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A review on influencing parameters of biodiesel production and purification processes

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ABSTRACT

Biodiesel is an alternate renewable, biodegradable, non-toxic fuel similar to conventional fossil fuel. It is usually produced from vegetable oil, animal fat, tallow, non-edible plant oil and waste cooking oil. Biodiesel emits fewer air pollutants, greenhouse gases other than oxides of nitrogen and easier to treat when compared with fossil fuels. However, with all these environmental benefits, biodiesel could not be extensively used as a complete alternative fuel to conventional diesel. Accordingly in this study apart from the scope and need of biodiesel, an attempt has been made to address the number of parameters that influence the production process of biodiesel. Lipid/fat content, type and catalyst concentration, oil to alcohol ratio and other purification process has been discussed to reduce the unit operation involved in biodiesel production.

1. Introduction

World's anticipated energy prerequisite in the year 2030 shall be 50% more than it is today. On one hand, world's economy is largely dependent on the transportation of goods and services, and on the other hand, transportation is mainly dependent on energy from petroleum fuels. The shipping sector alone consumes 30% of the world's total energy production and the last three decades have perceived a steep rise in the number of vehicles worldwide [1,2]. About, 96% of the shipping sector is reliant on fossil fuels [3]. Remarkably, accepted the use of fossil fuel has caused global warming conditions; therefore, fossil fuels as a source of energy should be replaced with renewable and clean energy sources to reduce the emission of carbon dioxide and greenhouse gases [4,5]. The global climatic change, rising crude oil price, rapid depletion of fossil fuel reserves, concern about energy security, land and water degradation have forced governments, policymakers, scientists and researchers to find alternative energy sources including wind, solar and biofuels [6–8].

The drawbacks of other renewable energy lead to high production of biofuel in particular biodiesel has gained as a sustainable source of fuel and it is considered as an important form of technological progress in diminishing pollution [9]. Biodiesel is renewable, sustainable, biodegradable, non-toxic and clean energy with a good flashpoint, better viscosity and calorific value similar to fossil fuels [10,11]. The price stability, reduce inter fuel competition, rich states, reduce the demand-supply gap and global demand for biodiesel have been projected to either doubled or tripled in many regions by another decade and beyond [12]. The commercial experience with biodiesel production has been very promising and this article addresses the relevant researches with many factors that have not been critically addressed for the commercial production of biodiesel as alternate biofuels.

1.1. Biodiesel production

Biodiesel can be produced from micro and macroalgae, animal fat and vegetable oil, food crops, lignocellulose material etc., Generally, biodiesel is typically produced via transesterification process, in which the reaction of vegetable oils with alcohol (methanol or ethanol) to produce alkyl esters and glycerol by using an appropriate catalyst [8]. Transesterification is a three-step reversible reaction and it takes place in a stepwise manner. In the initial step, conversion of triglycerides in the oil to diglycerides, diglycerides into monoglycerides and lastly glycerol. To favor the forward reaction, sufficient quantity (3:1) of alcohol to oil molar ratio is usually maintained in the transesterification process. However, an excess quantity of alcohol is usually added to drive the

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equilibrium towards the product side [13]. At the end of trans-esterification process, the reaction stream is separated into two phases: biodiesel phase (top layer) and glycerol rich phase (bottom layer) [14]. This excess alcohol would distribute in the biodiesel and glycerol phase. Fig. 1 shows the chemical equation for fatty acid methyl ester production from a triacylglycerides by the transesterification process in the presence of a catalyst.

1.2. Generation of biodiesel

First-generation of biodiesel which has been extracted from edible sources such as soybean, groundnut and canola which adversely affect the harvesting of food products for human consumption, environmental and climate change effects [15]. However, the first generation biodiesel has been effectively used as a replacement for gasoline on a large-scale basis of 5% mixture with gasoline since the 1930s. The second-generation biodiesel, made from cellulosic feedstock such as short-rotation forests, prairie grasses and municipal wastes [16,17]. *Jatropha*, an exemplified non-edible source requires vast amounts of arable land and results in low yielding oil production. From the above observations, search for alternative sources continued further to reduce the food cropland competition until using algae as a sustainable and rich source of biofuel which is known as third-generation biodiesel [18]. Algae-based biodiesel are considered to be a viable alternative third generation biodiesel since it do not have any influence on food supply. The use of microalgae is desirable since it can serve a dual role for bioremediation of wastewater as well as a source for biodiesel production with concomitant carbon dioxide sequestration [19]. Besides, algae can be grown on any available land, water or saline and produces more lipids, which is found to be a potential source in the production of biodiesel [20]. The up-gradation amenities of biodiesel industries to produce value-added products from the waste generated during the production process generally falls under a strategy of fourth-generation biodiesel [21].

