	This technique requires high temperature, thus high cost of energy.
Ultrasound-assisted extraction	This method is not capital intensive but yield good percentage of oil.	It can cause degradation of the oil.

Table 3. Summary of Oil Extraction Techniques for biodiesel production (Zulqarnain et al., 2020)

6.0 Biodiesel Production Techniques

There are different techniques by which biodiesel can be produced; some of the methods are highlighted below.

1.Direct Blending

To reduce the consumption of fossil fuel, crude oil from animal or plant source is blend directly with conventional diesel. Percentage ratio of mixing is very critical in achieving a good quality diesel. However, the biodiesel obtained from this method have some limitation such as high free fatty acid content, high viscosity and ease of gum formation. These make the biodiesel produced from this method unfit for many combustion engines (Chai et al, 2014).

2.Microemulsion

In this method, the oil is mixed with alcohol such as methanol, ethanol, propanol and butanol which are considered to be emulsifying agents. Other additives such as surfactant and alkyl nitrate are added to reduce viscosity, increase the cetane number and the volatile property of the diesel. The major problems associated with biodiesel produced via microemulsion include incomplete combustion, and accumulation of carbon in the engine which can lead to nozzle failure (Demirbas, 2009).

3.Thermal cracking (pyrolysis)

This is the application of heat in the absence of air to convert complex structure of hydrocarbon into simple compound with or without the aid of catalyst. This process helps in reducing density and viscosity of the biodiesel which are major parameters affecting combustion of biodiesel in diesel engines. Biodiesel obtained from this technique can be use directly without much modification. Pyrolysis process for biodiesel production is always performed between 250 °C and 350 °C with the use of catalyst such as alumina, and zeolite. the process is carryout in a reactor where the oil is been heated and then the vapour condensed to obtained biodiesel (Kansedo et al., 2009).

4. Transesterification

Transesterification or alcoholysis is a reaction by which triglyceride (TG) reacts with alcohol in nucleophilic manner to produce Fatty Acid Methyl Ester (FAME) and glycerol as by – product (see Figure 1). The reaction involves three steps (i) reduction of triglyceride to diglyceride (ii) reduction of the diglyceride to monoglyceride (iii) the conversion of monoglyceride to glycerol. At each step, ester is been formed, thus the overall reaction gives rise to three molecules of ester (Changmai et al, 2020). The reaction is aided by the use of catalyst and there are different categories of catalysts that can be used for this purpose (base catalyst, acid catalyst, enzyme, bifunctional catalyst etc). The choice of the catalyst depends on the free fatty acid content of the oil.

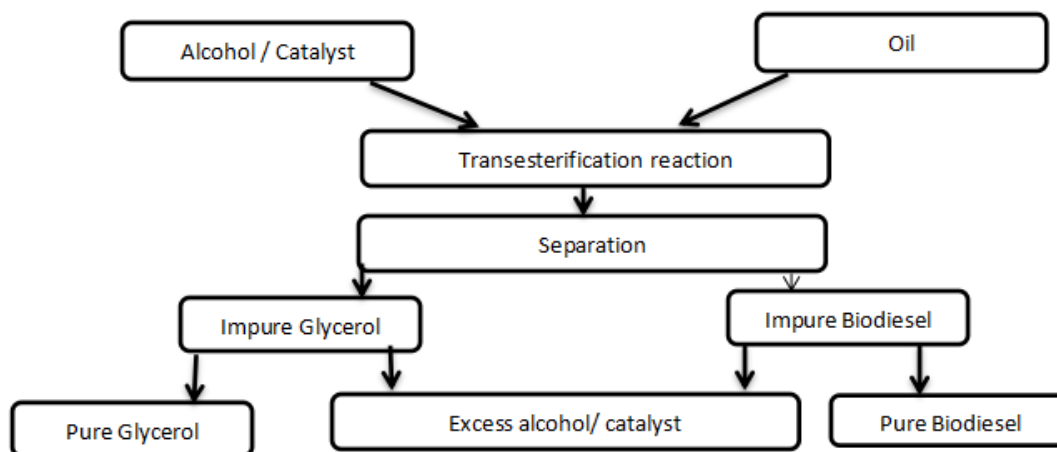


Figure 1 : Transesterification reaction scheme

7.0 Biodiesel production reactors

Reactors are equipment which provides an enabling condition for chemical reaction to occur. In a reactor, reactants are transformed to

products after been subjected to the required conditions. There are many configurations (types) of reactors that are used for biodiesel synthesis, depending on the production method either in batch or continuous process (Gerpen, 2005). Below are some of the reactors used in biodiesel production

