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Revisiting Trans-esterification to Produce Biodiesel : Novel Reactors, Separation Strategies and Economic Outlook

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Abstract — Biodiesel produced from vegetable oil and animal fats has been widely accepted as an alternative fuel source. Its production via batch transesterification process is constrained by long residence time, immiscibility of oil and methanol, and inadequate conversion. A number of novel reactor configurations have been developed in recent years to surmount these problems. The present article deals with the prospects and potentials of some of the new process technologies of trans-esterification. Reaction/separation coupled systems like membrane process and reactive distillation have also been highlighted. Other promising areas of technology improvement through heterogeneous catalytic continuous production, and catalyst-free supercritical trans-esterification are discussed. Finally, some aspects of operating and fixed costs of biodiesel by trans-esterification by various processes are analyzed.

Keywords : *Biodiesel, transesterification, novel reactors, enzymes.*

INTRODUCTION

Soaring oil prices, dwindling fossil fuel reserves, environmental degradation, and concerns about looming climatic changes have played the pivotal role to search for renewable energy sources. A large fraction of current fossil fuel consumption is due to the transportation sector which relies almost exclusively on the use of liquid fossil fuels. Partial or complete replacement of presently used carburants, gasoline or diesel, with a renewable energy carrier is thus key to averting or reducing the impending crisis. Biodiesel is a much touted energy resource of the recent times. Chemically

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it is mono alkyl ester of long chain fatty acids derived from a renewable lipid feedstock, such as vegetable oil or animal fat. These natural oils and fats are made up mainly of triglycerides having striking similarity to petroleum derived diesel and are called "Bio-diesel". Biodiesel has several merits to its credit. It is derived from a renewable, domestic resource, thereby reducing reliance on petroleum fuel imports. It is biodegradable and non-toxic. Compared to petroleum-based diesel, biodiesel has a more favourable combustion emission profile, such as low emissions of carbon monoxide, particulate matter and unburnt hydrocarbons. Carbon dioxide produced by combustion of biodiesel can be recycled by photosynthesis, thereby minimizing the impact of biodiesel combustion on the greenhouse effect [1, 2]. A life cycle analysis of biodiesel showed that overall CO₂ emissions were reduced by 78% compared with petroleum-based diesel fuel. Biodiesel has a relatively high flash point (150°C), which makes it less volatile and safer to transport or handle than petroleum diesel [3]. It provides lubricating properties that can reduce engine wear and extend engine life [4].

Transesterification of triglycerides produces fatty acid alkyl esters and glycerol. The glycerol layer settles down at the bottom of the reaction vessel. Diglycerides and monoglycerides are the intermediates in this process. The step wise reactions are reversible and a little excess of alcohol is used to shift the equilibrium towards the formation of esters. The process of transesterification is affected by various factors depending upon the reaction condition used. The important physicochemical factors include the effect of free fatty acid and moisture, catalyst type and concentration, molar ratio of alcohol to oil, type of alcohol, the effect of reaction time, temperature and the mixing intensity. Biodiesel production via trans-esterification has been a topic of basic and applied research for last few decades. With the advent of new catalyst materials, novel separation processes and improved process engineering, the biodiesel is fast making inroad into the fuel sector as a promising candidate. Intensive research on biodiesel is underway, and in the last few years a plethora of papers are published on several novel approaches of biodiesel production. Quite a few reviews on process intensification technologies in biodiesel production compile a number of novel reactor systems along with simultaneous reactor-separator devices. Notwithstanding, some of the technologies have been applied successfully in commercial production, these focus primarily on reaction and production. The quality of biodiesel remains to be one of the key issues towards its techno-commercial acceptance as an alternative fuel. Biodiesel quality depends not only on the reactor but also on downstream processing like product separation, water washing, and byproduct recovery. Therefore, efficient separation devices for biodiesel also assume paramount importance. Additionally, heterogeneous catalytic continuous production of biodiesel and enzymatic trans-

esterification are another two promising strategies towards the improvement of biodiesel production technologies.

The present paper aims at these aspects of biodiesel production with a critical analysis of the trends and drivers. It also touches upon the economic factors of biodiesel technologies. We discuss novel techniques, and improvements to existing techniques, that have been used in attempts to increase biodiesel production rates and yields. Some of the discussed techniques have permitted large increases in biodiesel production rates, and this advance has brought biodiesel production to the point where production rates with oil substrates (or wastes) under realistic conditions are approaching practical levels. Of course, it is too premature to be able to exactly define what might be a practical level for biodiesel production, but a rough yardstick can be obtained by examining a detailed process analysis of the existing production technologies.