1.3. Need for biodiesel

Over a decade, a significant base has been built for biodiesel on environmental and socio-economic impacts [22]. Due to the quick development of human activities, it has been estimated that oil and natural gas storage will be depleted in another few decades and become the largest challenge of the 21st century [23]. According to the organization of the petroleum exporting countries (OPEC) by 2040 world fuel oil demand will reach up to 109.4 million barrels per day from which, diesel fuel demands are expected to dominate by 5.7 million barrels per day [24]. Compounding these issues, volatile prices for fossil fuels are undermining energy security and eroding balances of payments by escalating the cost of energy imports [25]. Consequently, there is renewed interest in the production and use of fuels from plants or organic waste [17]. Biofuel; biodiesel is environmentally friendly and shows great potential as an alternative liquid fuel and energy [26]. It is an alternative fuel similar to conventional diesel.

1.4. Scope of biodiesel

In late 2000, an increase in the usage of fossil fuels transformed on the economic prospects of alternative transport fuels, including that of liquid biofuels like bioethanol and biodiesel [27]. Biodiesel production along with food production models are reviewed and best practices are identified that can co-exist to enhance and expand the productivity and income of farmers [28]. Advancing the technologies helps to complement each other instead of competing against each other. Using biodiesel blended gasoline fuel for automobiles can significantly reduce petroleum use and exhaust greenhouse gas emission. The fuels have higher octane numbers and are preferred in spark-ignition internal combustion engines. The combustion properties of biodiesel are very close to those of petroleum diesel [29]. The comparable physical and chemical properties indicate that biodiesel can be used as such in the diesel engine without any engine modification. Among the other form of energy sources, biomass is most likely to be applied on a wide scale without any environmental or economic penalties. Also, aquatic biomass presents easy adaptability to grow in different conditions, either in fresh or marine water or in a wide enough range of pH [30]. The cost associated with the harvesting and transportation of microalgae is relatively low compared to those of other biomass materials such as trees and crops. Besides, they do not directly affect the human food supply chain thereby eliminating the food versus fuel dispute [4]. Production of bio-ethanol from biomass is one way to reduce both consumptions of crude oil and environmental pollution [31]. Moreover, crude glycerol produced has a major byproduct during biodiesel production can be used as a sole carbon source for the production of high-value chemicals [32]. It can be used as animal feed and lost cost manures which in turn reduces the treatment of crude glycerol. Hence, biodiesel industries also enjoy numerous benefits like self-disposal of crude glycerol, zero liquid discharge which helps to develop economically as a whole [33].

2. Parameters affecting biodiesel production

'The major obstacle of biodiesel commercialization is the price of feedstock, which occupies 70% of the production cost of biodiesel and biodiesel production technology [34]. The main important factors to be encountered during biodiesel production are feedstock availability, catalyst type and concentration, the molar ratio of oil to alcohol, reaction temperature, reaction time, mixing intensity, water content and agitation speed [35]. Table 1 clearly shows the yield of biodiesel on different types of catalysts and their concentration on various feedstocks.

2.1. Feedstock

The availability of feedstocks is the critical parameter that affects the economic feasibility of biodiesel production. Since it accounts for around 80% of the biodiesel total cost. In this context, several efforts have been carried out in the search of low-cost feedstock and its availability round the year [36]. Fatty acid methyl esters from algae, vegetable oil and animal fats shown an evident feedstock for biodiesel production due to improved viscosity, volatility and combustion behavior when compared