Type of reactor	Description	Advantage	Disadvantage	References
Batch	It is a vessel with stirring system, thermometer and pressure gauge attached to it.	It is easy to operate	Poor control of mass transfer. Bulky size of reactor	Kraai (2009) Abdurakhman et al. (2017)
Continuous Stirrer Tank Reactor	Reactants and product(s) flow in and out continuously. Parameters includes input and output rate, agitation speed, residence time, mass transfer rate and mixing efficiency.	It produces quality product. Operation parameters are easily control.	It required much energy. High cost of operation.	Janajreh et al.(2016)
Fixed Bed Reactor	It is a cylindrical tube packed with some catalyst pellet in a fixed bed.	It promotes longevity and activity of heterogeneous catalysis. Reaction time is reduced.	High ratio of alcohol to oil is required for optimum yield. Accumulation of the by-product on the surface of the catalyst.	Hama et al. (2013)
Bubble Reactor	The reacting scheme of bubble column reactor is divided into two, vapour and liquid phase. Reaction occurred at very high temperature.	Reduces formation of soap. Oil with high free fatty acid can be used without pretreatment.	biocatalyst cannot be used because there are easily destroy by mechanical agitation	Adeleke. (2021)
Reactive Distillation Column	In reactive distillation The product formation and removal occur concurrently.	The major advantage of using this process is the combination of reaction and separation unit in single system	Complex arrangement of equipment	Adeleke. (2021)
Hybrid Catalytic Plasma Reactor	This reactor uses high energy electrons to energize reacting molecules.	It does not required catalyst, short resident time, no formation of soap.	The major challenge of the reactor is the regulation of the reaction parameter.	Istadi et al. (2014).

Membrane reactor	Here the reaction and separation of product(s) via membrane separation occur simultaneously in the same apartment	It has the ability to regulating the mixing of the reacting molecules and also possesses high selectivity	Sensitive to temperature different	Vares et al. (2014)
Sonochemical Reactor	This is a novel reactor that utilized energy from ultrasonic irradiation to generate cavitation	Low operating cost , high yield and selectivity, operating conditions are easy to control		Gogate et al. (2009) Colucci et al. (2005)

Table 4: Type of biodiesel reactors

8.0 Biodiesel Reagents

The two major reagents for biodiesel production are alcohol and fatty acid (oil). Alcohol is an important raw material for biodiesel synthesis. Several alcohols have been investigated for biodiesel production, but the most widely used are methanol and ethanol. This is because of their physical and chemical properties which makes them very reactive with triglyceride (Demirbas, 2008). Other lower chain alcohol like propanol, butanol, isopropanol and branch chain alcohol are also investigated. The ratio of alcohol to oil is another important factor to be considered during transesterification reaction. It affects the yield, rate of the reaction and cost of production. According to Barnwal and Sharma (2005), the ratio of oil to methanol when alkali catalyst is used is 1: 6, the high amount of methanol is to break the chain of fatty acid – glycerol (Agarwal, 2007), thus alcohol to oil ratio above 6 : 1 influences the production process negatively, and does not increase the amount of biodiesel produce. Silva et al. (2011) reported incomplete reaction with ratio less than 6:1 while higher ratio above 15:1 resulted in difficult separation of products and subsequent decrease in percentage yield.

9.0 Catalysts used for biodiesel production

Catalyst create alternative pathway which allowed for the utilization of minimum amount energy thereby cutting down the cost of the process (Robert 2017). In the process, it increasing the rate of formation of the desired product and lower the formation of the undesired product, this is term selectivity. Catalysts used for biodiesel production are categorized into four groups and each category comprises of sub-groups, there are homogeneous, heterogeneous, immobilized enzymes and bifunctional categories.

