



Biodiesel Production: A Mini Review

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Abstract – The challenges faced in production of biodiesel from edible and non-edible oils via the transesterification process are discussed. Identified process parameters such as level of FFA, moisture content, Fatty acid composition varies for both edible and non-edible oil affects product quality, as a result, the process continues to be modified using competitive alternative methods. Resources and process limitations are reviewed in this paper and in view of current state of the art processes, technical successes and limitations of biodiesel production from plant and animal fats and oils are compared based on reaction conditions and product formation/purification methods. Furthermore, the paper recommends a combination of production systems to overcome the inherent technical limitations in biodiesel production.

Keywords – Biodiesel, edible, non-edible oil, process method, transesterification.

1. INTRODUCTION

Ecological, political and economic concerns over petrodiesel, which is the single largest industry in terms of dollar value on earth, are the drivers behind biodiesel production from edible/ non-edible oils and fats. Although the growth rate of plantations for vegetable oil is expanding, much of it is due to oil palm at 5% per year. Conversely, there is a corresponding increase for biodiesel production. This has led to the emergence of the food versus fuel debate and the caveat of an ‘eco-nightmare’ [1] which suggests the negative consequence of the use of food crop for biodiesel/biofuel production. Reconsideration of the use of food-grade oil is being undertaken, particularly as the cost of biodiesel is about 70–75% of the total cost of raw material. Edible oil with food value like coconut, palm oil, soybean, corn oil has been under tremendous pressure for industrial use. The growth of the oleochemical industry has also resulted in exponential growth of these crops as plantation crops and has created an entire value chain making them one of the world’s valued crops. According to a database [2], India has over 90 species of plants producing non-edible oil. Other regions in Asia, South America and Africa are already earmarking huge expanse for non-edible oil plantation using *Jatropha*, *Pongamia*, *Karanja*. The overall energy balance between crop growth and use is another issue challenging biodiesel production from vegetable oils as the overall biodiesel demand is growing. Consequently, leading to the use of alternative raw materials like algae, waste cooking oils and non-edible oils to match demand. However, it is unlikely that non-food oils will completely replace food-grade oil for biodiesel production in the nearest future.

This paper seeks to highlight presents biodiesel production via the transesterification process from food and non-food oils and the current state of the art

processes, limitations. Particular focus is given to technical successes of biodiesel production from non-food oils. A comparison of reaction conditions, product formation and purification is made. The paper concludes by suggesting a combination of successful techniques to overcome inherent technical limitations in biodiesel production from non food oils.

2. FEEDSTOCKS

Plant Oils/Fats

Vegetable fats/ oil (edible and non edible) along with animal fat feed-stocks (main raw material for biodiesel production) contain monoglycerides (MGs), diglycerides (DGs) and triglycerides (TGs), (long-chain fatty acid groups) attached by ester linkages to a glycerol backbone [3]. They share a degree of physio-chemical similarity with petro-diesel but they are unsuitable for use in direct inject (DI) engines as a result of combustion residue of the straight oil. This problem is overcome by modifying vegetable oils via transesterification to forming alkyl esters referred to as biodiesel. The quality of alkyl esters are determined by TG components and could be used to predict the final product properties of biodiesel [3], [4]. Other sources of transesterifiable oil from micro-organisms (algae), fryer waste, minor non-edible oils [6], waste soap stocks from the oleo-chemical industries have been identified as a veritable source of biodiesel feed-stock [7]. The constitution of some vegetable oil by fatty acid content is as in Table 1. Fatty acid composition and type of alcohol has been reported to affect the fuel property of biodiesel. The higher the straight chain, the better the fuel property such as heat capacity [8], cetane number [9]. SBO, SFO, Tallow, *J. curcas* L, *P. pinnata* are examples of oils with high unsaturated fatty acid compared to palm oil. As the C8:0 and C16:0 methyl esters is reported to have a heating capacity and melting point of 1313 kg cal/mol and 16.5°C; and 2250 kg cal/mol, 30.5°C respectively compared to C18:1 methyl ester with melting point -20°C having 2828 kg cal/mol. The choice feedstock would naturally be that with the

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longer chain. The implication is discussed detail in the section on technical limitation and how it is mitigated using oxidant. The high melting point causes crystallization which affects engine performance.

The selection of desired biodiesel can be carried out with this relevant information with regards to the preferred fatty acid. While this may be desired, saturated fatty display higher cloud points and pour points than

unsaturates-dominate fatty acid [17]. Cold flow improvers such as olefin-ester copolymers (OECF) at 0.03% have been reported to act as a pour point depressant [18] whilst previously kerosene had been used [19]. Improvement of the CP with regards to specified biodiesel is discussed in the technical limitation section.

Table 1. Fatty acid composition of vegetable oils.