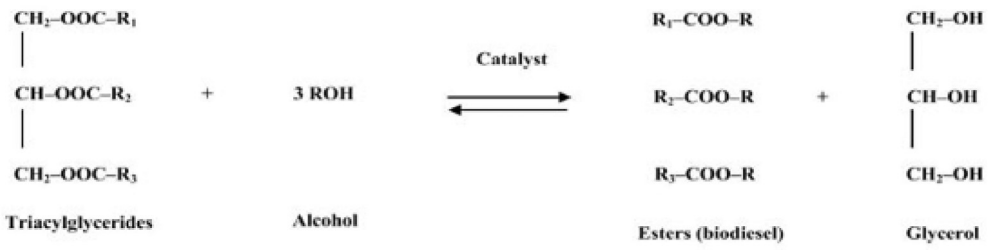


Fig. 1. Production of biodiesel from fatty acid by transesterification process.

Table 1
Biodiesel yield for different type catalyst on various feedstocks.

Catalyst	Concentration of Catalyst	Feedstock	Solvent	Oil to Alcohol ratio	Yield of Biodiesel	Reference
1.Heterogeneous						
CaO from egg shells	1.5wt%	Palm oil	Methanol	12:01	98%	[48,58]
CaO	1wt%	Sunflower oil	Methanol	6:01	91%	[48,59]
KF	4wt%	tallow seed oil	Methanol	12:01	96.80%	[48,60]
KNO	1wt%	Rape oil	Methanol	6:01	98%	[48,61]
ZnO	1.3wt%	Ethyl butyrate	Methanol	12:01	>90%	[48]
Al O	5.97wt%	Palm oil	Methanol	12.14:1	98.64%	[48,62]
MgO	4wt%	Mutton fat	Methanol	22:01	>98%	[48,62]
TiO	6wt%	Canola oil	Methanol	30:01:00	100%	[48,63]
2.Homogeneous						
Sodium hydroxide	1wt%	Sunflower oil	Methanol	6:01	87%	[40]
Potassium hydroxide	1wt%	Sunflower oil	Methanol	6:01	91.67%	[40]
Sodium methoxide	1wt%	Sunflower oil	Methanol	6:01	99%	[40]
Potassium methoxide	1wt%	Sunflower oil	Methanol	6:01	98%	[40]
3. Lipase Enzyme						
A. niger	1wt%	Palm oil	Methanol	3:01	69%	[64]
R. oryzae	1wt%	Soybean oil	Methanol	3:01	85%	[64]
4. Nano catalyst						
KF	3wt%	Canola oil	Methanol	15:01	82.1	[51]
MgO	3wt%	Soybean oil	Methanol	2:03	99%	[51]
ZnO	14wt%	Castor oil	Methanol	12:01	91%	[50]
CaO	1wt%	Soybean oil	Methanol	7:01	96%	[53]

with conventional fuels. Main animal fat sources are beef tallow, lard, poultry fat and fish oils similarly the vegetable oils like rapeseed oil, castor berry, palm pulp, palm kernel oil, sunflower seeds, coconut kernel, cottonseed, peanut grain, canola seed were used for the biodiesel production process [37]. Some microalgae can double their biomasses within 24 h and the shortest doubling time during their growth is around 3.5 h which makes microalgae an ideal renewable source for biodiesel production [6]. Its abundance and utilizing enriched nutrients from wastewater as a low-cost nutrient source are benefiting from microalgae cultivation [38]. A major drawback of algal species are obligate phototrophs and this requires light for their growth [39]. The content of FFA and the presence of impurities affect the type of biodiesel production process used and the yield of fuel from that process. In recent, alternatively, lipid residues as waste frying oil and inedible animal fats have also received considerable attention from the biodiesel sector. However, it is important to find new alternative sources that don't compete with food chains.

