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Study on Some Advanced Techniques to Produce Biodiesel from Non-Edible Oils

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ABSTRACT

This paper reviews various technologies that have been used for biodiesel production till date, with a view to comparing commercial suitability of these methods on the basis of available feed stocks and associated challenges. Homogenously catalyzed processes are the conventional technologies. However, their large-scale applicability is compromised due to their characteristic challenges. Batch processes and continuous processes are used for industrial purposes and heterogeneous catalysis may be sustainable for the continuous processes. Heterogeneous catalysts from renewable sources may be both environmentally and economically viable. Reactive distillation has the major advantage of combining the reaction and separation stages in a single unit, thereby significantly reducing capital costs and increasing opportunities for heat integration. This paper is a comprehensive overview of current technologies and appropriate options for scale-up development, providing the basis for a proposal for the exploitation of heterogeneous catalysts from natural sources to optimize biodiesel production.

Keywords: *Biodiesel; Homogeneous Catalyst; Heterogeneous Catalyst; Production Techniques.*

1.0 Introduction

Biodiesel is defined as a clean-burning fuel with low viscosity, biodegradable and environmentally friendly due to its comparative low emissions and reduction of SO2 production [1]. The main advantages of producing and using biodiesel come from the fact that foreign oil imports can be reduced, using the current installed distribution networks and the current engine technologies.

The use of renewable sources for this biofuel industry helps to increase not only job generation and incomes, but also promoting energy self-sufficiency in rural areas [2,3].

Biodiesel is composed by fatty alkyl esters produced using different chemical routes according to the initial feedstock [4]. Transesterification and fatty acid esterification reactions are currently the most used [5,6].

However, other routes such as interesterification and thermal cracking can also be employed [7]. The increase in the petroleum prices and the diesel fuel consumption as well as the promotion of several bioenergy fuels policies and consumption incentives, project the biodiesel production above 50 billion liters by 2030 [8,9]. As a result, biodiesel has a rising potential market, that can be classified according to its end-use applications in: transportation, non-road applications (mining, forestry, construction, etc.), marine and heating [10]. Biodiesel can be produced from different feedstocks, including animal fat, vegetable oils and algae oils, among others.

Various methods have been employed in the production of biodiesel from oils and fats feedstock [6,7,23]. The use of a homogeneous catalyst also poses an environmental concern as the disposal of the resulting quantities of glycerol may be challenging [27,28] and not economically viable.

Hence, the quest for more innovative and efficient processes is reflected in the number of publications on biodiesel production till date. Some advances in heterogeneous catalysis have also been reported [29,30].

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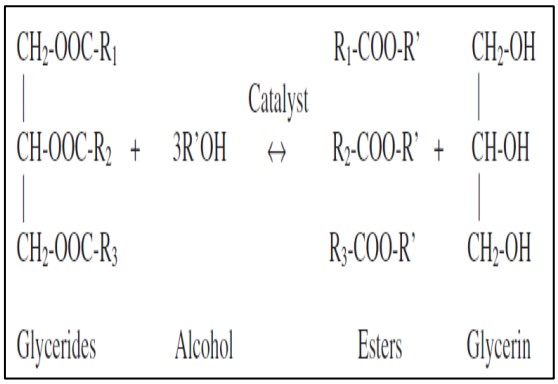
Heterogeneous catalysts from natural resources or biomaterials may be useful alternatives to conventional catalysts in view of the economics of production on commercial scale. This paper reviews various technologies that have been used for biodiesel production till date with a view to comparing commercial suitability of these methods on the basis of available feedstocks and associated challenges. The lessons gleaned from this review form the basis of a proposal for the exploitation of heterogeneous catalysts from natural sources to optimize biodiesel production, and to suggest an appropriate option for scale-up development.

2.0 Techniques for Biodiesel Production

The direct use of vegetable oils and its blends as fuel in diesel engines had been considered both unsatisfactory and impractical, primarily due to high viscosity, acid compositionand free fatty acid content of such oils, as well as gum formationdue to oxidation and polymerization during storageand combustion. Carbon deposits and lubricating oil thickeningare two of the more obvious problems [27]. As a result ofthese problems, efforts have been undertaken to convertthese vegetable oils to suitable and viable biodiesel fuels. Transesterification is the most popular and preferred, its preference having beenclearly reported in detail.Transesterification is the reaction of a fat or oil with an alcohol to form esters and glycerol. It should benoted that this equilibrium reaction needs greater amounts ofalcohol to shift the reaction equilibrium forward to produce more methyl esters as the desired product.

Fig 3: Transesterification Reaction



3.0 Transesterification of Vegetable Oil Using Homogeneous Catalysts

In the transesterification of different types of oils, triglycerides react with an alcohol,generally methanol or ethanol, to produce esters and glycerin. To make it possible, acatalyst is added to the reaction.

