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Biodiesel synthesis and bioreactor design – An overview

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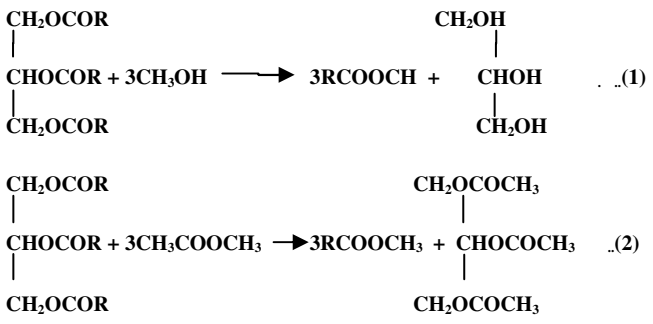
Biodiesel, an alternate, renewable, environment-friendly engine fuel, is making significant contribution to the world energy demand, particularly in the light of the diminishing petroleum reserves. In this paper, biodiesel synthesis from different feedstocks and use of different types of catalysts (both homogeneous and heterogeneous) has been reviewed. These feedstocks have been compared with respect to availability (yield of oil per unit area of cultivation), ease and fastness of transesterification, yield and purity of produced biodiesel. The comparison between homogeneous and heterogeneous catalysts including enzyme catalysts and relative superiority of each have been analysed and highlighted with respect to catalyst activity, formation of uncontaminated product and cost of downstream processing. The design features of different types of industrial bioreactors such as fluidised bed, semifluidised bed, diverging–converging fluidised bed and inverse fluidised bed reactors have been surveyed. Recommendations for future investigations have also been presented in this paper.

Keywords: Biodiesel, Bioreactors, Transesterification catalysts, Immobilised enzyme reactors, Computer aided design, Software development, Fluidised bed bioreactors, Semifluidised bed bioreactors, Inverse fluidised bed bioreactors, Diverging – converging fluidised bed bioreactors

Biodiesel is not a new product. For the past many years, the rise of energy demand, the reduction of fossil fuel-based reserves and the increase of global warming caused by the CO_2 emissions from conventional petroleum- based fuel engines have sowed the seeds for biodiesel invention, manufacture and utilisation. Many attempts have been made during the last few decades to develop technologies for the economical and commercial synthesis of biodiesel and for their efficient utilization as engine fuels/furnace fuels. It is well established that in spite of the legend that Rudolf Diesel ran the first diesel engine of the world using palm oil, vegetable oils are unsuitable for use as automobile fuels, mainly due to their enormously high viscosity (which makes the cost of atomisation of these oils exorbitantly high)[1]. Biodiesel is a short chain alkyl ester produced by transesterification of long chain triglycerides. Vegetable oils are thus converted to biodiesels by subjecting them to transesterification with low molecular weight alcohols or alkyl acetates in presence of a homogeneous catalyst (sodium alkoxide, dilute sulphuric acid) or a heterogeneous catalyst (immobilised lipase enzyme, metallic oxides, zeolites)[2-4]. This causes a drastic decrease in the viscosity of the oil, but the combustion characteristics of the oil (calorific value, flash point, ignition point) and its properties related to engine performance (diesel index, cetane rating) remain intact. Generally, in transesterification reaction, one mole of oil (triglyceride) reacts with three moles of alcohol to produce three moles of biodiesel (formed as upper layer) and one mole of glycerol (formed as a lower layer). The stoichiometry of the reaction can be represented as:



Recently, apart from vegetable oils, waste cooking oils and algal oils are also being used for the synthesis of biodiesel[5,6]. As a green fuel, biodiesel is much more environment - friendly than petroleum oils:

(i) It does not increase the concentration of greenhouse gases in the atmosphere and thus does not contribute to global warming[7].

(ii) Combustion of biodiesels does release CO_2, but this is reabsorbed by the plants from which the vegetable oil has been extracted, thereby maintaining a carbon cycle in nature.

(iii) Being an oxygenated fuel, it undergoes complete combustion and consequently, the exhaust gases from the engine cylinder would contain little unburnt C - particles or unburnt hydrocarbons.

(iv) It contains little S – compounds and pollution menace due to emission of S – containing gases (SO_2, H_2SO_4 mist) is practically eliminated[8,9].

(v) It is also photosynthetically renewable.

The economy of biodiesel synthesis heavily depends on (i) choice of raw materials (vegetable oil, alcohol or alkyl acetate, catalyst) and (ii) the efficient design of bioreactor for conducting the transesterification process.

Raw materials for biodiesel synthesis

The feedstock for biodiesel production mainly comprises of lipid feedstock (vegetable oils) and alcohol feedstock (alcohols, alkyl acetate).

Lipid feedstock (Vegetable oils)

As for the lipid feedstock, edible vegetable oils are practically ruled out due to their high market price. Non – edible oils obtained from industrial plantations (biodiesel plantations) are most recommended in this connection. Typical data on yield of biodiesel from different vegetable oils, waste cooking oils, algal oils are tabulated in Tables 1a and 1b. Among these, Jatropha oil, neem oil and algal oil are most promising. Among others, quite a few of them (rubber seed oil, tobacco oil, kusum oil, as for examples) suffer from limited availability. Waste oils (waste cooking oils, waste lard oil and the like) have the basic drawback of possessing uncertain composition and they also demand large scale pre-treatments.

An interesting feature observed from above tables is that the yield of biodiesel reported is different at different molar ratios of oil to alcohol, even if transesterification has been performed using the same edible oil / non – edible oil and the same alcohol. For example, Annapurna *et al.*[16] report that 94% yield of biodiesel can be obtained by reacting Jatropha oil with methanol at a molar ratio of 1:4, whereas Daniel *et al.*[17] observed from experiments that 90.8% yield of biodiesel is obtained by reacting the same oil (Jatropha oil) with methanol at a molar ratio of 1:15. Similarly, Abebe *et al.*[18] experimentally concluded that 100% yield of biodiesel is possible by reacting Jatropha oil with methanol at a molar ratio of 1:6, whereas Vivek *et al.*[23] and Siddharth *et al.*[24] obtained 96.8% and 90.1% yield of biodiesel by reacting Jatropha oil with methanol at a molar ratio of 1:10 and 7:3 respectively.

The land requirement for biodiesel plantations is another deciding factor. Jatropha plants (though provide a promising raw material) grow as tall trees and demand fairly large land area (see Table 2).

In comparison, microalgae could be cultivated even in waste land and waste ponds and the oil yield per hectare is significantly large (as compared to Jatropha and other oil seeds), as is evident from Table 2. The potential of algal oil as a feedstock for biodiesel synthesis is thus quite bright[35].

Neem oil is equally prospective[36,37], but at present, this oil lacks government subsidy and as a result, its market price is quite large. Once recommended as a commercial feedstock for biodiesel synthesis and accordingly cultivated in industrial plantations, this oil could be made available at subsidised price.

Alcohol feedstock (Alcohols, alkyl esters)

As for the alcohol feedstock, the choice is very much restricted to low molecular weight alcohols (methanol, ethanol, propanol) or alkyl acetates (methyl, ethyl or propyl acetate). This is to restrict the molecular weight of the synthesised biodiesel which also restricts its viscosity.

When the transesterification reaction for biodiesel synthesis is being catalysed by immobilised enzymes, then alkyl acetates are preferred over alcohols as the secondary reactant. This is because investigations have demonstrated that glycerol, which is formed as the byproduct during transesterification of vegetable oils with alcohols, tends to deactivate the immobilised enzyme (for example, immobilised lipase) and thus tends to hamper the overall rate of reaction[38-41]. When transesterification of oils is performed using an alkyl acetate, this problem does not arise since the reaction pathway then follows equation 2 and the byproduct formed is glycerol triacetate. This glycerol triacetate has little tendency to deactivate the immobilised enzyme and thereby diminish the rate of biodiesel synthesis.