Various reactor configurations :

Possible improvements to biodiesel production have been sought through specialized reactor configurations. This has led to systems with more robust and reliable performance that is stable over longer periods of time and resistant to short-term fluctuations in operational parameters. In addition, optimized volumetric production rates could be obtained. Batch mode of reactions shown is more suitable for initial optimization studies, but any industrially feasible process would most likely have to be performed on a continuous or at least semi-continuous (or sequencing batch) basis. Moreover, the batch transesterification is constrained by several limitations such as inadequate rate of reaction due to immiscibility of oil and alcohol and limited conversion due to reversibility of reaction. To surmount these problems several options including the use of excess alcohol, longer reaction time and high concentration of catalyst are explored. However, these in turn may lead to high operating cost and energy consumption to obtain the desired degree of purity and recover the excess amount of alcohol and catalyst in the downstream processing. Continuous process technologies are credited with reduced down-time, higher throughput, and more stable operation to overcome the challenges due to mass, heat and momentum transfer limitations, incomplete conversion and use of high free fatty acid (FFA) feedstock. But, fewer technologies have been successfully commercialized. New technologies have either used the novel kind of reactors or the combination of reaction along with separation units [5]. Some of the key features of the various novel reactors are presented in Table 1. Enhanced biodiesel production can be achieved by improvisation in the process technologies which in turn improves the production efficiency at the expense of low cost. Most of these reactors or process technologies increase the rate

TABLE 1.

Summary of various reactor configurations for the production of biodiesel

Sr. no.	Reactor configuration	Feed stock used	Reaction parameters	Percent conversion	Salient features
1.	Static Mixer ⁶⁻⁸	Canola oil, Palm oil	Catalyst : NaOH, KOH Temperature : 60–65°C Molar ratio : 6 : 1–10 : 1 Residence time : up to 30 min	96.5%	<ul style="list-style-type: none"> • No moving parts • Provides effective mixing • High quality biodiesel
2.	Micro tube reactor ⁹⁻¹⁰	Sunflower oil	Catalyst : KOH Molar ratio (methanol/oil) : 23.9 Temperature : 60°C Residence time : 100 s	100%	<ul style="list-style-type: none"> • improved heat and mass transfer efficiency • short diffusion distance • high volume to surface area
3.	Oscillatory Reactor ¹¹	Rapeseed oil	Catalyst: NaOH Temperature : 50°C Residence time : 30 min Molar ratio : 1.5 : 1	99%	<ul style="list-style-type: none"> • Plug flow reactor with simple construction. • Intensified radial mixing. • Improved heat and mass transfer.
4.	Ultrasound assisted reactor ¹²	Waste cooking oil	Catalyst: KOH Molar ratio (methanol/oil) : 2.5 : 1 (stage 1) : 1.5 : 1 (stage 2) Temperature : ambient Residence time : < 1 min	stage 1 : 81% stage 2 : 99%	<ul style="list-style-type: none"> • Cavitation provides simultaneous mixing and heating. • reduces the reaction time, reaction temperatures and energy input • increases the rate of mass transfer
5.	Microwave reactor ¹³⁻¹⁴	Cotton seed oil	Catalyst : 1% KOH Temperature : 50°C Residence time : 5 min	93.7%	<ul style="list-style-type: none"> • Quick and efficient desired temp. in no time. • Accelerate the rate of reaction. • Higher conversion in less time. • Uniform temperature
6.	Centrifugal contactor ¹⁶	Sunflower oil	Catalyst : 1wt% NaOH Molar ratio (methanol/oil) : 6 : 1, Temperature : 60°C Residence time : 30 min rpm : 1800	96%	<ul style="list-style-type: none"> • High-shear region for good mixing and mass transfer, • High inter-phase mass-transfer rates • Low residence time (typically ~ 10 s).

(Table-1 Contd.)

7. CSTR ¹⁷	Palm oil, rap seed oil, soybean oil, beef oil	Catalyst : NaOH, KOH Temperature : 60°C Molar ratio : 4 : 1-7.9 : 1 Residence time : 6-12 min.	99.2%	<ul style="list-style-type: none"> • Atomizing technology to have contact at micro level. • High heat and mass transfer rate • Less residence time.
8. Liquid-liquid Film Reactor ¹⁸	Palm oil, soybean oil	Catalyst : NaOH, Novozym 435 solid Temperature : 30-70°C Molar ratio 6 : 1-18 : 1 Residence time : up to 1 min.	92.2-97.5%	<ul style="list-style-type: none"> • No mixing or agitation, increased contact area. • Time for effluent phase decreases • prevention of glycerol back mixing • Drives reaction in forward direction
9. Ultra and high shear reactor ¹⁹	Canola oil, soybean oil	Catalyst : NaOH Temperature : 40-60°C Residence time : 40 sec-several min	up to 98%	<ul style="list-style-type: none"> • High free fatty acid feed can be handled, small reactor size. • Smaller size and negligible hold up time. • High mass transfer rate. • Enhanced reaction rate

of reaction by enhancing the transport processes and mixing between alcohol and oil. Static mixers can accomplish effective radial mixing as fluids pass through it. Even some of the novel reactors have achieved low total glycerin i.e. less than 0.24% by weight at a shorter residence time due to improved heat and mass transfer rate and vigorous agitation intensity.