The overall process is normally a sequence of three consecutive steps, which arereversible reactions.

In the first step, from triglycerides diglyceride is obtained, fromdigly-ceride-monoglyceride is produced and in the last step, from monoglycerides glycerin isobtained. In all these reactions esters are produced.

3.1. Alkali-catalyzed transesterification process

The homogeneous alkali-catalyzed transesterification has been the commonest method used at laboratory, pilot and industrial scale levels [32,33].

This process is catalyzed by alkaline metal hydroxides and alkoxides [34] as well as sodium or potassium carbonates [23].

The production cost of these catalysts is low and they show a very high performance when feedstocks (vegetable oils) with low free fatty acid are used. Also, this reaction leads to high conversion of triglycerides to their corresponding methyl esters in short reaction times.

However, this method also has its own shortcomings as it is energy intensive, recovery of glycerol is difficult, the catalyst has to be removed from the product, alkaline waste water requires treatment, free fatty acid and water interfere with the reaction, and low selectivity leads to undesirable side reactions [27,33].

3.2 Acidcatalyzed transesterification process

This way of production is the second conventional way of making the biodiesel. The ideais to use the triglycerides with alcohol and instead of a base to use an acid—the mostcommonly used is sulfuric acid [7,9,12] and some authors prefer sulfonic acid [13].

Thistype of catalyst gives very high yield in esters but the reaction is very slow, requiring almostalways more than one day to finish.

3.3 Two-step transesterification process

This method is useful when dealing with feedstocks containing high free fatty acids (FFAs). It has been shown that alkaline catalysts cannot directly catalyze the transesterification of oils containing high FFAs save for FFA levels ranging from a mass fraction of 0.5% to less than 3% of the oil [38].

The transesterification of high FFA oils can be achieved by employing a two-step transesterification process. In this technique, the first step is an acid catalyzed process which involves esterification of the FFAs to FAMEs [4,] as described in Section 3.1, followed by a second step, alkalicatalyzed transesterification, as described in Section 3.2.

Various studies have been conducted using this technique with reported high yields of biodiesel [16,37]. Although a limit of <3% FFA level in oils has been reported as acceptable for homogeneous alkaline catalysis for biodiesel production without pretreatment, the FFA contents may extend beyond this limit, as it has been reported that a two-step process can also be achieved using alkaline catalysis in both steps to maximize overall yield [43] at room temperature.

4.0 Transesterification of Vegetable Oil Using Heterogeneous Catalysts

The high production cost of biodiesel is due to both the cost of raw materials and processing costs. The application of heterogeneous (solid) catalysts in biodiesel production alleviates the problems associated with homogeneous catalysis. Heterogeneous catalysts can be recycled and re-used severaltimes with better separation of the final product, minimizingmaterial and processing cost.

The acidicand basic characteristics of heterogeneous catalysts are important properties suited for use in transesterification of triglycerides just as homogeneous catalysis [37].

The reaction mechanisms have been reported showing some similarities to those of homogeneous catalysis, and these have also been reported in detail elsewhere [30,26].

These solid catalysts can be divided into two categories based on their catalytic temperature: high temperature catalysts and low temperature catalysts.

The purity of methyl esters exceeds 99%, with yields close to 100%. In addition, the heterogeneous process produces glycerol as by-product with a purity of greater than 98% compared to about 80% from the homogeneous process [31]. Heterogeneous catalysts can easily be tuned to include desired catalyst properties so that the presence of FFAs or water does not adversely affect the reaction steps during transesterification. Other advantages of the heterogeneous catalysts include its prolonged lifetime for fatty acid methyl ester (FAME) production and the fact that it is relatively cheap in comparison to homogeneous catalysts [25].

4.1 Heterogeneous acid transesterification

Heterogeneous acid catalyst has the ability to catalyze both transesterification and esterification reactions simultaneously, which becomes quite important when using low quality feedstocks [28]. This catalyst is less corrosive, less toxic, and generates fewer environmental problems [38]. Industrially, heterogeneous acid catalysts have been determined to be useful because they contain a variety of acid sites with different strengths of Bronsted or Lewis acidity as compared to the homogeneous acid catalysts. Solid acid catalysts such as Nafion-NR50, sulphated zirconia and tungstatedzirconia, were chosen to catalyze biodiesel-forming transesterification due to the presence of sufficient acid sitestrength [41]. These heterogeneous acid catalysts could be either the low or high temperature type.

4.2. Heterogeneous alkali transesterification

The use of heterogeneous alkali transesterification has been interesting in biodiesel production as a result of its simplification of production and purification processes, the decrease in the amount of basic waste water, the downsizing of process equipment, and the reduction of environmental impact and process costs [17].