Oil	saturated				Mono unsat	Poly unsat	
	C12	C14	C16	C18:0		C18:1	C18:2
SFO [10]		11.5	11.5	4	24.5	53.0	7
SBFO [11]		1	11.5	4	24.5	53.0	7
SFSO			6.6	5.1	19.6	68.7	
WCO [12]			8.4	3.7	34.6	50.5	0.6
SBO [5]			11.3	3.6	24.9	53	6.1
PO	0.1	0.7	36.7	6.6	46.1	8.6	0.3
<i>P.pinnata</i> [13]	-	-	3.7-7.9	2.4-8.9	44.5-71.3	10.8-18.3	
<i>J. curcas</i> L [14]-[16]		0.1	14.1-15.3	3.7-9.8	34.3-45.844.7	29.0-44.23	0-0.3

Micro-organisms

Up to 70% of algae biomass is usable oils and theoretically they are a more efficient source of lipids. They are the fastest growing photosynthesizing organisms, completing an entire growing cycle every few days and sequestering up to 50 % of their dry body mass in oil. For instance *Botryococcus braunii* converts 61% of its biomass into oil [20]. Other micro algae that have produced significant outcome are *C. protothecoides*, *Microcystis aeruginosa* [21], Heterotrophic *C. protothecoides* [22] by manipulating their nutritional pathways through heterotrophic growth. The storage of energy as oil rather than as carbohydrates slows the reproduction rate of any algae so higher oil-strains generally grow slower than low oil-strains. Enclosed photobioreactors are now used to maximize growth rate and nutrient feed. The corresponding average biomass energy production according to [23] is not substantially better than land based oil crops although they have higher photosynthetic efficiency compared to other energy crops [24]. The net conversion of solar energy to energy for algae with respect of biodiesel production is not also encouraging. As the amount of growth is proportional to incident light acquired, region with low incident solar energy would need considerable augmented equipment to deliver the maximum energy needed for algae to photosynthesis. Only light within the wavelength range of 400 to 700 nm (photosynthetically active radiation, PAR) can be utilized by plants, effectively allowing only 45% of total solar energy to be utilized for photosynthesis. Furthermore, fixation of one CO₂ molecule during photosynthesis, necessitates a quantum requirement of ten (or more), which results in a maximum utilization of only 25% of the PAR absorbed by the photosynthetic system. On the basis of these limitations, the theoretical maximum efficiency of solar energy conversion is approximately 11%. However a system that resulted in a

power plant with a potential capacity of about 9 kW/ha of solar algal panel was reported [25], using mixed culture of freshwater algae, obtained from hydroponic plant growth systems, supplemented with *Chlamydomonas reinhardtii* and *Pseudokirchneriella subcapitata* in a 10L cylinder. It has prospects of reaching an output of 23 kW/ha. Conversely, in on-going research in the United States [26], [27], micro-algae as an alternative material for biodiesel production has not been viewed as technically efficient even though approximately 46 tons of oil/hectare/year production is estimated from diatom algae in raceway ponds and photo-bioreactors with some algae producing up to 50% oil by weight [26]. The production of algae to harvest oil for biodiesel has not yet been undertaken on a commercial scale [28], due the fact that growing high-lipid species require possesses technical challenges. Growth is in favor of a heterotrophic compared to photoautotrophical environment where exogenous carbon sources offer prefabricated chemical energy. *Chlorella protothecoides* has been shown to accumulate as much as 55% of its dry weight as oil, compared to only 14% in grown cells. Promoting growth with large scale culture using transgenic material has been proposed [29]. According to [28] an equivalent 111 million hectare of oil palm plant would be needed, as no other oil crops come close to microalgae in being able to sustainably provide the necessary amounts of biodiesel. More detailed review on micro algae can be found in [20], [27].

3. BIODIESEL PRODUCTION METHODS

Acid/Alkali Catalytic Transesterification

The review of [7] discusses biodiesel production by transesterification using various feed-stocks and their state of the art production. Molar ratio of alcohol: oil, concentration, temperature, FFA level, moisture and

reaction time constitute the most crucial factors in all the literature presented.

The two methods preferred for the industrial production of biodiesel from vegetable oils are alkaline and acid catalyzed transesterification. This is a cascade reversible reaction where the oil and alcohol react at a stoichiometric molar ratio of 1:3 in the presence of an alkali or acid catalyst. The convention is to use excess alcohols to push the reaction to completion for high ester conversion. The presence of FFA is widely considered also as a limiting factor in oil conversion because of the tendency to consume the catalyst and produce soap. Transesterification of vegetable oils at oil/ alcohol ratio between 1:3 to 1:45 and catalyst quantity (0.2-3% w/w) with the alkali is feasible for FFA level less than 1% [30]-[32]. May [33] posits FFA level of less than 5%. Acid-catalysis is preferred if there is significant quantities of FFA in the feed stock as with animal fat and waste fryer oils where the reaction time has been shown to be very slow (2-6 hr) and high levels of alcohols are needed to force the reaction equilibrium

towards the transesterified products [34]. Compared to previous processes carried out, the *in-situ* acid-catalyzed transesterification of hydrolytically-degraded oil recovered from the pulp of oil palm fruits (FFA, 25–26%) are converted into alkyl esters (96–97%) for both Methanol (MeOH) and Ethanol (EtOH) with accompanying low concentrations of FFA, TG, DG, and MG [35]. Yields of alkyl were significantly greater by up to 17.5% than those obtained from the conventional reaction. Similarly, [36] reported FAME synthesis of the oilseed lipid by drying soybean flake and the reaction takes place directly within the oil bearing material during incubation in alkaline alcohol as the oilseed is not isolated prior to transesterification in its raw agricultural form, exploiting the advantages of simultaneous easy extraction of neutral lipids. While this is advantageous where the oil-bearing cells are still maintaining a rigid structure holding the oil, this led to a marked reduction in the reagent requirements. A summary of optimized transesterification process parameter for vegetable oils is presented in Table 2.