High quality biodiesel can be produced from canola oil and methanol in a stand-alone closed loop static mixer (Fig. 1) [6]. The optimum conditions were temperature : 60°C, NaOH catalyst : 1.5 wt%, reaction time : 30 min and 6 : 1 molar ratio of methanol to oil. In another study 96.5% conversion of palm oil was achieved within 5 min of reaction time at a molar ratio of oil to MeOH of 1 : 10.5, 1% by wt. KOH, 65°C temperature [7]. A static mixer reactor for continuous biodiesel production and product separation are combined in a single unit [8]. Micro-reactor or micro-channel reactor is another promising option where reactions takes place in a confinement with typical lateral dimensions between submicrometers and submillimeters. The most typical form of such confinement is micro channel. The use

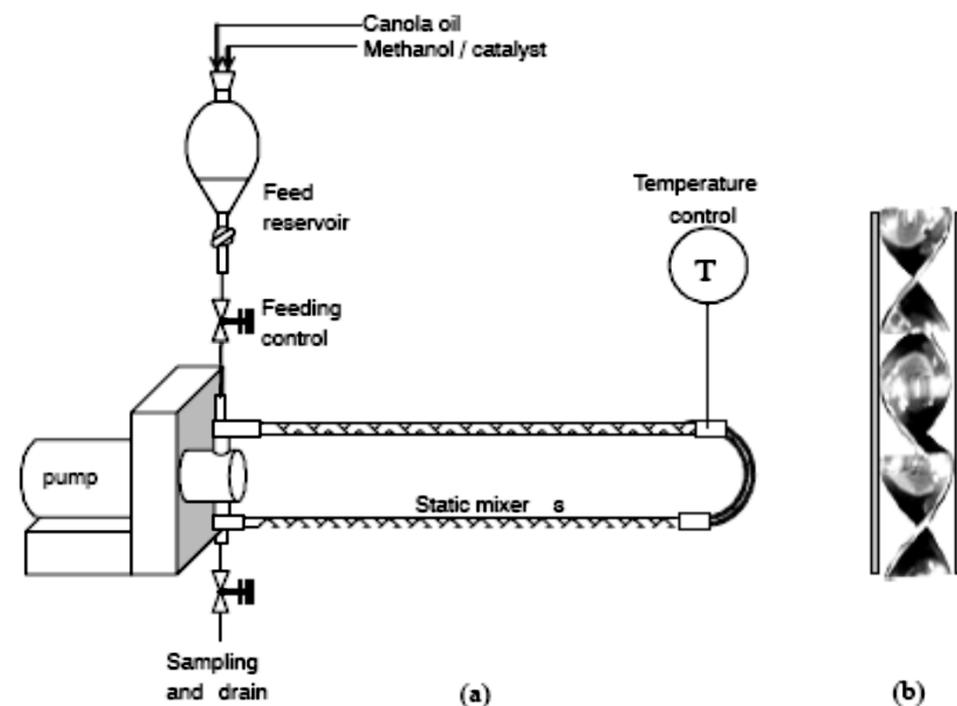


Fig. 1. Schematic of the experimental setup : (a) static mixer closed-loop system and (b) internal structure of static mixers [6].

of micro-reactor could considerably improve heat and mass transfer efficiency due to short diffusion distance and high volume to surface area [9, 10]. A continuous oscillatory flow reactor (OFR) in a pilot-scale plant can achieve up to 99% conversion of biodiesel from rapeseed oil at 50°C using 1.5 molar ratio of methanol to oil in the presence of NaOH catalyst within 30 min [11]. Oscillatory reactors can enhance radial mixing and transport process by independent and controlled oscillatory motion (Fig. 2). In cavitation reactors, the collapse of cavity or bubbles produces high temperature and pressure and turbulence locally resulting in rapid reaction rate [12].

Microwave irradiation can also reduce the reaction times for transesterification of cottonseed oil with methanol to 7 min compared to 30 min in conventional process for similar conversion at 60°C. The yield of biodiesel within 5 min at 50°C using 1% KOH as catalyst was reported to be 93.7% [13, 14]. A recent study indicates the use of commercial microwave ovens to provide the heat needed in the transesterification process [15]. Microwave reactors, thus offer the advantage of direct