(a). Homogeneous Catalysis

Homogeneous catalysts used for transesterification process are basically of two types; acid and base. These are the most widely used and investigated catalyst for biodiesel production because they are less expensive and properties are easy to study. The base catalysts are basically metallic hydroxides from group 1 and 2 elements (NaOH, KOH, NaOCl etc). Hassain and Boyce (2009) used KOH in pure sunflower cooking oil and waste sunflower cooking oil and reported yield of 99.5 % under the following reaction conditions 40 °C, stirring speed 320 rpm and methanol-to-oil ratio of 6:1. Buendia-Tamariz et al. (2015) synthesized biodiesel from chicken fat and pennycress oil via double steps method; in the first step, esterification of the oils were carried out using H₂SO₄ while second step, the transesterification make use of KOH catalyst. Homogeneous base catalyst gives a better yield than its acid counterpart but when oil feedstock with high free fatty acid is involved, the basic catalyst react to form soap via saponification and this would consumed the catalyst and reduces its activity thus some oils required acid catalyst. Daniyan et al. (2019) used HCl as catalyst for frying oil transesterification and reported yield of 93 %. Goff et al. (2004) carried out a study to evaluate alcoholysis of soybean oil using hydrochloric acid, formic acid, acetic acid, sulphuric acid and nitric acid and reported that sulphuric acid gave the maximum yield. Miao et al. (2009) investigated

biodiesel production from soybean oil using trifluoroacetic acid as catalyst. The result showed 98.4% conversion at optimal reaction conditions.

(b). Heterogeneous catalyst

Heterogeneous catalyst reduces process cost and improve the quality of product obtained in addition to been eco- friendly. Aside from the above mentioned advantages, it can be easily recover; can withstand harsh reaction conditions and has longer reusability than homogeneous catalyst. There are majorly two categories of heterogeneous catalyst, acid and base. Each of the categories comprise sub-groups which are derivative of the parent group. Acid heterogeneous catalysts are derived mainly from mineral acid; they show high activity in catalyzing biodiesel production from oil with high value of free fatty acid without formation of soap. It is a good substitute for homogeneous acid catalyst because it is ease to separate, minimal corrosiveness and toxicity. Umar et al. (2019), investigated the potential of Amberlyst 15 (ion exchange resin) in catalyzing biodiesel production from vulgaris seed oil and reported 93.2 % yield. A report from the work of Kansedo et al. (2009) has it that 80 % yield of biodiesel was obtained from transesterification of hydrolyzed sea mango oil using Amberlyst 15. Deboni et al. (2018) produced biodiesel from soybean oil using Amberlyst 26 and reported 99 % yield of FAME. Ilgen et al. (2009) reported 63 % yield when Amberlyst 26 was used to catalyzed biodiesel production from canola oil under optimum conditions. Heterogeneous catalysts from basic sources are the most widely investigated catalyst because of its excellent catalytic activity under mild reaction conditions. Alkaline earth oxides are the bases of these catalysts due to its high basicity and insolubility in methanol. It can maintain its efficiency up to 10 cycles (Liu et al, 2008). Several heterogeneous solid base catalysts have been reported in many literatures. Kouzu et al. (2009), prepared and investigated CaO catalyst for production of biodiesel from soybean oil and reported 95 % conversion. Dahkhoda et al. (2010) produced biodiesel from palm oil using KOH/activated carbon catalyst and reported 94 % yield.

(c). Sulfonated carbon- base catalysts

Sulfonated carbon is another potential catalyst that has shown a promising activity in transesterification reaction. This is basically due to its distinctive surface chemistry, high thermal and chemical stability aside from been biogenic and eco-friendly the feedstock are cheap. It can be prepared from different methods like incomplete carbonization of aromatic substances in tetraoxosulfate(vi)acid or treating carbon materials with sulfonated reagents like ClSO₃H, P-toluenesulfonic acid, gaseous SO₃ etc (Malins et al 2016). Nakajima et al. (2012) prepared amorphous cellulose originated carbon solid acid catalyst and used it for biodiesel production from oleic acid. The report has it that 99.9 % conversion was recorded.