Table 2. Reported optimized transesterification using homogeneous liquid catalyst on various feedstocks.

Oil	Catalyst (w/w _{oil})	Alcohol: oil ratio	Temperature / Time	Ester Yield (%)	Reference
WPO	H ₂ SO ₄ 2.25M, EtOH		Ambient / 3 h	90%	[34]
SBO (Magnesol aided separation)	NaOH 0.3% KOH 0.1% oil/ MeOH	12:1 12:1	70°C/ 60 min	97.2% 95.6%	[37]
<i>Raphanus Sativus</i> (Magnesol aided separation)	NaOH 0.6% oil /EtOH	11.7:1	38°C/ 1 hr	99.10%	[38]
Virgin oil SFO SBO WVO	NaOCH ₃ (0.6% oil/ MeOH) NaOH (.6% oil) NaOCH ₃ /NaOH (0.8% oil) NaOH (0.8% oil)	6:1	60°C/ 1 hr	97% 92%	[12]
SFSO	NaOH (2% oil, MeOH, EtOH)	7:1	-/2 h		[11]
PO Sludge	toluene-4-sulfonic monohydrate acid 0.75% (w/w) dosage of PTSA to SPO, 10:1 M	10:1	60°C / 1 hr	96%	[39]
Lard	NaOH 1.26% w/w oil, MeOH	7.5:1	65°C 1/3 hr	97.8 %	[40]

While the *in-situ* treatment can be referred to as a treatment in raw material embedded in a solid state, the use of acid/ alkali based transesterification continues to be employed for biodiesel because of the ease of raw material handling and portability of reaction. Oil pre-treatment methods often use acid catalyst. Ferric sulfate as solid acid has been used in esterification of waste cooking oil, and results show high activity and conversion of FFA to FAME compared to sulfuric acid [41] and recently FFA of SPO was reported to have been reduced by acid catalyzed esterification to less than 2% at 0.75% (w/w) PTSA [39]. More detail is given in Table 3 on this aspect.

Enzyme Catalysis

In this process, extracellular and intercellular lipases effectively catalyze the transesterification of TGs without the associated problems of waste-water alkaline treatment identified with alkali transesterification, FFA/ water interference, energy intensivity and glycerol recovery [42]. Twelve microbial producers of lipases are listed in [43] for biodiesel production systems in organic and non-organic solvent where enzyme activities, acidity (or basicity) (pH) of the solution, and substrate interaction with products are crucial parameters affecting synthesis. The compared effectiveness of enzymatic transesterification of soybean oil [44] reported unchanged activity of the lipase *C. antarctica*.

The same was also cited in the treatment of waste oil and industrial, oil-rich bleached earth using *Ashbya gossypii* [45]. Conversion of TGs was comparatively higher in the enzymatic process. The dynamics and equilibrium of enzymatic reaction reported [46] shows that increasing the initial EtOH concentration produces an increase in the initial production rate, the yield of Fatty Acid Ethyl Ester (FAEE) and lowers the final concentration of FFA whereas lower EtOH concentration led to a higher final concentration of FFA [21].

However, at present biodiesel from lipase (enzymes) is not economically competitive with conventional fuels worldwide and can only be used for a small fraction of existing demand for transport fuels [47] because of cost, recoverability, and re-usability. Many commercially available enzymes are too costly for the intended applications, even if they can be recovered and reused by immobilization [48]. Nevertheless, reduced enzyme prices could dramatically increase the number of applications and enable large-scale processes for the production of biodiesel from lipids. Self regeneration during immobilization of the enzymes in inert support and *in-situ* regeneration are areas that need to be explored. Sequential multi-enzymatic reactions can be employed to direct pattern-wise consecutive reaction where it is evident that some enzymes promote mass-transfer limitations at relatively low flow rates which are absent at higher flow rates [49].

4. CURRENT STATE OF THE ART PROCESSES AND CHALLENGES

Current state of the art techniques are modified alkali/acid process since the reaction is understood to be the 'stretching' of the fatty acid chain and removal of the glycerol back-bone, particularly in the presence of moisture and FFA as is the case with current feedstock. The review of [30] identified and examined different oil sources, the role of catalyst (liquid, solid, enzymes) and substitute raw material (algae) as being part of the growing areas of research. While consideration has earlier been given to algae as a source of oil, the dearth of information on biodiesel production from algae could be as a result of the engineering complexity. As this involve coupling between photosynthesis and irradiance parameters from experimental data which remains a bottleneck. However, the use computational analysis of such system [50] would remove many of the underlying factors particularly cost for design. Current biodiesel production systems now aim at overcoming one major obstacles preventing commercial success which is the mass transfer rates of protons and methanol to the oil phase through the oil-methanol interface by increasing the interfacial area [51].