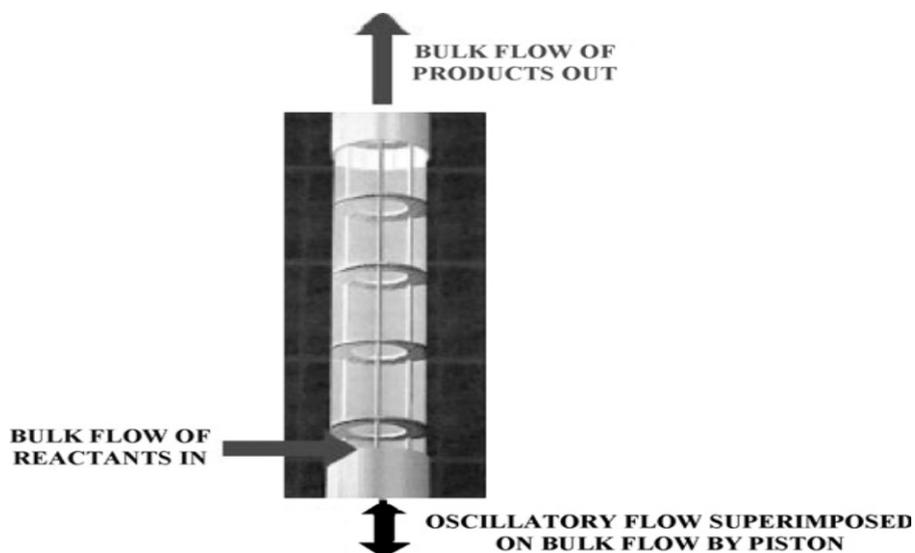


Fig. 2. The configuration of oscillatory flow reactor [11].

and intense localized heating thereby increasing the conversion in less time than in the conventional batch reactors. In essence, the goal of almost all the novel configurations of reactors is the process intensification which is expected to enhance physical processes including heat, mass, and momentum transfer in the context of biodiesel synthesis by transesterification. Another common characteristic of novel reactors is the small “footprint” required compared to conventional equipment. For example micro-channel reactors the diameter of channel is only several hundred micrometers. Oscillatory flow reactors can also be designed in shorter length-diameter ratio. Centrifugal contactors may obviate the need for a separate separation process for recovery of the glycerol from biodiesel product. Hence, small size of reactors and less processing steps reduce the cost of construction and maintenance. Nonetheless, detailed scale-up studies are required to be conducted for all these novel type reactors to assess their performance and flexibility towards a variety of feedstocks. In fact, there are many variations of different reactor types, as there are laboratories carrying out research in this area. Unfortunately, this also creates a situation in which it is very difficult to ascertain whether the differences in the various studies are due to different reactor configurations or to differences in operational parameters. Future studies could help to resolve this ambiguity by directly comparing different reactor configurations or, at the very least, by operating a novel configuration

under conditions used in other previous studies.

Byproduct recovery and utilization :

During biodiesel production, two phases are produced after transesterification and distillation of the excess alcohol. The upper ester phase (EP) contains the main product – biodiesel. The lower glycerol phase (GP) consists of glycerol and many other chemical substances such as water, organic, and inorganic salts, a small amount of esters and alcohol, traces of glycerides, and vegetable colors. The exact composition of the raw GP depends on the method of transesterification and the separation conditions of biodiesel production, but the glycerol concentration lies usually between 30 and 60 wt%.

A number of conventional as well as novel methods are employed in the separation and purification of glycerol from biodiesel reaction mixture. At the end of transesterification, biodiesel is mostly separated via gravitational settling or centrifugation. Biodiesel and glycerol are typically sparingly mutually soluble, and there is palpable difference in density between biodiesel (880 kg/m^3) and glycerol (1050 kg/m^3 , or more) phases respectively. More so, this difference in density is sufficiently enough for the application of simple techniques such as gravitational settling or centrifugation for the separation of biodiesel and glycerol phases. The crude biodiesel is then purified and dried to meet the stringent international standard specification provided by EN14214 [21]. Otherwise, the contaminants could reduce biodiesel quality and affects engine performance.

Many purification methods are based on the distillation of the glycerol phase to strip alcohol contaminants from glycerol [22] or using mechanically-agitated thin film processor to continuously evaporate and distill glycerol and other heat sensitive solids containing products [23]. Glycerol can also be recovered by heating a glycerol-containing effluent stream having a low molecular weight alcohol, water and fatty acid esters [24]. The reaction mixture is sparged with nitrogen to help remove water and low molecular weight alcohol. The crude glycerol phase can be purified by ion exchange on the strong acid resin Amberlite-252 and it has been suggested that the macroporous Amberlite could be useful for removal of sodium ions from glycerol/water solutions with a high salt concentration [25]. Another technology of purification of glycerol with high salt content is by ion-exchange Ambersep BD50 [26]. Use of ionic liquids has also been explored as a solvent for extraction. A Lewis basic mixture of quaternary ammonium salts - a eutectic based ionic liquid with glycerol was used to extract excess glycerol from biodiesel formed from the reaction of triglycerides with ethanol in the presence of KOH [27]. The effect of the cation on the partition

coefficient of glycerol was determined, together with the time taken for the systems to reach equilibrium.