(d). Zeolites

Zeolites are microporous crystalline of aluminosilicates. Depending on the preparation process, it can exist in different structural morphologies. The ease by which its structure can be modified makes them excellence catalyst for transesterification reaction. When the pore size and the ratio

of Si/Al are varied, the catalyst properties vary too. Different metal ions can be incorporated to improve the basicity of the catalyst. Several Zeolites have been prepared and used as catalyst for transesterification reaction. Xie et al. (2007) synthesized and investigated zeolites load with different concentrations of KOH and recorded 85.6 % yield of biodiesel with 10 % KOH loaded zeolite. Shu et al. (2007) synthesized La/Zeolites catalyst using $\text{La}(\text{NO}_3)_3$ as precursor through ion exchange approach and reported 48.9 % biodiesel yield when used for transesterification of soybean oil.

(e.) Hydrotalcites

Another promising group of catalyst is the hydrotalcite. It belongs to the double layer hydroxides with the general formulae $\text{Mn}^{2+}\text{Mm}^{3+}(\text{OH})_{2(m+n)}[\text{A}^x]_{m/x}\cdot\text{YH}_2\text{O}$ where M^{2+} is a divalent metal and M^{3+} is a trivalent metal and often A^{3+} , A^x is an anion with x in the range of 0.1 – 0.5. Many of this catalyst are currently in use. Nayajas et al. (2018) synthesized Mg/Al hydrotalcite catalyst via co-precipitation method and utilized it in transesterification of sunflower oil and reported 96 % yield. Ma et al. (2016) applied Mg/Al hydrotalcite catalyst for biodiesel production from waste-cooking oil and reported a yield of 95.2 %. In another study by Zeng et al. (2014) Mg/Al- CO_3 hydrotalcite catalyst was prepared with ratio of Mg/Al of 4:1 using Urea method. The report has it that conversion of 90.3 % biodiesel was obtained when the catalyst was used for transesterification of microalgae oil.

(f) Mixed metal oxides

It is obvious from many researches that when two metallic oxides of different basicity are combined, their individual properties change, one would behave like an acid while the other assumed basic nature. It is on this light that mixed oxides are used for catalyst synthesis. Several catalysts of this series have been prepared with report of high catalytic activity, increased basicity, good surface area, high stability and reusability. Kawashima et al. (2008) examined different calcium containing catalyst (CaTiO_3 , CaMnO_3 , $\text{Ca}_2\text{Fe}_2\text{O}_5$, CaZrO_3 and CaO-CeO_2) in transesterification of rapeseed oil and reported biodiesel yield of 90%. A mixed oxide of La_2O_3 loaded with ZrO_2 was prepared by (Sun et al, 2010) and reported biodiesel yield of 96% with sunflower oil.

(g) Biomass - based catalyst

Recently waste from biomass has been used to synthesize catalysts for biofuel and other chemical processes. Their variable composition of different oxides makes them promising area for research. Its usage aside from helping in coping the menace of environmental pollution also provide less expensive, less toxic, ecofriendly, sustainable and easily available source of catalysts. They can be derived from both animals and plants wastes in industries and households. Many of them are good sources of alkaline and alkaline earth oxides. Several works have been reported on the formulation and usage of biomass-based catalysts for biodiesel production. Wei et al. (2009) and Goli and Sahu (2018) reported a preparation of CaO catalyst from chicken eggshell, when applied in transesterification of soybean oil with a yield of 95 % and 93% were recorded respectively. Ayodeji et al. (2018) formulated catalyst using eggshell for biodiesel synthesis from soybean oil. According to the report 90 % yield of biodiesel was obtained.

(h). Enzymes

Enzymes catalysts are another promising set of catalysts that showed great potential in catalyzing transesterification reaction. They are very reactive and produce good quality biodiesel under mild reaction conditions with ease of separability. They can catalyze oil feedstock with high free fatty acid content without formation of soap. The catalyst can be used in free form or in immobilized lipase form. Jayaraman et al. (2020) applied lipase as catalyst to synthesize biodiesel from waste-cooking oil and reported yield of 88%. Marin-suarez et al. (2019) using process optimization synthesized biodiesel from low quality fish oil using lipase catalyst.