Ultrasonication

Ultrasonication is used to produce unique chemical and physical effects that arise from the collapse of the cavitation bubbles. Presently applied in the synthesis of nanostructured materials, the application has been extended to processing of biomass, sonofusion,

sonodynamic therapy, and the sonochemical degradation of pollutants and hazardous chemicals [53], [54]. Disselkamp et al. [53] contrasted differences in a heterogeneous catalytic reaction for cavitating and non-cavitating ultrasound incorporating an inert dopant to enable facile transition from high power non-cavitating to cavitating condition as not all liquid readily cavitate. Furthermore, transesterification of TGs was achieved with various alcohols under a low frequency ultrasonic irradiation (24 kHz) and showed conversion to be higher than those under the conventional stirring condition. Similarly, in [54] an optimal reaction condition was obtained with an alcohol to TG ratio of 6:1, combining a low frequency ultrasonication (24 kHz) and mechanical stirring (600 rpm) using MeOH to gave high yields of methyl esters (95%) after a short reaction time (20 min).

The mechanism for discriminating between the physical and chemical effects of ultrasound with different conditions has been coupled to bubble dynamics mode [37]. Due to the difference in intensity of micro turbulence produced by cavitation bubbles in oil and MeOH. Also noted is that non-thermal effect increase reaction rates 2-5 fold at all water activity level. The low intensity of micro turbulence generated by cavitation bubbles in oil, restrict an intimate dispersion of oil in MeOH for high alcohol to oil molar ratios. From the above, ultrasonication can be very efficient for the intensification of transesterification and design of cavitation reactors may offer a realistic solution to conventional transesterification.

Co-Solventing

Co-solvents enhance solubility to create a single phase in oil/ alcohol mixture and greatly accelerate reaction so that it reaches substantial completion in a few minutes [55]. In the transesterification of vegetable oil, the homogeneous flow is broken with the formation of immiscible glycerol, and transformed to a dispersed flow of fine glycerol droplets. The problem of the immiscibility of MeOH and vegetable oil leading to a mass-transfer resistance in the transesterification of vegetable oil [56] is overcome by using co-solvents. The technique is applicable for use with other alcohols and for the acid-catalyzed pretreatment of high FFA waste cooking oil [57]. Dimethyl ether (DME), Diethyl ether [58], tert-butyl methyl ether (TBME) and tetrahydrofuran (THF) to synthesize BDF from sunflower oil by using a KOH catalyst at 25°C in a closed batch reactor were compared. Addition of a co-solvent enhanced the transesterification rate at the MeOH/oil molar ratio of 6:1 at 25°C, and sunflower oil was almost completely converted into biodiesel after 20 min reaction while only approximately 78% conversion was reached in the absence of a co-solvent. The oil conversion was also influenced by the co-solvent/MeOH molar ratio and catalyst concentration. While co-solvents have been proven as an excellent material to create a monophasic environment, available literature scarcely discusses their separation. In a monophasic environment, a comparatively higher yield of 97.7% FAME and 0.74% FFA was reported in [10] within 13

min in the presence of DiEther Methyl (DEM) [59] to transesterify sunflower seeds at a molar ratio of 0.5:1 catalyst/oil, 101.39:1 and 57.85:1 of catalyst/oil, methanol/oil and DEM/ oil respectively at agitation speed of 150 rpm and reaction temperature of 20°C. Moisture content was not reported to have affected the yield with the use of DEM. Methyl TetrathydroFuran (MTHF) has been suggested as a better alternative to THF because of the lower solvent loss during reflux, higher stability in highly acidic environments, easiness to dry and the ability to produce a clean water phase along with its high boiling point (78-80°C) which places it for use with longer-chain alcohol.

Catalytic Conversion

According to [60], homogeneous catalysis is associated with the high consumption of energy and expensive separation from the reaction mixture compared with alternative heterogeneous catalysts in the transesterification of high FFA-containing oils. Although product conversion for most of the heterogeneous catalysts is not high enough to be used for industrial based production with high FFA [61] with the relatively prolonged reaction period [62], the need for aqueous quenching and removing metal salts is eliminated [63]. It has been reported that basic ammonium compounds such as Amines, aminoguanidines, nitroguanidines, and triamino(imino)phosphoranes is used as catalysts or reactants to replace sodium and potassium catalysts. The guanidines are the more active catalysts following their relative basicity, at a concentration of 3 mol %, similar to that of potassium carbonate [64]. The saturated aqueous solution of guanidine carbonate has a pH of 11 to 11.5; on the other hand, aqueous solution of free guanidine gives just as strong an alkaline reaction as lyes.

Biodiesel yield of 91.07% was reported [65] at temperature below 70°C within 2–3 h at a 1:15 molar ratio of palm oil to MeOH and a catalyst amount of 3–6 wt% KOH loaded on Al₂O₃ and Na_y elite support as heterogeneous catalysts, though leaching of potassium species in both spent catalysts was observed. Table 3 shows various conditions of the homogeneous and heterogeneous catalysts used in transesterification of various feed-stocks. As a result, the environmental benignity and re-usability, emerging heterogeneous catalyst impregnated in inert monolith could be used to address the simultaneous objective of eliminating catalyst poisoning, leaching and high basicity without reducing the biodiesel quality as expected for a successful industrial process.