Table 1a — Data on yield of biodiesel from different vegetable oil feedstock

Oil	Species	Alcohol	Oil: alcohol ratio	Catalyst	Yield	References
Karanja oil	*Pongamiapinnata*	Methanol, Ethanol	1:10.44, 1:8.42	Sulphuric acid, Potassium methoxide, Potassium ethoxide	91.05 %, 77.44 %	10
Mahua oil	*Madhucaindica*	Methanol	1:6	Sulphuric acid, Potassium methoxide	98 %	11
Rubber seed oil	*Heveabrasiliensis*	Methanol	1:6	Sulphuric acid, Potassium methoxide	96.8 %	12
Cotton seed oil	*Gossypiumhirsutum*	Methanol	1:6	Potassium methoxide	96 %	13
Linseed oil	*Linumusitatissimum*	Methanol	1:23	Dibutyltin diacetate	71%	14
Jojoba oil	*Simmondsiachinensis*	Methanol	1:23	Dibutyltin diacetate	39.66%	14
Neem oil	*Azadirachtaindica*	Methanol	1:23	Dibutyltin diacetate	50.78%	14
Tobacco oil	*Nicotianatabacum*	Methanol	1:18	Sulphuric acid	91%	15
Jatropha oil	*Jatropha curcas*	Methanol	1:4	Immobilised lipase *Enterobacter aerogenes*	94 %	16
Jatropha oil	*Jatropha curcas*	Methanol	1:15	Cesium modified sodium zirconate (Cs-Na_2ZrO_3)	90.8%	17
Jatropha oil	*Jatropha curcas*	Methanol	1:6	Li-CaO, $Fe_2(SO_4)_3$	100 %	18
Castor oil	*Ricinuscommunis*	Ethanol, Methanol	1:4 – 1:6	Sodium methoxide, sodium ethoxide, potassium methoxide, potassium ethoxide	68.3 – 87.3 %	19
Kusum oil	*Schleicheratriguga*	Methanol	1:6	Potassium methoxide	87%	20
Neem oil	*Azadirachtaindica*	Methanol	1:10	Copper doped zinc oxide(CZO)	97.18	21
Sesame oil	*Sesamum*	Methanol	1:6	Sodium methoxide	74%	22
Jatropha oil	*Jatropha curcas*	Dimethyl carbonate	1:10	Potassium hydroxide	96.8 %	23
Jatropha oil	*Jatropha curcas*	Methanol	7:3	Sulphuric acid, Sodium methoxide	90.1%	24

Table 1b — Data on yield of biodiesel from waste oils and microalgal oil feedstock

Other oils	Alcohol	Oil:Alcohol ratio	Catalyst	Yield	References
Waste cooking oils	Methanol	7:3	Sulphuric acid, Sodium methoxide	90.1%	25
Waste cooking oils	Methanol	1:12	Sodium methoxide	95%	26
Waste frying oil	Methanol	1:4.83 to 1:9.65	Calcinated crushed snail shells	87.28%	27
Microalgae oil	SupercriticalMethanol and Ethanol	1:10–1:42	-	90.8% (methanol) 87.8 % (ethanol)	28
Microalgae oil	Methanol	1:56	Sulphuric acid	60%	29
Microalgae oil	Methanol	1:30	Al_2O_3 supported CaO	97.5%	30
Microalgae oil	Methanol	1:3	Penicilliumexpansum lipase (PEL)	90.7%	31
Microalgae oil	Anhydrous ethanol	1:12	Candida Antarctica lipase (Novozyme 435)	98.10%	32
Waste land	Methanol	1:6	Immobilised *Candida antarctica Lipase B (CALB)*	96.8%	33

The use of higher alcohols such as butanol has also been investigated[42]. The results are encouraging, but not superior. Secondary alcohols (for example, isopropyl alcohol) are viable substitutes to primary alcohols, but no significant improvement in the yield and the quality of biodiesel produced has been noticed.

The molar ratio of vegetable oil (primary reactant) to alcohol or alkyl acetate (secondary reactant) is one of the most deciding parameters that affects the rate of transesterifcation reaction and the overall yield of biodiesel. Consequently, this ratio (usually denoted as y) is required to be

Table 2 — Oil yield per acre of land from different sources

Source	Oil yield (Gallons / Acre)
Corn	15
Soybeans	48
Safflower	83
Sunflower	102
Rapeseed	127
Palm oil	635
Jatropha oil	304
Microalgae	1850 (based on actual biomass yield)
Microalgae	5000 – 15000 (theoretical laboratory yield)

Source: Ref. 34

optimised. This has been discussed in more detail subsequently in this paper.

Catalysts for biodiesel synthesis

Transesterification catalysts broadly fall into two categories:

a. Homogeneous catalysts
   i. Alkali catalysts (sodium or potassium alkoxide)
   ii. Acid catalysts (dilute sulphuric acid)
b. Heterogeneous catalysts
   i. Immobilised enzyme catalysts (lipases)
   ii. Metallic oxide catalysts
   iii. Zeolite catalysts

Homogeneous catalysts

Most of the experimental investigations reported in literature are those employing homogeneous catalysts. Among them, alkali catalysts (sodium or potassium alkoxides) are more popularly used. The reason is obvious. These catalysts are easier to handle and they can be generated in situ. A calculated amount of well – ground caustic soda (NaOH) or caustic potash (KOH) is added to the alcohol and on intimate mixing, sodium or potassium alkoxide gets formed in solution

$$ROH + NaOH \longrightarrow NaOR + H_2O \quad ... (3)$$

where the alkyl group (R) can be methyl, ethyl or propyl group. Being a homogeneous catalyst, it blends uniformly with the reaction mixture and this enhances the rate of reaction (rate of transesterification). Caustic soda being an easily available chemical (reagent) and since the amount of alkoxide catalyst required is relatively small, the recovery of the catalyst from the product solution for recycle and reuse is often neglected.

Dilute sulphuric acid is the most popular homogeneous acid catalyst. Comparatively, it is a more efficient catalyst than alkoxide and it permits attainment of higher rate of transesterification.

In spite of their above desirable characteristics, homogeneous catalysts do have distinct disadvantages particularly with reference to the purity of biodiesel synthesized. With alkoxide catalysts (alkali catalysts), there is the danger of formation of soap (RCOONa, sodium or potassium salt of high molecular weight carboxylic acid) and this contaminates the biodiesel produced, demanding elaborate and expensive downstream processing. It is to be noted that soap is gelatinous in nature, and even very small particles of soap, if present, could tend to clog the atomisation nozzles. Also, being gelatinous, once deposited at the nozzle tip, it adheres to the surface very firmly and is difficult to get dislodged. In the case of acid catalysts (sulphuric acid), it has an annoying tendency to form acid sludge which is highly corrosive and toxic and if disposed to the environment (soil, water bodies) ,would cause serious pollution problems and serious damage to public health. A separate sludge treatment plant that enables efficient and economical recovery of the S – content (and C – content) of the sludge would have to be designed and operated.

Heterogeneous catalysts

Among the heterogeneous catalysts, immobilised enzyme catalysts, particularly lipase enzyme, are by far most popular. In most industrial applications, enzymes are used in the immobilised state, since this eliminates the need for recovery and reuse of enzymes which, by itself, is too expensive. Lipase enzyme can be immobilised in support particles made of polymer composites (polymer beads) or silica (silica granules) or activated carbon. The substrates (reactants) diffuse into the particles where they meet the enzyme catalyst and the reaction occurs. The products diffuse out. The product solution discharged thus does not contain the enzyme catalyst and this eliminates the entire cost of recovery and recycle of enzyme. In two phase heterogeneous systems like this, additional resistance thus comes into play which is the resistance to substrate transfer from the liquid bulk to the particle phase (solid phase). Due to this additional resistance, the overall rate of transesterification tends to get lowered. On the other hand, the concentration of immobilised enzyme within the particle is substantially large and this helps in maintaining the rate of reaction at an augmented magnitude. Enzymes are selective catalysts and consequently, do not cause formation of undesirable side products (soap, acid

sludge) and thereby yield purer and uncontaminated product (biodiesel). The cost of downstream processing is thus significantly reduced. No doubt, the overall rate of transesterification of vegetable oils is lower when immobilised lipase is used as the catalyst, as compared to processes employing alkoxide catalyst or sulphuric acid catalyst. Accordingly, the volume requirement of the bioreactor shall be larger. The popularly used lipase enzymes for biodiesel synthesis are *Candida rugosa, Thermomyces lanuginosu*[43], *Burkholderia cepaci*[44], *Aspergillus niger, Candida antarctica*[45], *Rhizopus oryzae, Rhizomucor miehei, Pseudomonas cepacia Pseudomonas fluorescens*[46].