(i). Bifunctional catalyst

Bifunctional heterogeneous catalysts are those types of catalyst that have both acidic and basic properties, they are prepared from oxides of either group one and three or two and three. The group three oxides are amphoteric in nature always assumed acidic properties while the other oxide shows basic properties. Thus, it can catalyze both esterification and transesterification simultaneously. They showed good activity during biodiesel process even with oil that has high fatty acid content. Its effectiveness in biodiesel production overshadowed the shortfall of both basic and acid catalysts. Farooq et al. (2013), prepared Mo-Mn/y- Al_2O_3 -MgO bifunctional catalyst and used it to catalyze waste cooking-oil having free fatty acid content of 3.37 mgKOH/g and reported 91.4 % biodiesel yield. Sulaman et al. (2016), developed Cu-Zn/y- Al_2O_3 bifunctional catalyst and used it for simultaneous transesterification and esterification of waste cooking oil and recorded biodiesel yield of 88.82 %.

10. Factors affecting biodiesel production via transesterification

The yield of biodiesel is influenced by some factors like temperature of the reaction, time of reaction, methanol to oil ratio, mixing rate, effect of water and free fatty acid content. These factors depend on the type of catalyst used for the transesterification.

(i). Alcohol to oil ratio

The ratio of alcohol to oil is very critical in biodiesel synthesis and it influences the yield significantly. It depends mostly on the type of catalyst used for the process. For example, when base catalyst is used, the alcohol to oil ratio is fixed at 6:1 according to (Zhang et al, 2003). A report from Jain et al. (2014) has it that when the quantity of methanol was increased from 10 to 30 % (v/v), a high yield of 90.6 % was obtained. It is imperative to note that, transesterification being a reversible reaction, requires large amount of methanol to keep the equilibrium in the product side. Increasing the ratio above particular critical value does not promote the reaction rate or percentage yield (Yaqoob et al, 2020). Nevertheless, excess use of alcohol would increase the overall cost of production due to alcohol removal and purification of the product.

(ii). Temperature

Reaction temperature is one of the most important factors that affect biodiesel yield in transesterification reaction. Temperature increase speed-up the rate of reaction and reduces the reaction time due to reduction of viscosity of the oil (Mathiyazhagan et al., 2011). During reaction, the energy possessed by the reacting molecules is proportional to temperature. Thus elevated temperature of the reaction would promote miscibility between non-polar oil and the polar alcohol. But the temperature has to be controlled in order not to exceed the maximum value that is necessary for the reaction because if it does, parallel reaction may occur which would decrease the yield of the biodiesel. Kumar et al., (2013) obtained optimum yield of 96 % biodiesel at 80 °C when using temperature range of 60 to 120 °C in transesterification of sunflower oil. In a similar work, Joshi et al. (2019) obtained optimum yield at 60 °C during transesterification using waste-cooking.

(iii). Reaction time

Reaction time is very essential in biodiesel synthesis; researches have been performed to ascertain optimum time for biodiesel production. Alamu et al. (2007) observed that the rate of conversion increases from the start to 90 mins after which no much effect was observed. Leung and Guo (2006) observed that longer reaction time beyond the peak lead to loss of biodiesel due to reversible reaction and formation of soap.

(iv). Amount of catalyst and type

Biodiesel yield during transesterification reaction depends largely on the type and amount of catalyst used. Utilizing large amount of catalyst promotes the rate of reaction and the subsequent increase in yield, this is due to the availability of more active site (Rashid, 2008). However, the use of excess catalyst can lead to high viscosity of the resultant biodiesel.

Thus, amount of catalyst must be controlled to prevent high cost of purification. Rathore et al. (2015), observed that when the concentration of KOH catalyst was increase from 2 to 12 %, the biodiesel yield increases from 20 to 95 %. Biodiesel yield increases until optimum load of catalyst is used.