Application of a combinatorial metallic oxide and other heterogeneous catalysts are areas worth further investigation. The effectiveness of separation of Mg-Al hydrotalcite from biodiesel after use is overshadowed by the low conversion of oil to biodiesel [61]. Increasing the basic site for reaction at higher calcination temperature did not improve biodiesel yield. However compared with the report of [74] for the continuous process which is described in the next part, limitation of

mass transfer is overcome at elevated temperature and pressure using a long chain alcohol. Whereas this is also similar to supercritical method, the continuity of the novel method using unmodified catalyst on feedstock with high FFA opens up the possibility of commercial biodiesel production. However it is unclear if other heterogeneous catalysts are amendable to mixed feed stock without imploring addition energy input such as microwave [68]. Calcinated egg shells at 1000°C yielded more than 95% FAME at MeOH:oil ratio 9:1 for 3 h at 65°C, which was reused 13 times with no loss in activity [71]. This is longer compared to Mg-Zr (2:1 wt/wt%) [60] at 65°C for 30–45 min with a marginal decrease in yield after 4th cycle reuse of 5%. The challenges in catalyst used are the reusability and recoverability, cost also being a major factor.

Continuous System

Most of the systems described would be batch or semi-batch systems, which promotes the mass transfer limitation earlier cited. The conventional batch reactor system for biodiesel production would remain very relevant for investigative purposes and scale-up. One of the early attempts to establish continuous production of biodiesel can be traced to [75] where the FFA, moisture and molar ratio of alcohol to oil was investigated for the effect on conversion rate. The reaction time was seen as too low in this study where a 3-step, second-order reaction was proposed. Subsequent works [76], [77] have validated this. Darnoko and Cheryan [78] study established a residence time of 60 min using a continuous stirred tank reactor (CSTR) and explained as a second order reaction. The comparison of a batch system to a continuous one by simulation [79] showed that a single CSTR requires more than 16 days of residence time to accomplish the same productivity that a batch reactor achieved in less than 62 minutes. However if CSTRs are connected in a series, the easier it is to achieve maximum batch productivity by also increasing the catalyst concentration. Nevertheless as it is not a simple task to arrange CSTR to replace batch reactor, industrial pressure would require greater competence at establishing the optimum CSTRs arrangement to replace the batch reactor.

Another process intensification process for continuous production is the continuous slit reactor [80], with hollow slit-channels. It was reported that this is to shorten average residence times for complete product conversion over a 1 mm and 10 mm slit-channel. It was also demonstrated that conversion efficiency is both a function of time and channel height. Fractional conversion efficiency of 0.923 was achieved where the slit channels with lower depth result in higher yield. As the main goal for the work is to use the slit channel as a solid catalyst similar to monolithic catalyst, higher throughput which is a major challenge in such design can be overcome using CFD.

The membrane reactor [81] was designed to overcome immiscibility of oil in methanol in providing a mass-transfer-free space in the early stages of the transesterification of canola oil in the production of fatty

acid methyl esters. With a pore size of 0.05 μm , inside and outside diameters of 6 and 8 mm in semi-batch mode, conversion was reported for flow rate of 2.5, 3.2 and 6.1 mL/min at 60, 65 and 70 $^{\circ}\text{C}$, 95-96%

respectively. The main advantage, as reported by the author, was the ability to produce a TG-free FAME, because reactor allows a phase barrier which limits the presence of TG and non-reacting lipids in the product.

Table 3. Various conditions of solid homogeneous and heterogeneous catalysts used in transesterification of various feedstock.