Apart from ease of catalyst recovery, it has been shown that activity of a heterogeneous alkali catalyst may resemble a homogeneous counterpart at the same operating condition [18].

Low tolerance to FFA and water in raw materials has been reported for heterogeneous alkali catalyst, and this has prevented their use for direct processing of crude oils with a high acid number [19].

4.3 Heterogeneous catalysts from natural sources

Some biomass materials have been shown to possess catalytic properties that render them suitable for biodiesel production [29].

The application of these renewable feedstocks and heterogeneous catalysts from natural sourcesfor biodiesel production will certainly lead to thedevelopment of a cost-effective process that is environmentally friendly.

An eco-friendly process for biodiesel production can also be realized. The catalytic activity of calcium containing natural and biological materials has been reported: namely, eggshell, limestone calcite, cuttlebone, dolomite and hydroxyapatite [24].

It has been shown that eggshell and dolomite can be used as catalysts in transesterification reactions yielding 95% and 98% biodiesel respectively [14]. The catalytic action of these materials can be attributed to the formation of calcium oxide during the calcination of these materials prior to transesterification.

5.0 Supercritical Method

While the catalyzed route of production of biodiesel is the most common route used industrially, the major drawbacks of this method include the necessity of treating the free fatty acids and the triglycerides in different reaction stages, the negative effects of any water present in the mixture, catalystconsumption, the necessity of removing traces of the catalystfrom the product mixture, the wastes produced, low glycerin purity, and generation of waste water.

Any non-catalyzed route bears an inherent attraction associated with the absence of most of these disadvantages due to the absence of the catalyst. Production of biodiesel at supercritical conditions is one such method, where the reaction is carried out at supercritical conditions. Under such conditions, the mixture becomes homogeneous where both the esterification of free fatty acids and the transesterification of triglycerides occur without the need for a catalyst, rendering this method

5.1. Types of supercritical processes

Supercritical fluid technology has been more extensively investigated for its application to the reaction stage of biodiesel production than for the extraction of oil. A survey of the literature reveals the following broad classifications of the research to date: classification based on 1) type of alcohol used (methanol or longer chain alcohols); 2) application as a catalyzed or non-catalyzed process; 3) whether or not it is used in combination with a different technology; and 4) oxidative stability and thermal decomposition of components in the reaction mixture.

6.0 Enzyme-Catalyzed Transesterification Process

The search for a truly environmentally-friendly approach for biodiesel production has intensified research into the use of enzymes as catalysts. The challenges faced when conventional catalysts are employed e feedstock pretreatment, catalyst removal, waste water treatment and high-energy requirement are alleviated in enzyme-catalyzed transesterification reactions.

Biocatalysis is mediated by a group of enzymes called lipases, produced by microorganisms, animals and plants [22].

There are two main groups of lipases: extracellular lipases and intracellular lipases. Intracellular lipases are usually employed in the whole-cell form, eliminating enzyme purification and separation processes [41].

In order to improve enzyme stability and reusability, lipases can be immobilized on several materials [14].

Further, glycerol recovery is easier and of high grade as compared to what is obtained in the alkaline process [27].

7.0 Cavitation Techniques

Cavitation has been recognized as an effective method to enhance mass transfer rate between immiscible liquid–liquid phases within a heterogeneous liquid reaction system. Such concept has been applied for biodiesel production [41].

Typically, caviation is broadly classified into two types: hydrodynamic cavitation and ultrasonic cavitation.It aids in achieving high local energy densities, temperature and pressure within the reaction mass through generation of cavities followed by their growth and subsequently violent collapsing of cavities, thereby delimiting the mass transfer and enhancing the reaction kinetics.

Hydrodynamic cavitation can be generated by using an orifice plate/ throttling valve/venture across the direction of a liquid flow.The mixing efficiency of a hydrodynamic cavitation is reported to be 160–400 times higher which consumes half of the energy compared to the conventional mixing method especially in case of immiscible liquids [41].

On the other hand, acoustic cavitation is induced by means of ultrasound to achieve the similar features as to hydrodynamic cavitation.

Ultrasonic waves are energy application of sound waves, which lies between 20 kHz and 100 MHz, are beyond human hearing limits (16 and 18 kHz) [17,25,30]. Ultrasonic irradiations are generated through piezoelectric materialwith the help of power converter (transducer).

This high frequency sound wave compresses and stretches the molecular spacing of a medium in which it passes through to create localized high energy densities within reaction mass. Ultrasonic irradiation holds three major effects; (1) variation of sonic pressure, (2) cavitation, and (3) acoustic stream mixing which causes solvent compression and rarefaction cycle, liquid will break down and cavities/bubble formation followed by disrupting the interfacial boundary layers respectively.