Other than immobilised enzymes, treated metallic oxides and zeolites have also been recommended for use as transesterification catalysts. However, all studies reported in this connection are on laboratory scale and little attempt has been made to develop kinetic equations or study the application of these catalysts in industrial bioreactors.

Feyzi and Norouzi[47] have investigated biodiesel synthesis from waste sunflower oil and methanol using a novel magnetic $Ca/Fe_3O_4@SiO_2$ nanocatalyst. 97% yield of biodiesel has been reported at 65°C and an alcohol to oil ratio of 15:1. Hu *et al.*[48] have studied transesterification of rapeseed oil with methanol in presence of KF/CaO catalyst and have observed that the maximum yield of biodiesel is 93.7% and it is attained at 81.5°C. In another investigation, Hu *et al.*[49] synthesised KF/CaO nano-magnetic catalyst and used it for the transesterification of Stillinga oil extracted from the seeds of Chinese tallow (S*apium sebiferum*) with methanol. The nano-magnetic catalyst reportedly assisted in attaining 96.8% yield of biodiesel of marketable quality.

Kawashima *et. al.*[50] have carried out experiments on catalytic activities of thirteen different metallic oxides for transesterification of rapeseed oil with methanol at 60°C and a 6:1 molar ratio of methanol to oil, out of which, calcium – containing catalysts were observed to give the highest biodiesel yield of 90%. The same authors[32] have reported that calcium oxide (CaO) activated by methanol provides 90% transesterification of rapeseed oil at 60°C. Fang *et al.*[51] have demostrated that calcined sodium silicate is an effective catalyst for the microwave-irradiated production of biodiesel from rapeseed and jatropha oils and methanol , biodiesel yield being about 96% from rapeseed oil and 92% from jatropha oil. Ibrahim[52] obtained biodiesel yield of 94% by transesterification reaction with rapeseed oil and methanol over K_2O/Υ-Al_2O_3 catalyst at a molar ratio of 12:1 methanol to oil at 700°C.

Attempts to use zeolite catalysts for transesterification have been on the rise during the recent past. Abbas and Abbas[53] have found that at an oleic acid to ethanol molar ratio of 1:6, a maximum biodiesel yield of 81% is obtained in presence of NaY zeolite at 70°C. Bhagiyalakshmi *et al.*[54] studied transesterification of Jatropha curcas oil with methanol over ceria impregnated ZSM-5 catalyst and reports 90% yield of biodiesel at 60 °C and oil to methanol molar ratio of 1:12.

Karmee and Chadha[55] have reported that 59, 47 and 83% conversion are obtained by transesterification of Karanja Oil (*Pongammia pinnata*) crude with methanol at 120°C with 10:1 ratio of alcohol to oil in presence of HBeta-zeolite, montmorillonite K-10 and ZnO catalyst respectively. Sathya Selvabala[56] have observed that transesterification reaction of neem oil with methanol at a molar ratio of 1:6 at 60°C gives a maximum biodiesel yield of 92.5% in presence of heterogeneous catalysts of phosphoric acid modified mordenite.

Shah *et al.*[14] have studied transesterification of a variety of oils such as jojoba oil, sunflower oil, neem oil, rocket seed oil and linseed oil using different catalysts such as tin powder, dibutyltin diacetate $(C_4H_9)_2Sn(OOCCH_3)_2$, dioctyltin diacetate $(C_8H_{17})_2Sn(OOCCH_3)_2$, dibutyltin oxide $(C_4H_9)_2SnO$, dioctyltin oxide $(C_8H_{17})_2SnO$, diphenyltin oxide $(C_6H_5)_2SnO$, dibutyltin chloride dihydroxide $(C_4H_9)_2Sn(OH)_2Cl$, butyltinhydroxide hydrate $(C_4H_9)Sn(=O)OH.xH_2O$, Ni nanoparticles and Pd nanoparticles. They report 71, 51, 50.9, 41 and 30.9% biodiesel yields during methanolysis of above f ive vegetable oils, respectively. Sirajuddin *et al.*[57] report that organotin (IV) carboxylates are effective catalysts for the conversion of corn oil to biodiesel. Biodiesel production from soyabean oil and jatropha oil using cesium impregnated sodium zirconate as a heterogeneous base catalyst has been reported by Rodríguez *et al.*[17]. Here also, laboratory studies reportedly predict satisfactorily high yield of biodiesel.

Adewale, Dumont and Ngadi[33] have conducted experiments on biodiesel synthesis from waste lard and methanol in presence of ultrasonic waves. The catalyst employed was immobilised lipase enzyme (*Candida Antarctica Lipase B, CALB*). Use of ultrasonic waves reportedly augmented the rate of transesterification. However, more elaborate studies are required to be conducted prior to

recommending the technique for industrial adaptation.

Kinetics of transesterification

Kinetics studies on transesterification process and biodiesel synthesis are relatively less reported in literature. Most investigations (referenced in the earlier section) have been confined to estimation of the yield and characteristics of biodiesel produced. For the industrial manufacture of biodiesel and for the design of industrial bioreactors for the same, we very much need the kinetic equation representing the transesterification process.

Most of the authors who have studied the kinetics of transesterification of vegetable oils using homogeneous alkali catalyst (sodium or potassium alkoxide) report that the process follows second order reversible kinetics, the first step involving transformation of triglyceride to diglyceride being the rate controlling step. Examples are Noureddini and Zhu[58] who studied transesterification of soyabean oil with methanol, Darnoko and Cheryan[59] who investigated methanolysis of palm oil with potassium methoxide catalyst and Issariyakul and Dalai[60] who studied the same and also methanolysis of mustard oil. All of them agree to second order, reversible kinetics. So are Okullo *et al.*[61] who experimented on biodiesel synthesis from Jatropha oil and methanol in presence of sodium methoxide catalyst and Richard, Roux and Prat[62] who handled sunflower oil and ethanol with sodium ethoxide catalyst, though the latter authors have listed third order kinetic constants as well, with dimensions $L^2 mole^{-2} s^{-1}$. Interestingly, Liu *et. al*[63] report that the same three step, second order, reversible kinetic mechanism is applicable to non-catalytic transesterification of microalgae oil with methanol at elevated temperatures (300–400°C) and elevated pressure (150–300 bar).

Kinetic data on heterogeneous catalysis are much more scattered. Allain *et al.*[64] report that as in the case of homogeneous catalysis, transesterification of triolein with methanol in presence of zinc-aluminium catalyst ($ZnAl_2O_4$) follows second order, reversible kinetics. Gurunathan and Ravi[21] have studied biodiesel synthesis from neem oil and methanol in presence of copper doped zinc oxide catalyst and they propose that the rate of product formation follows first order (or pseudo first order) kinetics. Since the process involves two reactants (oil and alcohol) and it is a three step reaction, it is difficult to conceive that the rate of formation of biodiesel is pseudo first order in biodiesel concentration. More experiments are required to confirm the reported kinetic equation.

The reported studies on kinetics of transesterification are summarized in Table 3.

Table 3 — Reported studies on kinetics of transesterification reaction

Oil, alcohol	Oil: alcohol	Temperature	Kinetic model	Kinetic parameters	References
Rapeseed oil, methanol	1:42	270–487°C	First order irreversible	$7.0 \times 10^{-4} – 8.0 \times 10^{-2}$ s^{-1}	65
Sunflower oil, methanol, ethanol	1:40	200-400°C	First order irreversible	$1.67 \times 10^{-6} – 1.07 \times 10^{-3}$ s^{-1}	66
Soyabean oil, ethanol	1:40	275–300°C	First order irreversible	$2.12 \times 10^{-4} – 1.67 \times 10^{-3}$ s^{-1}	67
Soyabean oil, methanol	1:6	30–70°C	Second order reversible kinetics	0.050–0.007 $L.mol^{-1}.min^{-1}$	58
Palm oil, methanol	1:6	60°C	Second order reversible kinetics	0.018–0.191 $L.mol^{-1}.min^{-1}$	59
Sunflower oil, butanol	1:3 – 1:5	40°C	Non – linear reaction kinetics (equation 4)	$r_1 = 250 \mu mol.min^{-1}.g^{-1}$, $K_1 = 5.3$mM, $K_m = 55$mM, $K_{Si} = 13$mM	42
Soyabean oil, methyl acetate	1:12	40°C	Non – linear reaction kinetics (equation 4)	r_1 = 1.9 moles/(L.min), = 16.0 moles/L, = 1.0 moles/L and = 0.0455 moles/L	68
Neem oil, methyl acetate	1:3 – 1:9	Room temperature	Non – linear reaction kinetics (equation 4)	$r_1 = 4.78 \times 10^{-5}$ $mol.s^{-1}.g^{-1}$, $K_1 = 1.12$ moles/L, $K_m = 15.837$ moles/L, $K_{Si} = 0.053$ moles/L	69
Jatropha oil, methanol	1:3	45°C	Non – linear reaction kinetics (equation no. – 4)	r_1 = 0.00022 mole/ (L.min), = 0.0067 millimoles/L, = 2.212 millimoles/L, = 0.042 millimoles/L	71