Catalyst	Remark	Reference
Combined acidic/ alkali	Addition of co-solvent THF and dioxane Pre-esterification with dioxane was more effective than THF for PO	[65]
Mg-Al hydrotalcite	Methanolysis of SBO oil to methanol of 15:1, a reaction time 9 h and a catalyst amount 7.5%, 67% FAME yield	[61]
Iron doped HTC	Dopant cations incorporated into HTC lattice, after 80 min 100% FAME yield using SBO	[66]
Mg-La Oxide (3:1) oil:catalyst ratio	Easy and inexpensive method to prepare catalyst. At 65 $^{\circ}\text{C}$ for 0.3 h and Reaction time for 2.2 h FAME yield 100% edible and non edible oil	[67]
acid base catalyst	microwave reactor used and FAME yield 98% in 40 min using mixed feedstock and <i>n</i> -butanol	[68]
NaOCH ₃ (0.6% oil) NaOH (0.6% SFOil) NaOH(0.8% WFO) NaOH (0.8% WFO)	FAME of 99.4% purity yield	[12]
macrospherical magnesia-rich magnesium aluminate spinel catalysts (MgO · Mg Al ₂ O ₄)	Degree of methanolysis not stated. MgO/MgAl ₂ O ₄ had higher catalytic activity in the methanolysis of SBO compared with an MgO/MgAl ₂ O ₄ / γ -Al ₂ O ₃ using SBO	[69]
Mg, MCM-41, Mg-Al hydrotalcite, K impregnated Zirconia (i) 24 KHz ultrasonication (U), (ii) 600 rpm mechanical stirring (M)	ZrO activity increased with more K in SBO. Ultrasonication significantly increased reaction compared with mechanical stirring Mg-Al HT, MCM-41, ZrO yield - 97%, 85%, 89% at 24 h mechanical stirring and 96%, 89%, 83% at 5 hrs ultrasonication respectively	[11]
KOH/Al ₂ O ₃ (25%), KOH/Na ₂ O (10%)	Catalyst (3-6 wt%) yielded 91.7% FAME at <70 $^{\circ}\text{C}$, 2-3h MeOH:oil ratio 15:1 using PO	[64]
Mg-Zr 2:1(w/w _{oil})	transesterification at 65 $^{\circ}\text{C}$ for 30-45 min. Marginal decrease in yield after 4 th cycle reuse of 5% using SFO and JO	[60]
Heterogeneous KF loaded nano- γ Al ₂ O ₃	15:1 MeOH:Oil ratio using 3 wt% catalyst. Yielded 97.7% FAME at 338K. Observed leaching lead to 30-40% activity loss using CO	[70]
Calcinated egg shells at 1000 $^{\circ}\text{C}$	Yielded more than 95% FAME at MeOH:oil ratio 9:1 for 3 h at 65 $^{\circ}\text{C}$. Reused 13 times with no loss in activity using SBO	[71]
KNO ₃ / Al ₂ O ₃ solid catalyst	yield over 84% FAME under the conditions of 70 $^{\circ}\text{C}$, methanol/oil mole ratio of 12:1, reaction time 6 h, agitation speed 600 rpm and catalyst 6% (catalyst/oil) using JO	[72]
Al ₂ O ₃ supported CaO and MgO catalysts	At 50 $^{\circ}\text{C}$, biodiesel yield was 97.5% over 80% (w/w _{oil}) CaO/ Al ₂ O ₃ catalyst, which increased to 97.5% from 23% when methanol/lipid molar ratio was 30. Al ₂ O ₃ supported CaO and MgO catalysts were more active than pure CaO and MgO in the production of biodiesel from the microalgae <i>Nannochloropsis oculata</i> . CaO/ Al ₂ O ₃ could are reused twice.	[73]
Tri-potassium phosphate, triNaPO ₃ , diKHPO ₄ , THF	catalyst regenerated in KOH. 97.3% ester yield at 60 $^{\circ}\text{C}$, 120 min. FAME yield at 88% co-solvent reduced yield from SBO	[62]

From the foregoing, it can be deduced that continued effort is being made to increase the conversion rate and yields of biodiesel. No singular approach can be sufficient, where the efficient mixing, energy-intensive methods employed to address the interphase dispersion by increasing interfacial contact have been presented.

5. TECHNICAL LIMITATIONS / SUCCESSES

The EU Purity standard of 96.5% in a single-step transesterification are difficult to attain, if not, economically impractical to reach [32]. Official standards list 25 parameters that must be determined to certify biodiesel quality, and these analyses are expensive and time-consuming for the fuel sample are to be determine [82]. Currently, specification EN14214

limits the amount of free glycerin, Mono, Di, Tri-, total glyceride and total glycerine to a maximum of 0.20, 0.80, and 0.20, 0.20 and 0.25 (% m/m), respectively, while ASTM D6571 limits free glycerin and total glycerine to 0.02 and 0.24 (% m.m) with no data for Mono, Di, Tri-glyceride [83]. Residual glyceride content in biodiesel at low levels are analyzed by on-column injection as required by ASTM D-6584 and EN-14105, using 0.32mm analytical columns coupled with a 0.53mm retention gap. The column must be operated at temperatures up to 380°C, which puts strong challenges on the mechanical stability of the capillary tubing, the stability of the phase, and the leak-tightness of the coupling. Figure 1 shows characteristic GC-MS signals of MG, DG, TG and glycerol for FAME of WCO.