(v). Effect of water and FFA content

Water and free fatty acid content in reactants are critical in the choice of reaction route during transesterification. There are percentage limits of each of these (water and free fatty acid content) that can be allowed in feedstock before the reaction can be effective. For example base-catalyst can only be used in oil with free fatty acid content of less than 1 % to avoid formation of soap via saponification reaction. Similarly acid catalyst can lead to ester formation in oil with high water content. Nevertheless, transesterification that occur at supercritical condition does not required the removal of water and free fatty acid content from the oil.

(vi). Mixing intensity

Alcohols and oils are not perfectly soluble when mixed, thus at rest (when the mixture is not agitated) the reaction occurred at the interface between the two liquids. This makes transesterification reaction to be slow at the beginning. Intensity of mixing is very important factor during transesterification reaction because it allows for oil and solvent interaction which in turn increases the rate of reaction. Many literatures have acknowledged that moderate agitation speed of 400rpm gives the optimum yield Tabatabaei et al, 2019. It has been noted that lower agitation speed slow the rate of reaction while high agitation speed causes the formation soap due to irreversibility.

11. Life Cycle Assessment (LCA)

Life Cycle Assessment is a means through which impact of process or product on the environment is evaluated. It assesses the raw material(s) acquisition, energy utilization, production process; transportation of raw materials and finish product, product usage and product disposal and this approach is called Cradle to Grave analysis. Knowing the impact of a product to the environment is very necessary because it helps in decision making process about the product either to improve on the production route or to abandon the utilization of the production. There are basically four stages in LCA and are goal and scope, inventory analysis, impact assessment and interpretation. Life cycle Assessment of biodiesel is very important because it help to ascertain the impact of biodiesel to the environment so that if the negative effect is much, the impact can be reduced or processes leading to such impact can be improved. LCA performed by Sebitso et al. (2015) on biodiesel using Simapro 7.3.3 as analyzing tool with waste cooking and NaOH as oil source and catalyst respectively. The outcome of the finding indicated that during transesterification process, electricity has the highest environmental impact followed by alcohol. The grand analysis showed that the use of van for the distribution of biodiesel had the highest environmental impact than any other stage. According to Liang et al. (2013), different feedstock have different environmental impact, but concluded that biodiesel usage mitigate environmental pollution as compare to fossil diesel.

12. Economics feasibility

Economic feasibility study is an important aspect of production process because it helps to evaluate the economic validity of the final product whether it would yield profit or not. This is done after the pilot production has been optimized (Mathew et al, 2021). The feasibility study takes into consideration the cost of raw materials, transportation, energy, labour and equipment, sometime the cost of alternative product(s) in the market. Biodiesel economic feasibility studies have been performed by various researchers to ascertain the economic validity of the product. Using Aspen Hysys v 7.0 El-Galad et al. (2015) studied the production of biodiesel using fatty acid from oil and soap industries and concluded that biodiesel production using fatty acid from these is feasible and cheap with a yield of high quality biodiesel. Another study on the use of Pongamia oil for

biodiesel synthesis performed by (Prasad et al., 2020) indicated positive Net Present value and Benefit Cost Ratio of greater than 1, which means that the production process is economically viable. Raw material and catalyst cost are major challenges in biodiesel production. According to Edeh (2020) this can be mitigated by using alternatives and advance technologies. Mizik et al. (2021) ascertain that the use of waste cooking oil or algae oil as feedstock is economically viable than other feedstock.

13. Conclusion

The use of biodiesel as alternative fuel has come to stay and it has been proven to be efficient, economically viable, means by which greenhouse gases emission can be mitigated as well as a good way of waste management. Various raw materials for its production are readily available and researches are ongoing for development of novel feedstock that will enhance optimum production. Likewise, several production techniques have emerged over the years and new ones are still emerging geared towards improving product yield and process efficiency. Its utilization as alternative source of energy cut across manufacturing and transportation sectors without modification of the combustion chamber of the engine. Life Cycle Assessment conducted by several researchers pointed at positive index from raw materials acquisition to product disposal (cradle to grave) and is economically sustainable. Thus, it is imperative for government and other regulatory bodies to encourage the production and utilization of biodiesel by providing the enabling environment for it to strive.

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