When immobilised lipase is used as the catalyst, then the intrinsic kinetics of transesterification must be anticipated to follow a modified form of Michaelis–Menten scheme. Dossat, Combes and Marty[42] have proposed such a kinetic equation as given below, in the case of transesterification of high oleic sunflower oil with butanol in presence of immobilised Lipozyme in *n*–hexane solvent:

$$-r_s = r_{\max} C_s C_B / \left[K_m C_B + K_m (C_B^2 / K_{si}) + K_1 C_s + C_s C_B \right] \quad \ldots (4)$$

Where C_s, C_B = molar concentration of vegetable oil and that of alcohol respectively

k_m, $r_{\max}$ = kinetic constants

k_{si} = substrate inhibition coefficient

Experimental values of kinetic constants reported by them are,

$r_{\max}$ = 250 µmole/ (min.g catalyst)

k_1 = 5.3 millimoles/L

k_m = 55.0 millimoles/L

$k_{si} K_1$ = 13.0 millimoles/L

As can be deduced from the proposed kinetic equation, at high concentrations, the alcohol (here, butanol) tends to inhibit enzyme activity and thereby tends to diminish the rate of transeserification.

Xu, Du and Liu[68] have proposed a similar kinetic equation for lipase–catalysed transesterification of soyabean oil with methyl acetate, with $r_{\max}$ = 1.9 moles/(L.min), $k_{m'}$ = 16.0 moles/L, k_1 = 1.0 moles/L and k_{si} = 0.0455 moles/L. Tripti, Sikder and Narayanan[69] have also experimentally observed that a kinetic equation of above type is applicable to transesterification of neem oil with methyl acetate in presence of immobilised lipase *Pseudomonas cepacia*. Very recently, Li *et al.*[70] have confirmed the above observation with respect to lipase-catalysed methanolysis of soyabean oil. Veny, Aroua and Sulaiman[71] have developed a kinetic equation of the type of equation (4) based on their experiments on biodiesel synthesis from Jatropha oil and methanol in a circulating batch packed bed reactor composed of immobilised lipase catalyst particles. The kinetic constants reported by them, are, $r_{\max}$ = 0.00022 mole/ (L.min), K_m = 0.0067 millimoles/L, K_1 = 2.212 millimoles/L and k_{si} = 0.042 millimoles/L.

Catalyst handling

Once the system is heterogeneous (multiple phase) in nature, then the question of catalyst handling comes into play. All heterogeneous transesterification catalysts (discussed above) are in the solid state. In the case of lipase enzyme, it is immobilised in solid particles. The feed solution (vegetable oil – alcohol or oil – alkyl acetate mixture) is in the liquid phase. Thus, prior to the design of industrial reactor, we have to decide the mode of catalyst handling. The popular choices are,

a. Packed bed reactors
b. Fluidised bed reactors
c. Semifluidised bed reactors
d. Inverse fluidised bed reactors

Each category of reactors have their own merits as well as demerits. To make a judicious choice therefore, we have to critically analyse the performance characteristics of each of them.

Packed bed reactors are restricted to low capacity installations. Here, the superficial velocity of the feed solution, *U (sup)*, cannot be maintained above the minimum fluidisation velocity, U_{mf} Channelling (non – uniform wetting of catalyst particles by the feed solution) and clogging due to presence of fine particulates in the feed solution are two additional problems associated with packed bed reactors. Further, in the case of immobilised enzyme reactors, if large scale deactivation of enzyme is being apprehended, then continuous reactivation and recycle of immobilised enzyme is not possible in the case of these reactors.

For the large scale manufacture of biodiesels therefore, we have to employ fluidised bed, semifluidised bed or inverse fluidised bed reactors.

As stated earlier, among the heterogeneous reactors for biodiesel synthesis, only the immobilised enzyme bioreactors have received commercial acceptance. Others are more or less in the laboratory experimental stage. We shall, therefore, focus our discussion on reactors employing immobilised lipase catalyst.

In ***fluidised bed bioreactors***, the superficial velocity of the feed solution, *U (sup)*, is maintained

higher than U_{mf}, but lower than the terminal free settling velocity (V_t) of the solid particles (catalyst particles or support particles accommodating the lipase enzyme). A popular choice is

$$(1.20)U_{mf} \le U_{\sup} \le 0.8V_t \quad \ldots (5)$$

Initially, the reactor column is composed of a static bed (packed bed) of particles of height L_s and of voidage (or void fraction), $\in_p$. Once the feed solution is admitted from the bottom at a velocity chosen as per equation (5), the bed gets fluidised or expands. The solution moves upward keeping the particles suspended in it (Fig. 1).

The height (measured from the bottom liquid distributor) to which the particles are raised or suspended in the ascending stream of solution, called the expanded bed height or fluidised bed height, L_f (see Fig. 1), depends on the size and density of the particles (d_p,p_s) and the density and the viscosity of the feed solution p_L, μ_L. The voidage of the bed $(\in_f)$ shall be larger than that of the initial static bed $\in_p$. The product solution leaves from the top of the column. In many industrial applications, the feed solution is first admitted at the prescribed velocity and thereafter, calculated amount of solid particles (that would pack to form a bed of height L_s and voidage $\in_p$) is fed from the side inlet (feed hopper).

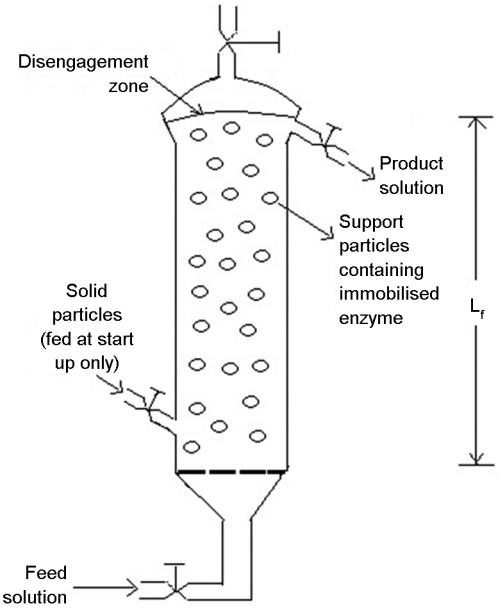


Fig. 1 — Schematic diagram of conventional fluidised bed bioreactor

The minimum fluidisation velocity, U_{mf}, in the case of liquid fluidised beds (as in the case of biodiesel synthesis) can be computed from the correlation proposed by Wen and Yu[72] way back in 1966. Though Wen and Yu's correlation involves a few simplifying assumptions, it predicts the order of magnitude of U_{mf} that can be used in design computations. It is to be kept in mind that for the design and analysis of fluidised bed reactors /bioreactors, we need to compute an order of magnitude of U_{mf} only since the actual fluid velocity employed (the operating fluid velocity), U (sup), is 20 to 25 % higher than U_{mf}.