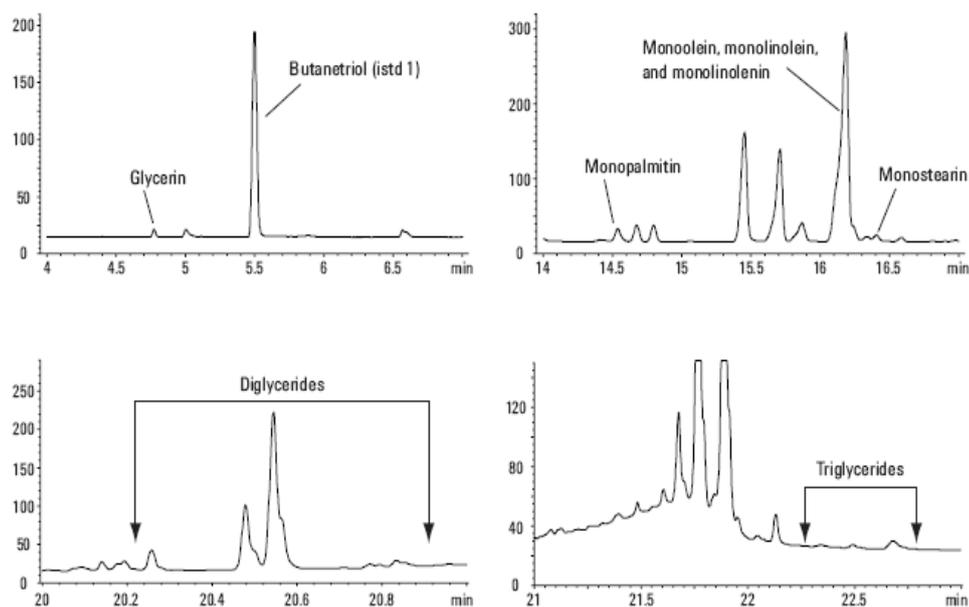


Fig. 1. Characteristic GC-MS signals of MG, DG, TG and Glycerol of sample of rapeseed B100 biodiesel [82].

This method required long preparation of sample and standard. Other methods have proposed due to the challenges of time and quantities of test which are as follows;

UV spectroscopy was used to investigate biodiesel blends in visible wavelength range of 380-530 nm. The relative absorbance was proportional to the blend level of biodiesel and a single wavelength between 470 and 490 nm was used to measure the biodiesel blend level with $\pm 1.85\%$ standard error at 95% confidence level. It was found that the shape of the absorption curve varied according to biodiesel feedstock [84]. HATR-FTIR spectroscopy associated with multivariate analysis [85] was used for determination of sulfur content, flash point and specific gravity in biodiesel blends in concentrations ranging from 1% to 30% of biodiesel content. Over the regions between $650\text{--}1909\text{ cm}^{-1}$ and $2746\text{--}3165\text{ cm}^{-1}$, quantification of these properties was attained using the variant partial least square method with a correlation of 0.9996. Monitoring reaction can be slow and tedious for these properties and several works using FTIR, spectroscopic sensor techniques, and artificial neural

networks [86], [87] have shown the applicability of these methods to help rapid and accurate analysis of other biodiesel and other biofuel.

Earlier mentioned in Table 1 is the saturated and unsaturated fatty acid composition of the feedstock. The degree of biodiesel stability is related to fatty acid composition. Sample biodiesels from different feedstocks have different properties as a result of the fatty acid composition which influences the physical and fuel properties of a fatty ester molecule, which in turn affects fatty esters cetane number and ultimately exhaust emissions, heat of combustion, cold flow, oxidative stability, viscosity, and lubricity [8].

This structural features of the various fatty esters are determined by the C=C bond and the rate of oxidation increases as the number of unsaturations in the biodiesel ester molecule [88]. The fatty acid chain, hence biodiesel property, can be predicted from knowledge of the feedstock knowing the proportion of C18:2 and C18:3 fatty acids present. This is directly related to acidity, peroxide value [89] and iodine value (IV), acid value (AV) of biodiesel responsible for

biodiesel stability [90]. Bouaid *et al.* [91] investigated acid value (AV), peroxide value [89], viscosity (η), iodine value (IV) and insoluble impurities [66] value of sunflower, high and low erucic *Brassica carinata* oil (HEBO and LEBO) respectively and used frying oil (UFO) over a period of 30 month and found that AV, PV, η and IV increased, while IV decreased with increasing storage time of biodiesel. By means of the 232 and 272 nm absorption peaks, ascribed to double bonds and carbonyl groups, respectively it was confirmed that oxidative decomposition increase the dynamic viscosities in corn biodiesel [92].

Most common fatty esters contained in biodiesel are those of palmitic, stearic, oleic acid, linoleic and linolenic acid as shown in Table 1. Cetane number describing ignition quality of a diesel fuel, decreases with a decreasing chain length, an increased branching, and an increasing unsaturation in the fatty acid chain. This would have been a good property as higher cetane number indicates better ignition quality. However the saturated esters possess poor cold-flow properties. Conversely, unsaturated and polyunsaturated fatty esters have lower melting points, which are desirable for improved low-temperature properties but also have low cetane numbers and reduced oxidative stability, which is undesirable for a diesel fuel [93]. A comprehensive review on oxidative stability can be found in [94].

To ensure that the official standards are met various effort will be needed from the initial preparation of the feed-stock to storage.