2.2. Homogeneous catalyst

The Homogeneous catalyst includes alkalis and acids. The most commonly used homogeneous catalyst are alkali catalyst which includes sodium hydroxide, sodium methoxide and potassium hydroxide [40]. In the transesterification of Karanja oil, KOH performed excellently with a methyl esters yield of above 90% at 1% and 1.25% catalyst dosage, in 1 h reaction at 65c with a stirring speed of 600 rpm [41]. In a homogeneous catalytic process the undesired side reaction, saponification occurs which leads to an additional separation process to remove catalytic impurities which ultimately increases the final production cost [42–44]. Considering homogeneous alkali catalytic systems; (1) optimum temperature tends to be the one which is the closest to the boiling point of the alcohol used; (2) excess alcohol is necessary to promote a good conversion (6:1 is considered as the best methanol/oil molar ratio) [45]. A comparison is made for different basic catalysts (sodium methoxide, potassium methoxide, sodium hydroxide and potassium hydroxide) for methanolysis of sunflower oil and all the reactions were carried out under the same experimental conditions in a stirred batch reactor and the subsequent separation and purification stages in a decanter. Methoxides are more effective than hydroxides and show maximum yield nearby 100 [40]. The advantages of the homogeneous catalyst using biodiesel production are modest reaction conditions, high activity of base catalysts results in high yield in a short time, base catalysts are much more active than acid catalysts. The major constraints faced on the homogenous catalysts are separation problems after reaction and wastewater treatment, saponification forms a stable emulsion, catalysts cannot be reused, and basic catalysts are sensitive to the presence of FFA and water [46].

2.3. Heterogeneous catalyst

Heterogeneous catalysts are promising for the transesterification reaction of vegetable oils to produce biodiesel. Unlike homogeneous, heterogeneous catalysts be reused, regenerated and could be operated in continuous processes [47]. More recently, there has been an increase in the development of both acidic and alkali heterogeneous catalysts to produce fatty acid methyl esters, because of their utilization in the transesterification reaction greatly simplifies and economies the post-treatment of the products (separation and purification) [40,41]. In general, the heterogeneously catalyzed biodiesel production processes have less number of unit operations, with simple product separation and purification steps and no neutralization process is required [48]. The heterogeneous catalysis is influenced by the type of catalyst either solid or base, amount of catalyst, stream reaction time, a degree of mixing or stirring, alcohol/oil content and purity index of the feedstock [12]. The replacement of homogeneous catalysts by heterogeneous catalysts would have various advantages like simple procedures and efficient catalyst separation from the reaction mixture and the reduction of environmental pollutants [49]. The advantages of the heterogeneous catalyst using biodiesel production are environmentally friendly, nor corrosive, recyclable and with fewer disposal problems, easy separation of products, higher selectivity, longer catalyst life, acid catalysts are insensitive to the presence of FFA and water. Major snag on the heterogeneous catalyst is currently less effective than common homogeneous base catalysts, high alcohol-to-oil molar ratio and has mass transfer limitations in the multi-phase reaction systems [46].

2.4. Enzymatic catalyst

The potential of biocatalysts in biodiesel production is attracting continuous attention and the catalysts perform equally well with their chemical-based counterparts [41]. The utilization of lipases for the production of biodiesel has been reported as an effective means of circumventing the aforesaid problems. The first difficulty of using lipase is that it is more expensive than the base catalyst like NaOH. Immobilized lipase is distinguished from free lipase because of its easy recovery from the reaction mixture facilitating its repeated use [50]. The enzymatic reaction selectivity is high and the enzyme can be immobilized in the support

material include how far the fuel can be recovered using enzyme catalyst [42].

2.5. NanoCatalyst

The effects of using a nano-sized alumina catalyst support on the transesterification of the triglyceride to fatty acid methyl esters, FAMEs [51]. Nano-MgO with supercritical/subcritical methanol can improve the transesterification reaction of soybean oil yield about 78.5% [52]. The biodiesel is also produced from castor oil using ferromagnetic zinc oxide nanocomposite as a heterogeneous catalyst by a transesterification reaction. A single phase of nanocatalyst was confirmed by x-ray diffraction analysis [53]. Biodiesel produced from soybean oil using nanopowder calcium oxide (NanoCaO) under room temperature showed a low reaction rate was low and it required 6–24 h to obtain high conversion even after eight cycles with soybean oil and three cycles with poultry fat [54]. The usage of nanomaterial is expensive and however, it yields more than 95%.