The terminal free settling velocity of particles (V_t) may be estimated from the generalised law of settling as,

$$V_t = \left[(4/3)(P_s - P_L)gd_p / (P_L f_D)\right]^{1/2} \quad \ldots(6)$$

where f_D is the drag coefficient which is to be estimated from the standard f_D versus Re_p plot (on log – log coordinates). In other words, equation (6) is to be solved by trial with the help of the standard f_D versus Re_p plot[73]. Here, Re_p is the particle Reynolds number and is defined as

$$\mathrm{Re}_p = (d_p V_t p_L / \mu_L) \quad \ldots (7)$$

The voidage $(\in_f)$ of liquid fluidised beds, as the one under consideration, can be estimated with reasonable accuracy from the correlation proposed by Richardson and Zaki[74] way back in 1954. A modified form of this correlation has been proposed by Al–Dibouni and Garside [75]. To note that in the case of liquid fluidised beds (two phase systems), the fractional liquid holdup $(\in_{fL})$ in the bed may be taken equal to the total voidage $(\in_f)$ of the bed. Once the voidage of the fluidised bed is known, the height of the expanded bed L_f can be deduced from a simple solid balance, as given below:

$$L_f(1-\in_f) = L_s(1-\in_P) \quad \ldots (8)$$

or

$$L_f(1-\in_{fL}) = L_s(1-\in_{PL}) \quad \ldots(9)$$

One of the interesting features of the fluidised bed systems is that once the bed is fully fluidised, the pressure drop across the bed remains more or less constant and does not increase with increase in fluid velocity. As a result, the bioreactor could be operated at high feed flow rates (high capacities) without sacrificing much on the operating cost.

A *semifluidised bed bioreactor* combines the advantages of both packed bed and the fluidised bed. The terminology "*semifluidised*" could be misleading since this may be interpreted as a bed that is half fluidised. This is absolutely wrong since the fluid velocity employed in a semifluidised bed is much higher than that employed in a conventional fluidised bed (Fig. 1). A schematic of a two phase (liquid – solid) semifluidised bed bioreactor is shown in Fig. 2. The bed is fully fluidised using a high fluid velocity, but the expansion of the bed is restricted by fixing another porous plate (called the top restraint) at a height L_{sf} from the bottom liquid distributor (Fig. 2). L_{sf}, in fact, constitutes the total height of the semifluidised bed. The ratio $R = (L_{sf}/L_s)$ is called the bed expansion ratio (R). In other words,

$$R = (L_{sf}/L_s) \quad \text{... (10)}$$

One of the popular choices is R = 2.0, that is, the total height of the semifluidised bed (L_{sf}) is twice the height of the initial static bed prior to fluidisation (L_s) Due to the presence of the top restraint, those particles which reach this restraint accumulate below it, thereby forming a packed bed of height L_P there. The

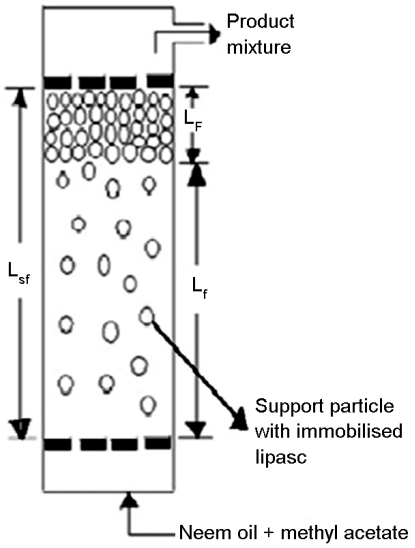


Fig. 2 — Schematic diagram of semifluidised bed bioreactor

reactor column becomes thus composed of a packed section of height L_P at the top and a fully fluidised section of height L_f at the bottom. The magnitude of L_p depends on the operating liquid velocity (U_{SL}), size and density of particles and density and viscosity of the feed solution P_L, μ_L and is hence a hydrodynamic parameter. Experimental correlations have been developed by many researchers for the estimation of L_P. Examples are correlations proposed by Kurian and Rao[76], Singh *et al.*[77], Roy and Sharma[78] and Mydlarz[79]. Based on the size and density of the particles handled and the liquid velocity or range of liquid velocities employed, the most applicable correlation must be selected for the computation of L_p. Once the height of the packed bed formed is known, the height of the fluidised section L_f can be obtained by difference, as

$$L_f = (L_{Sf} - LP) \quad \text{... (11)}$$

The operating superficial velocity of liquid, U_{SL}, must be selected in such a way that it exceeds the minimum semifluidisation velocity (U_{sm}), but is well below the terminal free settling velocity of the particles (V_t). A popular choice is

$$(1.25)U_{sm} \le U_{SL} \le 0.8V_t \quad \text{… (12)}$$

The minimum semifluidisation velocity is the liquid velocity at which the first particle reaches the top restraint. When $U_{SL} = V_t$, all the particles enter the top packed section and the bottom fluidised section shall be devoid of particles. Both of these situations are not acceptable nor desirable for the real life operation of an industrial bioreactor. Experimental correlations are available for the estimation of the minimum semifluidisation velocity U_{Sm} as well. Examples are those proposed by Kurian and Rao[76], Roy and Sharat Chandra[80] and Rao and Sharma[81]. The most appropriate correlation for a given application is to be selected from among them based on the magnitudes / range of magnitudes of the system parameters $(dp, P_s, P_L, \mu_L R)$.

Investigations have demonstrated that the voidage of the top packed section does not vary materially with increase in fluid flow rate. Accordingly, it shall not be too wrong to assume that $\in_P = \in_{PL} = 0.35$ to 0.40

The voidage of the fluidised section (which shall be equal to the fractional liquid holdup in the section, in

the case liquid – solid systems) can be estimated from the correlation proposed by Richardson and Zaki[74] mentioned earlier.

As the liquid velocity (velocity or flow rate of feed solution) is increased, more particles enter the packed section and the height or thickness of this section (L_P) increases. In the case of semifluidised bed bioreactors, this has been observed to be advantageous since the major share of transesterification occurs in this section. This is discussed more elaborately in the subsequent section.

Semifluidised bioreactors can be operated at higher capacities (at higher feed flow rates) than conventional fluidised bed bioreactors. Due to the presence of the top restraint, there shall be no problems associated with entrainment loss of particles in the outgoing product solution, which is often a head-aching problem during the operation of fluidised bed reactors. The operating cost of semifluidised bed reactors shall be nevertheless higher than that of the conventional fluidised beds due to the presence of the additional packed section at the top. Also, continuous reactivation of enzyme catalyst and recycle is not possible in the case of these reactors, since semifluidised beds cannot be operated in the circulating mode.

Inverse fluidised bed bioreactors are relatively new additions to the family of bioreactors. However, inverse fluidisation is not a new concept. Muroyama and Fan[82] have discussed on three phase inverse fluidised beds in their review article published way back in 1985. As the name implies, in an inverse fluidised bed, the feed solution is admitted from the top (and not from the bottom) and it flows down the column under gravity. The solid particles remain suspended in this descending stream of liquid and thus form a fluidised bed within the column. How is this achieved? As for two phase, liquid–solid systems, inverse fluidisation could be brought about by two means:

a. The first category of inverse fluidised bed reactors employ catalyst particles that are lighter than the feed solution. In the case of immobilised enzyme bioreactors, lipase enzyme is immobilised in polymer beads whose density is lower than that of the feed solution. Consequently, these particles remain suspended in the liquid stream though it is executing down flow, thereby constituting a fluidised bed inside the reactor column (Fig. 3).

b. The second category of reactors[83] are those which employ catalyst particles or support particles of nano size. For example, lipase enzyme can be immobilised in nanosilica particles and though silica is much heavier than aqueous solutions (density of silica is around 2500 kg /m^3), these nanoparticles shall remain suspended in the down-flowing liquid stream due to their enormously low size. However, in this case, the nanoparticles are to be mixed with the feed solution in advance in an overhead mixing tank and the resulting fine suspension is made to flow down the reactor column under gravity (Fig. 4). The suspension of nanoparticles in the product solution leaves the bottom of the column and is sent to a nano - membrane filter to separate the nanoparticles. The product solution passes through the nano – membrane as the permeate, while the nanoparticles (that are retained by the membrane) are conveyed upward