The transesterification double step process (TDSP) is an instance, where conversion of 97% FAME was achieved. At an alcohol: oil ratio of 10:1, an acid-basic catalyst was used on sunflower and linseed oils in a two-step protocol [5]. Another notable advance is the BIOX process [59] in its use of inert reclaimable co-solvents in a single-pass reaction taking only seconds at ambient temperature and pressure. The establishment of a single phase transesterification process warrants greater attention as the immiscibility problems (reactant/product) usually encountered can be eliminated through co-solventing and microwave/ ultrasonication, although at the expense of higher pressure and temperature [95]. The primary concerns with these methods are the additional complexity of recovering and recycling, if the co-solvents are not inert. Although this can be simplified by choosing a co-solvent with a boiling point near that of the solvent being used. Process type has a high impact on product purity and the most important aspects of biodiesel production to ensure trouble-free operation in diesel engines are: (i) complete transesterification reaction [66] (ii) removal of glycerine (iii) removal of catalyst (iv) removal of alcohol (v) removal of free fatty acids. However, purification remains a challenge in the biofuels industry as there is a paucity of technical data on product separation and purification. Product separation by the membrane method, resin, silica gels, water and phosphoric acid washing are summarized on Table 4 to give an insight into likely alternatives for commercial biodiesel purification.

Table 4. Biodiesel purification methods.

Material	Method of purification	Ref
Pure glycerol water wash	Addition of pure glycerol to upper layer of product and hot water washing to remove catalyst, with mixed alcohol and tannic acid	[77]
Membrane	Phase separates at room temperature into FAME. permeate consistently separated to yield a FAME-rich non-polar phase containing a minimum of 85 wt.% FAME	[81]
Absorbent BD10 (900 μ m) Purolite PD206 (600 μ m) Magensol (60 μ m)	All methods demonstrated removal of glycerol and soap only. Water washing has real effect on MeOH and none on glycerides, OSI, AV and water content	[97]
Silica gel, 5% phosphoric acid, water	Two-step alkali transesterification of waste sunflower oils (WFOs). Results showed that silica gel and phosphoric acid treatments gave the highest (~92%), while the hot water treatment the lowest yields (~89%),	[98]

Of all the methods reviewed so far, each has its merits and demerits. The reduction of FFA using acid catalyst is offset by the slow reaction. Although solid heterogeneous catalyst outperformed homogenous catalyst with high FFA feedstock subsequent leaching, recovery of catalyst and contamination of product is a major concern in the industry. Yet acid catalyst [39] would continue to be used to eliminate FFA. A major achievement is the use of Magnesol [96].

It is an active filtration medium with strong affinity for polar compounds, methanol, glycerine, glycerides, metals, soap which is recommended for dry

wash process of biodiesel. Although the particle remains undissolved, a long settling time is recommended for the removal. A list of purification process, as found in literature is listed in Table 4. The presence of glycerol in the biodiesel phase also possesses another challenge. Using membrane reactor will physically restrain and separate glycerol which has a higher density compared to biodiesel. The act of membrane recovery is however subject to degree of use. A novel method to further reduce glycerol content would be the using of surfactant also known as "deep eutectic solvents" (DES) reported at DES:biodiesel molar ratio of 1:1 [99]. Although non

active with water, relatively few studies has been done on the environmental effect. The aim of using ionic liquid is to be able to use an environmentally- benign liquid for glycerol removal.

At the moment, technical details about the use of some of these absorbents are not available and need to be worked out for various feed-stocks. See Table 5. An alternative heterogeneous catalyst scenario presented in [100] seem to be a more positive as a future technology. While the extent of catalysts can be limited by the ability to 'create' them, recourse to naturally occurring material (egg shell and oyster shell) has shown interesting outcomes [71], possibly opening an area to reduce cost.

The conditions that have provided the beneficial effects of ultrasound on bioprocesses are case-specific and so far ultrasonication has been demonstrated to provide sufficient and effective mixing for the production of biodiesel of various sources. The degradation of feed-stock and products during ultrasonication has not been reported hence it looks as if the technology will continue to enjoy patronage in the instance of overcoming mass transfer limitations.

6. CONCLUSION

Transesterification via the alkali/acid-catalyst route is the preferred alternative for biodiesel production. Catalyst types and amount, oil/ alcohol ratio, and temperature have been confirmed to be the most critical factors in biodiesel production. Process type and product quality is largely depended on feedstock where food oils are more congenial to the single step process. With the FFA and moisture content are not enough to aid soap formation. However, continued prospecting for complimentary feedstock such as non-food oils, waste/ used oil, micro-organism and algae is expanding available feedstock alternatives. The technical complexity (hydrodynamics, reaction kinetics) in using algae could be overcome using coupled computational fluid dynamics method that have been used in other complex biological systems. Harnessing the potentials of algae would also be advantageous in the quest for increasing energy sequestering similar to plants that have been domesticated. Genetically modified microalgae strains may surpass naturally existing ones in activity; however, long-term feasibility is questionable compared to other low-cost biodiesel production processes. This is due to inadequate thermodynamic data.

High quality biodiesel, as required by official standard could be realized even before production. The fatty acid composition and properties that are now available can be used to design product that would fulfill these standard using innovative monitoring techniques as discussed. Also there is the need to standardize and liberalize the specification protocol across the biodiesel producing region. It can be seen that a number of environmental factor also contribute to biodiesel quality which would be difficult to undo

Overcoming the technical limitations, using of low-cost microbes and extension of *in-situ* transesterification

to other feed-stocks could reduce production input but substantial quantities of reagents are required for high efficiency transesterification. The state of the art technology for commercial product would be a combination of the methods discussed if the balance between ecology and productivity is to be attained.

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