Glycerol (or glycerin) is a by-product of biodiesel production and can be used in a wide range of existing markets, having over 1500 end uses. Pharmaceuticals, toothpaste and cosmetics account for around 28%; tobacco 15%; foods 13% and polyether polyols for urethanes 11% of its market with the remainder being used for alkyd resins, cellophanes, explosives and other miscellaneous uses throughout industry. Supply of glycerol in Europe has significantly increased since the mid 1990s and this has been strongly influenced by an increase in biodiesel production. However this has been combined with a 20% increase in consumption since 2000 due to several factors, including the development of new markets for glycerine [28]. The microbial conversion of glycerol to various compounds are investigated by different authors with particular focus on the production of 1,3 propanediol, which can be applied as a basic ingredient of polyester [29, 30]. Moreover, biological production of hydrogen and ethanol from glycerol is also attractive because hydrogen is expected to future clean energy source and ethanol can be used as a raw material and a supplement to gasoline [31]. The fermentation of glycerol to 1, 3-propanediol has been studied using a number of microorganisms such as *Klebsiella pneumoniae* [32], *Citrobacter freundii* [33], *Clostridium butyricum* [34], *Enterobacter agglomerans* [35], *Enterobacter aerogenes* HU-101 [31] and so on.

Market value of glycerol produced as a by-product is an important factor in biodiesel economics. Glycerol market is limited; any major increase in biodiesel capacity would undoubtedly lead to glycerol prices to decline, thereby affecting the overall economics of biodiesel. Notwithstanding the potential of microbial conversion of glycerol into biohydrogen or bioethanol, there are some problems that need to be solved before this technology can have practical applications. For example it is necessary to increase glycerol concentration used in the production of H₂ and ethanol because an excessive dilution of biodiesel wastes using the medium increases the cost for the recovery of ethanol and waste water treatment [31].

Efficient separation strategies :

Various novel reactors, as stated earlier, can achieve low total glycerin (<0.24 wt%) in shorter residence times because reaction is intensified by improving mass and heat transfer rate and mixing intensity. But the quality of biodiesel may be still affected by other downstream processing steps. In addition, reaction/separation coupled technologies can strategically require less downstream processing steps than the novel reactors.

Membrane reactor cum separator :

The successful application of membrane technology to purify crude biodiesel has re-ignited the interest in the struggle to develop commercial biodiesel production. Membrane reactors can realize high quality biodiesel because membranes selectively permeate products while retaining bound glycerides and soaps. Membrane reactor is a device for simultaneously carrying out a reaction and membrane-based separation in the same physical enclosure. Due to the immiscibility of lipid feedstock and alcohol, lipids form droplets which are excluded from passing through the membrane pores. The micro-porous inorganic membrane selectively permeates free fatty alkyl ester (FFAE), alcohol and glycerol while retaining the emulsified oil droplets, thus increases the conversion of equilibrium limited reactions. Contrary to both wet and dry washing techniques, membrane biodiesel purification process does not require both water and absorbent. Membrane processes are usually based on the theory that higher permeates fluxes are followed by lower selectivity and higher selectivity is followed with lower permeates fluxes.

The kinetics of canola oil transesterification in a membrane reactor was also reported by several researchers [36-38]. The membrane reactor study showed the advantage of no bound glycerin, enhanced reaction rate, easy separation of products, high FFA feedstock handling, continuous flow, blocks most impurities, high purity biodiesel. Maintaining a separate lipid phase is a key factor to assure high-quality biodiesel production with the membrane reactor system [39]. Use of inorganic (ceramic) membrane to purify biodiesel from impurities such as glycerol, soap and catalyst is also been explored using different membrane pore sizes (0.6, 0.2 and 0.1 μm) at temperature of 60°C and pressure of 0.15 Mpa [40]. The removal of glycerol was less difficult due its formation of reverse micelle with soap forming molecule size of 2.21 μm which was analyzed by zeta potential analyzer and showed to be bigger than that of biodiesel molecule, and therefore was easily removed by membrane.

A membrane separator with porous ceramic disk membranes can be also integrated with liquid-liquid extraction process for the oil- FAME-MeOH system. The effective membrane area of 13.1 cm^2 , the pore size of 0.14 μm , and molecular weight cut off (MWCO) of 300 kDa are used [41]. The membrane active layer consisted of zirconia oxide supported on carbon. Zhu studied membrane extraction using hollow fibre polysulfone and polyacrylonitrile membranes in combination with conventional extraction techniques to purify crude biodiesel [42]. The biodiesel obtained from polysulfone fiber membrane gave purity of 99%, besides properties such as kinematic viscosity (3.906 mm^2/s), density (0.876 g/cm^3) and water content

(0.042 wt%) conforming the ASTM D6751 specification [42]. However, the criteria for selecting membranes are complex and this depends on the application. Important considerations on productivity and separation selectivity, as well as the membrane's durability and mechanical integrity at the operating conditions must be balanced against cost issues in all cases. The relative importance of each of these requirements varies with the application. However, selectivity and permeation rate are clearly the most basic properties of a membrane. The higher the selectivity, the more efficient the process, the lower the driving force required to achieve a given separation. The higher the flux, the smaller the membrane area is required. Further the driving force is often pressure or concentration gradient across the membrane. Inorganic membranes favor applications under higher temperature and chemical conditions, whereas polymeric ones have the advantages of being economical. While these membrane processes have frequently shown great promise their wider use at a large scale is often prevented by the problem of fouling. The formation of a forming layer at the septum during membrane separation can cause rapid decline in permeate flux and results in low separation rates.