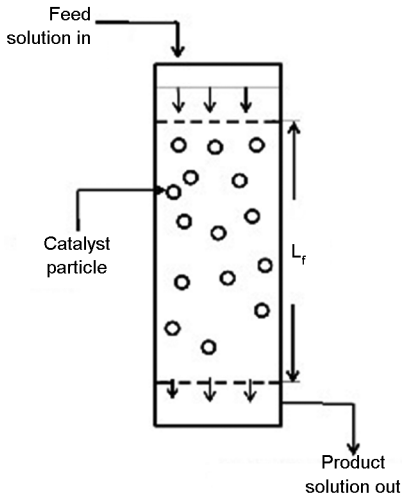


Fig. 3 — Schematic diagram of inverse fluidised bed bioreactor

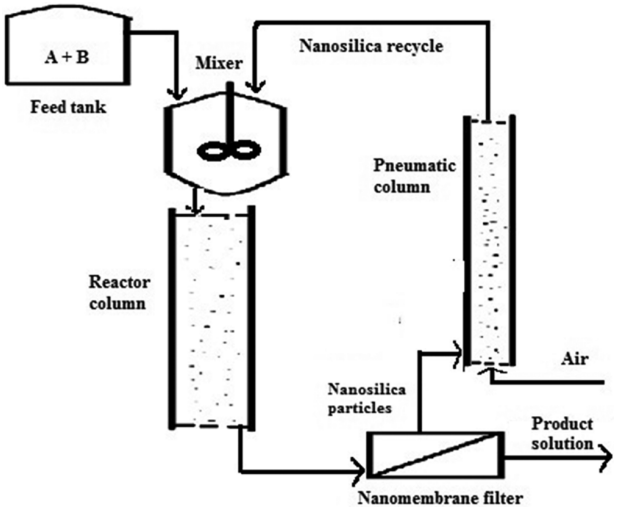


Fig. 4 — Schematic diagram of inverse fluidised bed bioreactor (with nanoparticles)

pneumatically using compressed air through the vertical pneumatic column and thus recycled back to the overhead mixing tank (Fig. 4)

Aditi and Narayanan[84] have shown that inverse fluidised bed bioreactors of second category (that handle nanosilica support particles) can be economically employed for the commercial manufacture of biodiesels. Due to the downflow mode of operation, the operating cost of inverse fluidised bed bioreactors shall be much lower than that of fluidised bed or semifluidised bed bioreactors. Bioreactors of first category (that handle particles of low density and that are lighter than the feed solution), circulating mode of operation is not possible and therefore, do not permit continuous re –activation and recycle of catalyst particles. However, in the second category of inverse fluidised beds, this can be successfully accomplished.

In the case of inverse fluidised beds of first category, the operating superficial velocity of feed solution, $U(\text{sup})$, is to be selected to be 20–25% higher than the minimum inverse fluidisation velocity, $U_{mf}(inv)$, which is to be estimated from one of the selected experimental correlations such as that proposed by Ulaganathan and Krishnaiah[85], Banerjee *et al.*[86]. These authors have developed correlations for the estimation of the expanded bed height (L_f) as well, which is obviously a function of the operating liquid velocity, $U(\text{sup})$ and the properties of the particles and the feed solution (d_p, p_s, p_L, μ_L).Once the expanded bed height (L_f) is known, the voidage of the bed $(\in_f)$ could be obtained from the solid balance given in equation (8) or (9).

Design of bioreactors

As stated earlier, most of the studies on biodiesel synthesis have been conducted on laboratory scale and relatively less attempt has been made to design industrial bioreactors for the same. Even if attempted, most researchers have incorporated gross simplifications into their analysis (either cent percent backmixing or zero percent backmixing, both of them being too idealistic). Only very recently, real life investigations have been taken up with a view to perform computer aided design (CAD) and analysis of industrial bioreactors for biodiesel synthesis[35,69,84]. What is to be kept in mind is that for industrial adaptation, we have to follow a two – fold approach:

a. The performance of the bioreactor must be studied mathematically and a reliable software package be developed.

b. The accuracy of above–developed CAD (software) package must be verified through experimental data on laboratory scale and pilot plant scale.

Once the performance of the bioreactor has been ascertained mathematically as well as experimentally, then its industrial adaptation could be carried out with confidence.

CAD of fluidised bed immobilised enzyme bioreactors

To analyse the performance characteristics of the fluidised bed bioreactor mathematically and to thereby develop a reliable software package (CAD package), it would be most rigorous to assume it to be equivalent to a Plug Flow Dispersion Reactor (PFDR). A PFDR is nothing but a plug flow reactor, but with a given degree of axial dispersion. The extent of axial dispersion is decided by the magnitude of the axial dispersion coefficient (D_{Lf}) incorporated into the analysis (see Equation 13 given below). The performance of a PFDR shall be thus intermediate between that of a PFR (in which true plug flow exists and the degree of backmixing is zero) and an ideal CSTR (in which cent percent backmixing is assumed to occur). The PFDR approach is thus quite realistic for modelling the performance of industrial reactors. Based on the PFDR approach, the performance equation for the bioreactor is

$$-U_L(dC_2/dz) + D_{Lf}(d^2C_2/dz^2) = \eta(-r_s)(\text{int}) \quad \text{... (13)}$$

where $U_L = \left[U(\text{sup})/\in_{fL}\right]$ ... (14)

η = effectiveness factor

$(-r_s)(\text{int})$ = intrinsic rate of transesterification process (from equation – 4)

The axial dispersion coefficient, D_{Lf}, is, in fact, a hydrodynamic parameter and is to be estimated from available experimental correlations. For fluidised beds, a typical average value of this coefficient is, $D_{Lf} = 0.0315\ \text{m}^2/\text{s}$.

The effectiveness factor (η) takes care of the resistance to substrate transfer from the particle surface (from the liquid to particle interface) to the particle interior (where it meets the enzyme catalyst).

The magnitude of η depends on the particle diameter (d_P), effective diffusivity of substrate (s) into the particle (D_ϵ) and the intrinsic kinetics of transesterification at hand. For the present case of enzyme-catalysed biodiesel synthesis where the kinetic equation is too nonlinear (equation – 4), estimation of η is to be done based on the generalised equation as given below:

$$\eta = \left[3\phi \coth(3\phi) - 1\right](3\phi^2) \quad \ldots (15)$$

where ϕ = Thiele – type modulus

$$= L^*(-r_s)(\text{int}) / (2D_\epsilon I)^{1/2} \quad \ldots (16)$$

$$I = \int_0^{c_s} (-r_s)(\text{int}) dC_s \quad \ldots (17)$$

The integral in the above equation is to be evaluated numerically using Simpson's rule or Trapezoidal rule, after substituting the expression for the intrinsic rate (Eq. 4) in it. The boundary conditions governing the system are,

BC – 1 At z=O, C_s=C_{SO} … (18)

BC – 2 At $Z = L_f$, $C_s = C_{S\epsilon} = C_{SO}(1-\alpha)$, … (19)

The performance equation (Eq. 13) is to be solved numerically based on the above boundary conditions using any of the well-established numerical techniques such as the fourth order Runge–Kutta method. Tripti *et al.*[69] have solved the above performance equation numerically using a numerical algorithm, NUMCM, that involves a modified version of the fourth order Runge–Kutta method. The package has been re-executed at different values of feed flow rate (Q_O), at different molar ratio of neem oil to methyl acetate (y) and at different sizes of support particles (d_p). They have also conducted pilot plant experiments and have demonstrated that the results obtained from the developed software package agree reasonably with the experimental results (the maximum deviation being ± 11 %). Typical performance data reported by them are listed in Table 4.

Table 4 — Typical performance data of fluidised bed bioreactor. Molar ratio of oil to acetate = 1:3,= 0.5 m, = 1.0 mm

Feed flow rate L/hr	Expanded bed height m	Fractional conversion of neem oil %
20000	2.9259	73.57
21000	3.0391	79.79
22000	3.1579	84.99
23000	3.2829	89.12

Source: Ref. 69

Typical performance data of fluidised bed bioreactor. Molar ratio of oil to acetate = 1:3, D= 0.5 m, d_p = 1.0 mm.

It can be observed from Table 4 that more than 89% transesterification of neem oil is possible to be attained within an expanded bed height (L_f) of 3.3 m, at a feed flow rate (Q_0) of 23000 L/h, when the molar ratio of oil to methyl acetate (y) is maintained at 0.33 (1:3). Higher values of y have been observed to lower the degree of transesterification (α) attained. In other words, a high excess of methyl acetate has been found to be not advantageous. As stated earlier, once fully fluidised, the pressure drop across the bed becomes practically independent of feed flow rate (Q_0). However, too high feed flow rates promote carry over of particles and increase entrainment loss. This tends to restrict the capacity of the bioreactor (as compared to semi fluidised bed / inverse fluidised bed bioreactors).