In total, these effects improve mass transfer, create high local pressure (up to 1000 atm) and temperatures (~5000 K), increasedcatalytic surface areas, and thus finally accelerate the rate of reaction[41].

8.0 Microwave Assisted Transesterification

Themicrowave-assisted transesterification is an energy efficient route for rapid biodiesel production. Microwaves assisted transesterification have gain research interest for their direct mode of energy transfer to the reactant molecules. This nonionizing radiation influences the molecular motions such as ion migration or dipole moment, and does not affect the molecular structure (34).

Typically, induced molecular friction generates in situ heat for the reaction by employing continuous magnetic field on polar molecules and ions. It employs microwave frequency of 2.45 GHz and 900 MHz, which are permissible for use at domestic and industrial level, respectively. Such route encompasses the advantage of volumetric heating of polar reaction mass (methanol) under the influence of microwaves.

Therefore, transesterification is efficiently accelerated in a short reaction time due to instantaneous localized superheating thereby enhancing the reaction kinetics.

9.0 Reactive Distillation Technology of Biodiesel Production

Reactive distillation (RD) is a promising multifunctional reactor to improve an ordinary process, as chemical reaction and thermodynamic separation are combined in a single unit [8]. This is highly advantageous in esterification-type processes, when the feed has a high content of free fatty acids [16]. The use of excess methanol becomes unnecessary withthis method as this can shift the reaction equilibrium towardsthe key product (ester) by continuous removal of by-product(water) [8]. An additional flash and a decanter are used to guarantee the high purity of the products. A reactive distillation column (RDC) consists of a core reactive zone completed by rectifying and stripping separation sections, whose extent depends on the separation behaviour of the reaction mixture. Since methanol and water are much more volatile than the fatty ester and acid, these will separate easily at the top [26]. Researchers have considered various aspects of this technique, including optimization of reaction conditions, heatintegration, use of thermally-coupled distillation columns, dual reactive distillation and catalysis [41]. This process has several advantages over conventional biodiesel production processes: 1) short reaction time and high unit productivity; 2) no excess alcohol requirements; 3) lower capital costs due to the small size of RDC and the lack of need for additional separation units; and 4) no neutralization and separation of the catalyst, as solid acids are used instead of homogeneous catalysts.

10.0 Membrane Technology of Biodiesel Production

A membrane reactor is a reaction system in which membranes and chemical reactions are combined.

It is a device for carrying out a reaction and a membrane-based separation simultaneously in a particular physical enclosure or in close proximity. Membrane reactor technology has been successfully applied to many chemical reaction processes.

The transesterification of lipids is a classic reversible chemical reaction that could also be combined with membrane reactor technology [16]. This method has been decidedly advantageous over conventional means as it ends with a FAME-rich phase, a controlled contact of incompatible reactants, and an elimination of undesired side reactions.

11.0 Challenges & Opportunities

Biodiesel is eco-friendly, renewable and sustainable fuelwhich offer carbon neutral cycle by utilization emitting CO2 in the growth of oilcrops. India has over 300 different species of trees, which produces oilbearing seeds and can manageWCO (waste cooking oil) by implementing policy Thus, there is asignificant potential for non-edible oil and WCO for biodiesel production as an alternative to fossils fuel. In fact, Indian approach towards the development of biodiesel program is different than the other parts of world and depends exclusively on non-food feedstocks. In view of environmental perspective, the combustion of biodiesel has reported to emit less CO2 or green house gas (GHG) and other pollutants [38,36, 20,22]. The economic performance of a biodiesel plant (e.g., fixed capital cost, total manufacturing cost, and the break-even price of bio-diesel) can be determined once certain factors are identified, such as plant capacity, process technology, raw material cost and chemical costs [32]. However, biodiesel price majorly driven by feed stock cost, which is about 80% of the total operating cost. Other important costs are labor, methanol and catalyst, which must be added to the feedstock .Out of various feed stocks available for biodiesel production, non-edible oils are the potential option.

12.0 Conclusions

Ever increasing demand for transportation fuel, depleting oil reserves and stringent emission norms have added motivation for development of processes for biofuel production. Among the targeted biofuels, biodiesel production processes have been well developed and commercialized. Various technologies employed to date for biodiesel production were described and reviewed in this paper. Membrane and reactive distillation technologies have the significant advantage of combining the reaction and separation stages in a single unit, thereby reducing capital costs in a continuous process.

The latter has the further advantages of increasing opportunities for heat integration and having a purer FAME-rich phase, but it is still necessary to conduct detailed experimental and economic studies to garner support concerning the simulations done by researchers. Heterogeneous catalysts from biomass sources stand out as grossly underexplored on the basis of both environmental and economic viability.

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