Reactive Distillation :

Reactive distillation (RD) is the simultaneous execution of reaction and separation within a single unit of column. This combined operation is especially suited for the chemical reaction limited by equilibrium constraints, since one or more of the products of the reaction are continuously separated from the reactants. Currently much attention has been focused on reactive distillation and has been used extensively [43] due to its advantages over conventional process such as reducing the capital costs and operating costs of a biodiesel plant and also of producing consistently high quality biodiesel. Silva et al. reported biodiesel production from soybean oil and bioethanol by reactive distillation [44]. The catalyst concentration (0.5–1.5 wt%), the ethanol to oil molar ratio, column reflux and reaction time were optimized to achieve 95% biodiesel conversion using novel type RD, KOH as catalyst and 4 : 1 methanol to canola oil ratio [45]. In their study Kusmiyati et al. achieved 95.7% conversion using 1% H₂SO₄ as catalyst, 8 : 1 methanol/oleic oil molar ratio, 180°C temperature and 90 minute reaction time [46]. Kiss et al. used a novel sustainable esterification process based on catalytic reactive distillation. Biodiesel via fatty acid esterification using metal oxide (niobic acid, sulfated zirconia, sulfated titania, and sulfated tin oxide) solid acid catalysts were investigated [47]. Thus reactive distillation shows variety of advantages apart from conversion such as reduction in capital cost in terms of pumps, piping and instrumentation, improvement in product selectivities due to continuous removal of product and the requirement of least amount of alcohol.

Supercritical method :

An alternative, catalyst-free method for transesterification uses supercritical methanol at high temperatures and pressures in a continuous process. In the supercritical state, the oil and methanol are in a single phase, and reaction occurs spontaneously and rapidly. The supercritical transesterification with methanol was found to be very effective in producing a conversion of more than 95% in only 4 minutes [48]. Although the process requires high temperature 350°C and pressure up to 20 bar (Exceeding the critical condition of methanol), high methanol to oil ratio 42 : 1, energy costs of production are similar or less than catalytic production routes. Many researchers studied the supercritical biodiesel production process in comparison with the conventional alkali based batch processes in terms of economical and experimental aspects [49, 50]. The continuous transesterification of soybean oil was carried out in a tube reactor using supercritical methanol. The tube reactor was equipped with a pre-heater, blender, condenser and separating funnel along with an electric thermostat to control the temperature of the reactor (Fig. 3). The optimum condition of 40 : 1 methanol to oil molar ratio, 25 minute residence time, 35 MPa pressure and 310°C temperature, at which the maximum production yield was 77%.

Supercritical trans-esterification, or biodiesel production in supercritical alcohols (SCA), has many advantages over conventional catalytic processes, especially in

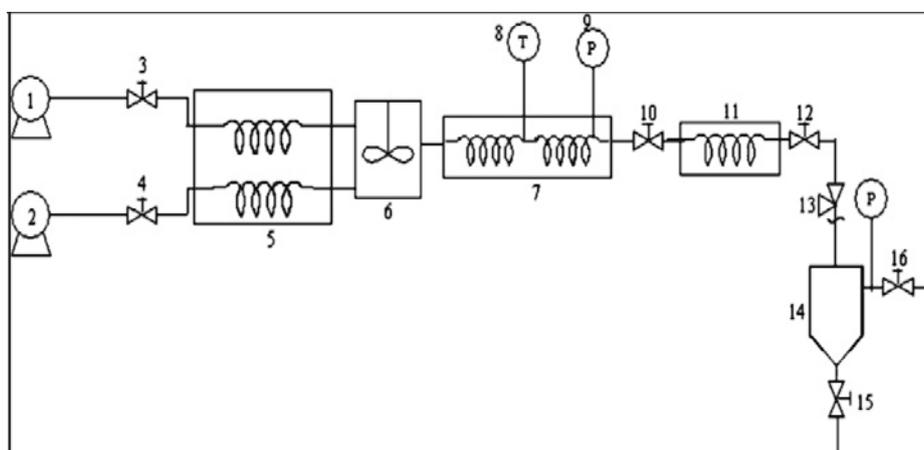


Fig. 3. A schematic of the supercritical continuous reaction device for biodiesel production [50]. (1, 2. High-pressure pump; 3, 4, 10, 12, 15, 16. valve; 5. preheater; 6. blender; 7. tube reactor; 8. thermometer; 9. manometer; 11. condenser; 13. pressure regulator; 14. separatory funnel.)