An improved design of fluidised bed bioreactor has been proposed by Tripti *et. al*[69]. As per this modified design, the reactor column is of diverging–converging geometry (and not uniform cylindrical geometry) with maximum diameter D_2, minimum diameter D_1 and segment length, L_s (Fig. 5). From the geometry shown, it can be deduced that the angle of divergence / convergence (θ) is related to the column dimensions as

$$\tan(\theta) = (D_2 - D_1) / L_s \quad \ldots (20)$$

In the given construction, D_2, D_1 and L_s have been so chosen that $\tan(\theta)$ = 1/ 12 and thereby, $\theta \approx 5^0$. This is the optimum value of θ for all equipment employing this type of geometry as recommended by previous investigations[87-89]. At larger values of θ, there could be boundary layer separation at the wall and this would cause increase in pressure drop penalty.

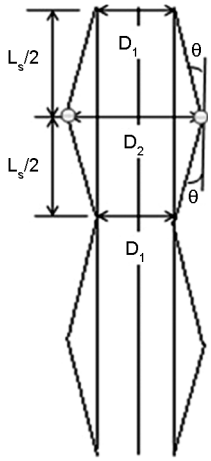


Fig. 5 — Schematic diagram of diverging – converging reactor column

The performance equation for this bioreactor shall be same as that given in equation (13), except that the term U_L will have to be replaced by $U_L(z)$ and D_{LF} by D_{LD} (axial dispersion coefficient in diverging–converging fluidised bed). To note that in a diverging–converging column like this, the liquid velocity changes continuously along the height / length of the column and so is the direction of flow of liquid. In the diverging section, the liquid flows towards the wall, while in the converging section, it flows towards the axis of the column. The average liquid velocity, $U_L(z)$, at any section of the fluidised bed is given by

$$U_L(z) = U_{\sup}(z) / \in_f (z) \quad \ldots (21)$$

where

$$U_{\sup}(z) = Q_0 / \left[\pi \left[D(z)\right]^2 / 4\right] \quad \ldots .(22)$$

$D(z)$ = diameter of bioreactor column at any z

From the geometry of the column, it can be deduced that

$$D(z) = D_1 + 2z\tan(\theta), \text{ for } 0 \le z \le (L_s / 2) \quad \ldots (23)$$

$$= D_2 - (2_z - L_s)\tan\theta,$$

$$\text{for } (L_s / 2) \le z \le L_s \quad \ldots (24)$$

The above two expressions are for the topmost segment (extending between z= 0 and $z = L_s$). Similar expressions can be easily derived for all other segments. To note that the axial distance (z) is measured from the top of the column.

Investigations (tracer experiments) have shown that the axial dispersion coefficient (D_{LD}) in a diverging – converging fluidised bed is much lower than that in a cylindrical fluidised bed[90]. Typically, D_{LD} = 0.02 m^2/ s (in comparison to D_{LF} = axial dispersion coefficient in conventional, cylindrical fluidised bed = 0.0315 m^2/ s).

From the software package developed by Tripti *et al.*[69], which has also been verified by comparing against elaborate experimental data, it is observed that a diverging–converging fluidised bed bioreactor provides 20-25% higher degree of transesterification of neem oil (when treated with methyl acetate and catalysed by immobilised lipase) as compared to a conventional fluidised bed bioreactor of cylindrical geometry and of the same volume per unit length (at all feed flow rates, at all oil to acetate molar ratios and at all sizes of support particles). Typical performance data are illustrated in Table 5.

Typical performance data of diverging–converging fluidised bed bioreactor. D_1 = 0.48 m, D_2 = 0.52 m, L_s = 0.5 m. Molar ratio of oil to acetate = 1:3, d_p = 1.0 mm.

The fabrication cost of bioreactors of this geometry shall be, no doubt, higher. However, it has been observed that the pressure drop across the diverging – converging fluidised bed is not materially higher than that across the equivalent cylindrical column. The operating cost of diverging–converging fluidised bed bioreactor shall be thus only marginally higher than that of conventional fluidised bed bioreactor.

The augmented performance of fluidised bed bioreactors of diverging–converging geometry is mainly due to the lower degree of axial dispersion (lower value of axial dispersion coefficient) and consequently closer approach to plug flow. Improved radial mixing of fluid elements due to the continuous change of flow direction and average fluid velocity along the length of the column also contributes to the enhanced performance of the bioreactor.

This observation has been confirmed by other investigators as well, such as by Ghosh *et al.*[91] who studied the performance of a diverging–converging bubble column and also by Narayanan *et al.*[92] who studied lactic acid synthesis from molasses and cheese whey in diverging–converging fluidised bed bioreactor.

Table 5 —Typical performance data of diverging – converging fluidised bed bioreactor. = 0.48 m, = 0.52 m, = 0.5 m. Molar ratio of oil to acetate = 1:3, = 1.0 mm.

Feed flow rate	Expanded bed height	Fractional conversion of neem oil
L/hr	m	%
16000	3.0	97.59
17000	3.0	97.81
18000	3.0	98.01
20000	3.0	98.35

Source: Ref. 69

CAD of immobilised enzyme semifluidised bed bioreactors

A schematic of semifluidised bed bioreactor has already been shown in Fig. 2. The PFDR approach may be used for the performance analysis of this bioreactor also and in such a case, the analysis shall be similar to that for the fluidised bed bioreactor as discussed earlier. The major difference is that separate performance equation is to be written for the packed section and for the fluidised section of the reactor. In other words, the bioreactor is assumed equivalent to two PFDRs in series, PFDR–1 representing the fluidised section and PFDR–2 denoting the packed section. The degree of axial dispersion shall be different in these two sections, being relatively lower in the packed section (that is, $(D_{Lp} < D_{Lf})$.

Based on these PFDRs in series model, the performance equation for PFDR–1 (the fluidised section) is

$$(U(\text{sup})/\in_{PL})(dC_s/dz) + D_{LP}(d^2C_s/dz^2) = \eta(-rs)(\text{int}) \quad \ldots (25)$$

The boundary conditions are,

BC – 1: at z=0 (top of the fluidised section) $C_s=C_{sb}$ …(26)

BC – 2: at $z=L_f$ (bottom of the reactor) $C_S=C_{SO}$ … (27)

Here, C_{sb} is the concentration of the principal substrate (for example, the vegetable oil) in the solution leaving the fluidised section and entering the packed section. In other words, C_{sb} is the substrate concentration at the interface between the fluidised section and the packed section. The value of C_{sb} is not known at the outset, but is computed during the numerical solution (during the execution of the numerical algorithm).

The performance equation for the packed section (PFDR – 2) similarly is

$$(U(\text{sup})/\in_{PL})(dC_s/dz) + D_{LP}(d^2C_s/dz^2) = \eta(-rs)(\text{int}) \quad \ldots (28)$$

where D_{LP} = axial dispersion coefficient in packed section

= 0.0075 m^2 /s (average experimental value)

The boundary conditions shall be

BC - 1: at z=0 (bottom of packed section) $C_s=C_{sb}$ … (29)

BC - 2: at $z=L_P$ (at the top of reactor column) $Cs = C_{s\theta} = C_{so}(1-\alpha)$ … (30)

Tripti *et al.*[69] have solved the above two performance equations successively using the numerical algorithm, NUMCM (involving a modified form of fourth order Runge–Kutta method) and have thus simulated the bioreactor's performance. They have also compared the computed results from the simulation model with experimental data collected on a laboratory-scale bioreactor as well as a pilot plant bioreactor so as to establish the accuracy of the simulation model developed. The agreement between model results and experimental data had been reportedly very satisfactory (maximum deviation = ± 10%, minimum deviation = ± 5%).

From the simulation model (software package), they observed that the value of C_{Sb} is very close to C_{SO} at all feed flow rates and at all molar ratios of oil to acetate. This means that the degree of transesterification occurring in the fluidised section is relatively low and the packed section contributes maximum to the conversion of neem oil to biodiesel, though the effective height of the packed section is lower than that of the fluidised section. This is due to the fact that the degree of axial dispersion is lower in the packed section (D_{LP} is lower than D_{Lf}) and the substrate flow through this section is close to plug flow. Table 6 presents typical performance data of semifluidised bed bioreactor with reference to biodiesel synthesis as reported by Tripti *et al.*[93].