2.6. Alcohol to oil ratio

The stoichiometric relation between alcohol and oil is 3:1. However, to drive the transesterification process in forwarding reaction excess alcohol usage is detrimental [55]. Methanol and Ethanol are the most common alcohols employed in the transesterification process. More than 80% biodiesel yield was obtained from soybean oil with 0.1% $NaOCH_3$ in a 2.5 h reaction time at 65c with 10:1 Me OH/oil molar ratio at 450 rpm shaking speed [41]. It is also reported that waste cooking oil at 65 °C with a molar ratio of 30:1 methanol to oil, took 69 h to obtain more than 90% oil conversion to methyl esters[56]. At the optimal alcohol to oil molar ratios of 12:1 and 18:1 for the supercritical methanol (SCM) and supercritical ethanol (SCE) [57].

2.7. Reaction temperature

The reaction temperature is one of the most important parameters that affect the yield of biodiesel production. The higher reaction rate was achieved with an increase in temperature by the reduction of oil viscosity. However, an increase in temperature beyond the optimum temperature leads to a decrease in biodiesel production because the higher temperature may accelerates the saponification of triglycerides [35]. Usually, the transesterification reaction temperature should be less than the boiling point of alcohol to prevent the evaporation of alcohol. The type of catalyst and oil used determines the optimum temperature in the range of 50 °C–60 °C for biodiesel production.

2.8. Agitation speed

Agitation speed plays an important role in the formation of fatty acid methyl esters because agitation of oil and catalyst mixture enhances the reaction [35]. For example, the mixing intensities chosen were 200 rpm, 400 rpm, 600 rpm and 800 rpm for 60 min while other parameters were kept constant. At 400 rpm higher conversion of the end product was obtained. At higher agitation speed soap formation occurs and at lower agitation shows a poor product formation. This is due to the reverse behavior of the transesterification reaction [39].

3. Purification of biodiesel

The main objective of biodiesel washing is to remove free glycerol, soap excess alcohol and residual catalyst. The drying of alkyl ester is needed to achieve the stringent limits of biodiesel specification on the amount of water content in the purified biodiesel product [65]. Table 2 shows the yield of biodiesel from the various purification processes. According to the main mechanism, the purification methods used till today for refining crude biodiesel can be classified in the following groups (a) wet washing, (b) dry washing(c) membrane extraction, (d) precipitation, (e) complexation and (f) simultaneous biodiesel synthesis and purification all methods can come under a single heading.

3.1. Wet washing

Wet washing is performed by distilled water or acidulated water (aqueous mineral acid solution). Water is used either at room temperature or as hot before entering into the wet washing step, the excess of alcohol is sometimes separated by distillation or evaporation. Comparison of purified ethyl esters of castor oil by water washing at different temperatures and pH. At the temperature of 30 and 70 °C with a pH of 2 and 7 showed a significant result when compared with other temperatures (20–90 °C) in the pH range of 1–7 [66,67]. The advantages of wet washing are very simple and effective method for purifying biodiesel, very effective removal of glycerol and methanol, possible use of aqueous of acids then disadvantages are requiring a large amount of water, drying of washed product is required to remove the trace amount of water increasing energy cost, requires washing and settling tanks occupying a large surface area.

3.2. Dry washing

Dry -washing is developed to replace water washing by environmentally friendly water -free purification methods. It removes the impurities from crude biodiesel using waterless washing agents: adsorbents and acid resins. Crude biodiesel was treated with 2 wt% magnesol at 65 °C after stirring for 20 min, the adsorbent was collected by filtration. However, a higher biodiesel yield was achieved by water washing (96%) than by, because a part of biodiesel remained in the column after purification. In this process of decalcification protons of the functional groups on the resin are exchanged by calcium ions of calcium soaps, glyceroxide, methoxide and hydroxide that are believed to compose the leached catalyst. Thus, the removal of leached calcium is by absorption into cation exchange resin with the help of its [68]. The advantages of dry washing are no risk of water in the fuel, allows for continuous operation, decrease the total time

Table 2
Yield of biodiesel from various purification process.