feedstock flexibility. Supercritical methanol process, in particular, involves a much simpler purification of trans-esterified products and is more environmentally friendly. Moreover, it requires lower reaction time, and lower energy use [51]. Another advantage with supercritical methanol is that the conversion gets 95% complete in 10 min. It was reported that hydrated ethanol (5% (v/v) water content) could still be employed for supercritical transesterification. Since hydrated ethanol has a lower price than absolute ethanol, it could make the FAEE based biodiesel production process more feasible and economically similar to that which uses methanol as feedstock for FAME production. However, the optimal parameters for biodiesel production in SCA are a high pressure (19–45 MPa), a high temperature (320–350 °C) and a high alcohol to oil ratio (40 : 1–42 : 1). To reduce these parameters, and so reduce the environmental and economic costs of biodiesel production by the SCA system, the addition of a suitable heterogeneous catalyst is an attractive idea

Heterogeneous Catalytic Continuous Production :

Separation cost of homogeneous catalyst and high consumption of energy has driven the need for the growth and development of heterogeneous catalysts for the production of biodiesel. Heterogeneous catalysts are not dissolved or consumed during transesterification. Therefore, they are easily separated from the crude biodiesel product and recyclable. This characteristic limits impurities and reduces cost of final biodiesel product separation. Additionally, the catalysts can be regenerated and reused and as added advantage, the catalysts are environmentally friendly since the need to use acids, solvents and water during separation stage is minimized [52]. McNeff et al. developed a novel type continuous fixed bed reactor for the biodiesel production using metal oxide-based catalyst for varying feed stocks such as soybean oil, acidulated soap stock, tall oil, algae oil, and corn oil with different alcohols [20]. Porous zirconia, titania and alumina micro-particulate heterogeneous catalyst were investigated for transesterification and esterification reaction under high pressure of 2500 psi and 300–450°C temperature and as low as 5.4 s residence time. Phosphate modified zirconium particles and hydroxide modified zirconia, titania, and alumina catalyst were used to prepare the catalyst bed. The round shaped catalysts were compressed in the two different sized reactors of 0.46 cm and 1 cm i.d. × 15 cm length to produce the biodiesel. The different feed stocks (soybean oil, acidulated soap stock, tall oil, algae oil, and corn oil) were tested for varying condition of reactor volume, catalyst type, pre-heater temperature, column inlet and outlet temperature, pressure, molar ratio of alcohol to oil and total flow rate. The conversion in the range of 86–95% was achieved. Park et al. investigated heterogeneous catalyst system for the production of biodiesel from used vegetable oil (VOs) using continuous process [53]. The free fatty acids (FFA) were converted to fatty acid methyl esters (FAME) prior to the

main biodiesel production process. The heterogeneous catalyst used were Cs-heteropoly acid (Catalyst of a metal heteropoly acid salt that is insoluble in a polar solvent on a non-metallic porous support), $\text{SO}_4^{2-}/\text{ZrO}_2$, $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3$, $\text{SO}_4^{2-}/\text{SiO}_2$ and WO_3/ZrO_2 (powder type), H-zeolite, WO_3/ZrO_2 (Pellet type). The esterification was carried out in packed bed at 75°C, and oleic acid to methanol molar ratio of 1 : 19.4 was used. The catalyst $\text{SO}_4^{2-}/\text{ZrO}_2$ and WO_3/ZrO_2 showed the highest activity for esterification of FFA to FAME. 65% conversion was achieved for a period of 140 h. A shell-core Ca $(\text{C}_3\text{H}_7\text{O}_3)_2/\text{CaCO}_3$ catalyst (A product of calcination of CaCO_3 particle followed by glyceride reaction) was employed in a continuous flow packed-bed system [54]. 95% FAME yield of soybean oil at 60°C with 30 : 1 methanol-to-soybean oil molar ratio with the 168 min retention time was achieved without disturbing the catalyst activity up to 5 cycles. A rotating packed bed reactor (RPB) was employed with potassium hydroxide as catalyst. The maximum FAME conversion of 97.3% and productivity of 0.828 mol/min from soybean oil were obtained [55].

Economic outlook :