Typical performance data of semifluidised bed bioreactor. D= 0.5 m, d_p = 1.0 mm, molar ratio of oil to acetate = 1:3

From Table 6, it can be observed that the semifluidised bed bioreactor provides higher degree of transesterification of neem oil at higher feed flow rates, but within a lower reactor volume

$L_{sf} + L_p + L_f$ 1.2 m, D = 0.5 m). For instance, the bioreactor provides 91.34% conversion of neem oil to biodiesel at a feed flow rate of 33567 L/h at y = 1/3. Another interesting observation is that the degree of transesterification of neem oil (α) increases with increase in feed flow rate (Q_0). This is an exclusive characteristic of semifluidised bed bioreactor, since in all other categories of reactors, the fractional substrate conversion decreases with increase in feed flow rate as the residence time of fluid elements within the reactor decreases. This special feature of semifluidised bed reactor is not difficult to explain. In this category of bioreactors, there occurs a rearrangement of reaction zones within the column as the feed flow rate is increased. At higher value of (Q_0), more particles enter the packed section and consequently, the height of this section (L_p) increases, while that of the fluidised section (L_f) decreases relatively (see Table 6). Since the major share of transesterification is provided by the packed section, when its height or volume increases, the degree of transesterification attained also increases. This phenomenon has been confirmed by Shrijita and Narayanan[94] with reference to lactic acid synthesis from cheese whey and molasses and also by Narayanan and Biswas[95] in the case of aerobic biological treatment of industrial effluents.

As stated in the earlier section, the operating cost is higher for these bioreactors as compared to fluidised bed bioreactors. The additional packed bed at the top provides additional resistance to substrate flow. This bioreactor cannot be operated in the circulating mode and hence, continuous re-activation and recycle of catalyst particles shall not be possible. No doubt,the top restraint prevents (practically eliminates) the entrainment loss of catalyst particles.

Table 6 — Typical performance data of semifluidised bed bioreactor.= 0.5 m,=1.0 mm, molar ratio of oil to acetate = 1:3

Feed flow rate L/h	Height of packed section m	Height of fluidised section m	Fractional conversion of neem oil %
32507	0.4335	0.7665	87.37
33567	0.4439	0.7561	91.34
34627	0.4537	0.7463	94.15
35334	0.460	0.740	95.46

Source:Ref.93

CAD of Inverse fluidised bed immobilised enzyme bioreactors

Aditi and Narayanan[84] have conducted computer aided analysis of biodiesel synthesis in inverse fluidised bed bioreactor that employs nanosilica particles as support media for immobilising the lipase enzyme catalyst. The scheme is thus that sketched in Fig. 4. The feedstock used by them is neem oil and methyl acetate. In a system like this, the influencing parameters are feed flow rate (Q_0), molar ratio of oil to acetate (y) and the catalyst loading (C_L), apart from the geometrical dimensions of the reactor column (height, L and diameter, D). The column employed is of smaller diameter such as 25.4 mm ID, but a large number of vertical columns / tubes could be used to improve the capacity of the bioreactor.

Performance analysis of this bioreactor has also been done based on the PFDR approach (discussed in earlier subsections). The developed software package has been successfully tested and verified by them based on pilot plant experiments.

A bioreactor of this category reportedly provides more than 88% conversion of neem oil to biodiesel at a feed flow rate of 360 L/h (with single column construction) and a catalyst loading (C_L) of 0.70. The reactor column is 6.0 m in length and 25.4 mm in diameter, the molar ratio of oil to acetate used being 1:3. By using a bundle of around 50 tubes, the capacity of the reactor can be easily increased to 18000L/h. The degree of transesterification of neem oil increases with increase in catalyst loading, (C_L) (which is nothing but the mass ratio of nanosilica particles to feed solution, g/g).

This bioreactor is characterised by the low operating cost (due to downflow mode of operation) and the fact that the effectiveness factor (η) is equal to 1.0 at all feed flow rates, feed composition and catalyst loading and consequently, the global rate of reaction is practically equal to the intrinsic rate itself. This is due to the enormously large specific surface of the nanoparticles and this enhances the performance of the bioreactor. The reactor operates in circulating mode (see Fig. 4) and this could be an advantage on occasions.

Conclusion

The importance of biodiesel as a versatile green fuel need not have to be overemphasised. Technology of biodiesel synthesis has seen a lot of progress during the recent years. An exhaustive survey of all the recent and past developments in the synthesis of this

green fuel including design of industrial bioreactors for the same has been attempted in this paper. What is strongly observed is that in spite of the large potential biodiesel possesses as the most promising green fuel of the day, investigations have been confined to laboratory shake flasks. More extensive studies on the utilization of non-edible oils such as algal oil, neem oil, waste cooking oil are required to be attempted.

Except for immobilised enzyme catalyst (lipase), investigations on heterogeneous catalysts are far from adequate. Most studies are restricted to reporting yield and quality of biodiesel synthesised, with little attempt to perform kinetic analysis of the transesterification process and development of kinetic equations. The recommended catalysts can be used for commercial manufacture of biodiesels only if the kinetic models are available.

Successful attempts towards computer aided design and analysis of industrial immobilised enzyme bioreactors (fluidised bed, semifluidised bed, inverse fluidised bed, diverging –converging fluidised bed) and development of well-tested CAD (software) packages have been thoroughly surveyed. Industrial adaptation of these packages has been strongly recommended.

Nomenclature

C_B	concentration of alcohol, moles/L
C_S	concentration of oil, moles/L
C_{sb}	concentration of neem oil at the exit of fluidised section, or inlet of the packed section, moles/L
$C_{S\theta}$	concentration of neem oil in the product stream, moles/L
C_{S0}	concentration of neem oil in the feed stream, moles/L
d_p	diameter of support particles, m
D	diameter of reactor column, m
D_1	minimum diameter of diverging – converging bioreactor, m
D_2	maximum diameter of diverging – converging bioreactor, m
$D_\in$	effective diffusivity of substrate solution into the particle, m^2/s
D_{Lf}	axial dispersion coefficient in fluidised section of the bioreactor, m^2/s
D_{LP}	axial dispersion coefficient in packed section of the bioreactor, m^2/s
D_{LD}	axial dispersion coefficient in diverging – converging bioreactor, m^2/s
$D(z)$	diameter of diverging – converging fluidised bed bioreactor at any z, m
f_D	drag coefficient, dimensionless
K_1, K_2, K_m	kinetic constants, moles/L
K_{si}	substrate inhibition coefficient, moles/L
L^*	characteristic length, m
$L_{S'}$	height of initial static bed ; length of each segment of diverging – converging fluidised bed, m
L_f	height of the fluidized section, m
L_p	height of the packed section, m
L_{sf}	total height of the semi – fluidised bed, m
Q_0	volumetric flow rate of substrate solution /feed solution, m^3/s
$r_{\max}$	kinetic constant, moles/ (g.sec)
$(-r_s)$(int)	intrinsic rate of trans – esterification reaction, moles/ (L.sec)
R	bed expansion ratio, dimensionless
Re_p	particle Reynolds number, dimensionless
U_{mf}	minimum fluidisation velocity, m/s
U_{sm}	minimum semi - fluidisation velocity, m/s
$U_{mf}(inv)$	minimum inverse fluidisation velocity, m/s
U_L	operating fluid velocity through the bioreactor, m/s
$U_L(z)$	actual velocity of substrate solution through the bioreactor at any z, m/s
$U(\mathrm{sup})$	superficial velocity of substrate solution through the bioreactor, m/s
$U_{\sup}(z)$	superficial velocity of substrate solution at any z, m/s
V_t	terminal free settling velocity of the particles, m/s
y	molar ratio of neem oil to methyl acetate in the feed solution, dimensionless
z	axial coordinate

Greek Symbols

α	fractional conversion of neem oil, dimensionless
θ	angle of constriction of diverging – converging fluidised bed bioreactor, degrees
$\in_f$	total voidage of fluidized bed, dimensionless
$\in_p$	total voidage of packed bed/ static bed, dimensionless
$\in_{fL}$	fractional liquid holdup in the fluidised section, dimensionless
$\in_{PL}$	fractional liquid holdup in the packed section, dimensionless
η	effectiveness factor, dimensionless
p_L	density of feed solution, kg/m^3

P_s density of support particles, kg/m^3

μ_L viscosity of feed solution, kg/(m.s)

ϕ Thiele – type modulus, dimensionless

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