S.No	Purification method	Feed Stock	Oil: Alcohol ratio	Solvent	Ester content	Reference
1	Wet washing					
	Water	Curcas oil	1:09	Methanol	98%	[13,46]
	Complexation (EDTA)	Curcas oil	1:09	Methanol	98%	[46]
	Precipitation (Citric acid)	Curcas oil	1:09	Methanol	98%	[46]
2	Dry washing					
	Sulfonic resin	Sunflower oil	1:14	Methanol	95.70%	[46,69]
	Ion exchange precipitation (Na_2CO_3)	Sunflower oil	1:14	Methanol	95.70%	[46,69]
	Cation- exchange resins	waste cooking oil	1:20	Methanol	95.70%	[46,69]
4	Membrane extraction	waste cooking oil	1:2°	Methanol	95.70%	[46,69]
5	Distillation	yellow grease	1:30	Methanol	98%	[46,70]
6	No washing	pork lard	1:18	Methanol	95.70%	[46,71]

of production, drastic reduction of wastewater, the disadvantages are ion exchange resins do not remove methanol, need extra equipment, little higher running costs than water washing basicity [46].

3.3. Membrane extraction

Membrane-based separations are well-known technologies used in water purification and protein separations. At present, these membrane technologies are commercially applied in separations of aqueous solutions, but the treatment of non-aqueous fluids by membrane separation is currently emerging. The membrane can be organic or inorganic. Owing to their chemical and thermal stabilities, the latter type especially the ceramic membranes, is more suitable to use with organic solvents. Ceramic membrane coupled with liquid-liquid extraction for the continuous crossflow rejection of triglycerides from fatty acid methyl ester mixture. The average pore size for an oil emulsion was determined to be 44 μm with lower and upper limits of 12 μm and 400 μm respectively. Tubular ceramic membrane and Ultrafiltration membrane are the two membranes are more efficient of environmentally benign in the purification process when compared with other membranes [65]. The advantages are high potential in separating sodium soaps and alcohols, operational simplicity and flexibility, low energy requirements, easy control and scale-up, disadvantages are membrane must be cleaned, increases of biodiesel production cost, decreases of throughput by possible contaminations.

3.4. Precipitation

This purification method is based on the use of precipitating agents to remove calcium ions from crude biodiesel. When the precipitating agent, such as oxalic acid or citric acid, is added to crude biodiesel containing calcium ions, an insoluble compound is formed in the reaction mixture. The precipitated compound can be separated from the purified biodiesel by filtration or centrifugation. The advantages are high yield of purified biodiesel, reduced amount of water used in the process, simple removal of the precipitate by filtration. The disadvantages are successful precipitation depends on operating conditions, further studies are needed to optimize the precipitation conditions [46].

3.5. Complexation

Complexation is the combination of individual atom groups, ions or molecules to create one large ion or molecule. This method for purifying crude biodiesel uses a complexing agent to remove calcium ions, so far, only ethylenediaminetetraacetic acid (EDTA) has been used as the complexing agent for decalcifying crude biodiesel. EDTA forms a complex with calcium ions in 91:1 agent to calcium molar ratio. The advantages are calcium forms a complex with EDTA soluble in water, calcium remains in solution without ionic reactions. Several disadvantages of complexation are preparation of aqueous EDTA solution with difficulty, medium decalcification efficiency, EDTA is a hazardous substance.

4. Economic impacts of biodiesel

Replacing fossil fuels with biodiesel has the potential to stimulate several benefits. Biodiesel can be produced domestically, which lower the need for fossil fuel imports and reduces its price and generate economic sustainability of the nation [72]. If biodiesel production and use reduce the consumption of imported fossil fuels, the adverse impacts of supply disruptions can be avoided. Biodiesel production energy security to the nation which does not possess oil resources. The economic impact of biodiesel is not limited to biodiesel industry and the agriculture sector, they spill over throughout an economy due to the inter-linkages between production sectors.

5. Conclusion

To reduce CO_2 emissions and fulfill the increasing energy demands, a horde of research endeavors have been commenced to develop renewable and sustainable energy resources, which must be environmentally friendly, and cost-effective. Though the researchers could obtain more than 95% yield from various feedstock and catalyst yet, the commercialization of biodiesel has not been accomplished. The feasibility of production and utilization of biodiesel from various sources has been affected by several parameters. Apart from the conventional catalyst, several catalysts have been prepared from waste and cheap material like eggshell, crustacean shells, biochar from coconut shell and kraft lignin. The major purification processes which are used up to date are addressed with its merits and demerits. The low -cost feedstock has many impurities and low lipid or fat content which ultimately leads to increased pretreatment of the separation process and product quality improvement.

Declaration of Competing interest

None.

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