The feasibility of a biodiesel production process includes both technological and economic aspects. Thus, apart from assessing the technological feasibility of the different process designs for biodiesel, an economic evaluation of these processes is highly needed. The real topic that is debated hotly today is whether biodiesel is an economically sustainable idea, given the costs of production, fossil and non-fossil energy spent for producing energy from biodiesel, opportunity costs for the respective plant oils, and the competing fuels (mainly fossil fuels) already available. Van Kasteren and Nisworo carried out an economic assessment of a supercritical transesterification process for biodiesel continuous production from waste cooking oil [56]. The economic assessment of the biodiesel plant showed that biodiesel can be sold at US\$ 0.17/l (125,000 tonnes/year), US\$ 0.24/l (80,000 tonnes/year) and US\$ 0.52/l for the smallest capacity (8000 tonnes/year). The sensitive key factors for the economic feasibility of the plant are: raw material price, plant capacity, glycerol price and capital cost. Haas et al. developed a computer model to estimate the capital and operating costs of a moderately-sized industrial biodiesel production facility [57]. The major process operations in the plant were continuous-process vegetable oil transesterification, and ester and glycerol recovery. Crude, degummed soybean oil was specified as the feedstock. Annual production capacity of the plant was set at 10×10^6 gal). At a value of US\$0.52/kg (\$0.236/lb) for feedstock soybean oil, a biodiesel production cost of US\$0.53/l (\$2.00/gal) was predicted. The single greatest contributor to this value was the cost of the oil feedstock, which accounted for 88% of total estimated production costs. An analysis of the dependence of production costs on the cost of the feedstock indicated a direct linear relationship between the two,

with a change of US\$0.020/l (\$0.075/gal) in product cost per US\$0.022/kg (\$0.01/lb) change in oil cost [57]. The production cost of biodiesel was found to vary inversely and linearly with variations in the market value of glycerol.

Zhang et al. assessed the economic feasibilities of four continuous processes to produce biodiesel, including both alkali- and acid-catalyzed processes, using waste cooking oil and the standard process using virgin vegetable oil as the raw material [58]. Although the alkali catalyzed process using virgin vegetable oil had the lowest fixed capital cost, the acid-catalyzed process using waste cooking oil was more economically feasible overall, providing a lower total manufacturing cost, a more attractive after-tax rate of return and a lower biodiesel break-even price. The authors also carried out the sensitivity analyses for these processes. Plant capacity and prices of feedstock oils and biodiesel were found to be the most significant factors affecting the economic viability of biodiesel manufacture. In comparison, the cost of crude oil, the raw feedstock for petroleum-based fuels, ranges from \$1.19 per gallon for \$50 per barrel oil to \$1.67 per gallon for \$70 per barrel oil. Thus, the feedstock costs for biodiesel are substantially higher than for the conventional feedstock, putting biodiesel at a cost disadvantage to conventional diesel.

Biodiesel is currently more expensive than petroleum based fuels. Thus, if technology improvements succeed in bringing down costs, it is likely to play a major role in the economy in the future. Although rigorous techno-economic analyses are necessary to draw a cost-effective comparison between biodiesels and the various other conventional fossil fuels an economic survey, based on fuel cost estimation, turns out to somewhat complicated when applied in practical terms. This is because of the intervening large number of other techno-economic parameters. The socially relevant costs of bringing any fuel to market must also include such factors as pollution and other short-term and long-term environmental costs, as well as direct and indirect health costs. When these factors are taken into consideration, together with the initial cost competitiveness, biodiesel is surely the most logical choice as a worldwide energy medium.

CONCLUSION

Indeed, in spite of a large amount of research in the past and at present, major hurdles remain to be overcome before a feasible practical process can be demonstrated for any approach to biodiesel production. Here we have concentrated on recent progress in biodiesel production. As shown here, there have been substantial recent improvements in both the yield and quality biodiesel. Yet, to be practical, the question of economic feasibility still remains unanswered. As part of the climate change

agreement the Government have made a commitment for energy to be supplied from renewable sources. This ensures that the energy produced is from sustainable sources and deliver carbon savings. At present no carbon accreditation scheme operates for biofuels in the India, but as the industry develops, Government is expected to implement a scheme. All the continuous production technologies along with novel separation strategies have shown great advantages and potentials over conventional batch processes. Improved rates of heat and mass transfer have shown the greater potential and scope for continuous production technologies to be commercialized. The higher rate of conversion at the low molar ratio of methanol to oil, reduced temperature and lesser quantity of catalyst as compared to conventional batch processes. Also fewer technologies have shown great potential of handling variety of feed stocks. Ultimately these processes have proved to be more efficient in terms of energy utilization and economic production of biodiesel which is going to be one of the key features in the near future due to depletion of fossil fuel recourses and sky high prices of fossil fuels. The selection of appropriate technology for production of biodiesel requires careful selection of processing steps, catalyst and downstream process integration. The quality of feed vegetable oil particularly FFA content plays an important role in identifying the suitable technology. Another important criterion for the quality of biodiesel is the storage stability. Vegetable oil derivatives especially tend to deteriorate owing to hydrolytic and oxidative reactions. Their degree of unsaturation makes them susceptible to thermal and/or oxidative polymerization, which may lead to the formation of insoluble products that cause problems within the fuel system, especially in the injection pump. In conclusion, biodiesel is a very small industry compared to its ethanol companion in renewable fuels. Current projections show that biodiesel may grow relatively rapidly over the next few years, but it will likely remain a small part of the overall diesel market. For the foreseeable future, cheap inedible oils may likely be the dominant feedstock, but the search for technological improvements may lead to alternative crops being the primary source for biodiesel production in the future.

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