Processing of vegetable oil for biofuel production through conventional and non-conventional routes

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ABSTRACT

Ever growing world energy demands, depletion and price of petroleum reserves, and environmental concerns are enormous challenges in today's scenario. For meeting the demand, alternate fuels are considered as an obvious choice owing to their renewability and environmental friendliness. Among the possible alternatives, processing of vegetable oil for biofuel production has gained considerable attention due to its ease of operation and integration with existing oil refining processes. Typically, transesterification based processes have been developed for production of biodiesel whereas hydroprocessing routes are developed to convert vegetable oil to green diesel and Bio-aviation turbine fuel (Bio-ATF) fraction using non-edible/edible vegetable oils as a feedstock. Accordingly, the present review is aimed at understanding of process aspects of various available processes. Based on the reviewed processing options, the merits and demerits of the developed routes have been highlighted and possible approaches for development of glycerin free biodiesel routes are envisaged.

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Introduction

Today, stringent environmental norms and depletion of oil reserves have added impetus for development of eco-friendly and sustainable fuel options. This has resulted into emergence of biofuels from sustainable bio-resources. In this context, fuels of bio-origin, such as bio-alcohols, biodiesel, biogas, green diesel and Bio-aviation turbine fuel (Bio-ATF) are found to be potential alternatives and are increasingly becoming important. Among these, vegetable oil based biofuel options i.e. biodiesel, green diesel and bio-ATF have become more attractive in recent time because of their ease of production from available vegetable oil feedstock options.

The direct use of vegetable oil as an alternative for diesel has been attempted in the past due to its portability, heat content (80% of diesel fuel), ready availability and renewability. However, its major disadvantages namely high viscosity, lower volatility and presence of unsaturated hydrocarbon have hampered its direct use as a diesel fuel (Pryde, 1983). Therefore, different ways have been evolved to transform vegetable oil to compatible diesel fuel option. This has led to development of (a) dilution, (b) micro-emulsions, (c) pyrolysis, (d) catalytic

processing and (e) transesterification approaches to convert vegetable oil to viable biofuel option (Ma and Hanna, 1999). Among all these alternatives, transesterification of vegetable oil with methanol leads to fatty acid methyl esters (biodiesel) formation and their physical characteristics that are very close to the diesel fuel (Selmi and Thomas, 1998; De et al., 1999). Typically, oil/triglycerides undergo transesterification reaction with low molecular weight alcohols such as methanol in the presence of catalyst as shown in Fig. 1a. For this purpose, alkali catalyst viz. sodium or potassium hydroxide prevails as the cheapest catalyst. However, reaction of sodium and potassium hydroxides produces water while reacting with alcohol in the formation of their alkoxide (Ma and Hanna, 1999). This reaction is naturally undesirable, because water can react with triglycerides, fatty acids, or esters in hydrolysis reactions as presented in Fig. 1b & c. In fact, the presence of water competes with alcohol which inhibits transesterification, thereby promotes ester hydrolysis, leading to formation of FFAs (Haas, 2005). The formed FFA favors saponification, leading to soap formation as shown in Fig. 1d. Hence, performance of alkali catalyzed transesterification are majorly affected by the presence of water by various side reactions which turns into loss of methyl ester to glycerol phase, and often result into high purification costs and less biodiesel yield (Zadra, 2006; Singh and Singh, 2010; Huang and Chang, 2010). Therefore, feedstocks containing considerable amount of water (>0.06 1 wt.%) and FFA (>3 wt.%) prior to transesterification undergo pre-treatment via esterification reaction using acid catalyst (H_2SO_4) as shown in Fig. 1e. The product (refined feedstocks) obtained with less FFA content (≤3 wt.%) and water content (<0.06 wt.%) is then used for alkali-catalyzed transesterification to produce biodiesel.

Transesterification

(a)

$$CH_2OCOR^1 \qquad \qquad CH_2OH \qquad R^1COOCH_3$$
$$| \qquad \qquad \qquad \qquad |$$
$$CHOCOR^2 + 3\ CH_3OH \xrightarrow{\text{Catalyst}} CHOH + R^2COOCH_3$$
$$| \qquad \qquad \qquad \qquad |$$
$$CH_2OCOR^3 \qquad \qquad CH_2OH \qquad R^3COOCH_3$$

Triglyceride   Methanol   Glycerol   Biodiesel

                                               (Methyl ester)

Side Reactions

(b)

$$CH_2OCOR^1 \qquad \qquad CH_2OH \qquad R^1COOH$$
$$| \qquad \qquad \qquad \qquad |$$
$$CHOCOR^2 + 3\ H_2O \rightleftharpoons CHOH + R^2COOH$$
$$| \qquad \qquad \qquad \qquad |$$
$$CH_2OCOR^3 \qquad \qquad CH_2OH \qquad R^3COOH$$

Triglyceride   Water   Glycerol   FFA

(c)

$$R^1COOCH_3 + H_2O \longrightarrow R^1COOH + CH_3OH$$

Methyl ester   Water   FFA   Methanol

(d)

$$R^1COOH + KOH \longrightarrow R^1COOK^+ + H_2O$$

FFA   Potassium hydroxide   Soap   Water

Esterification

(e)

$$R^1COOH + CH_3OH \underset{\ }{\overset{H_2SO_4}{\rightleftharpoons}} R^1COOCH_3 + H_2O$$

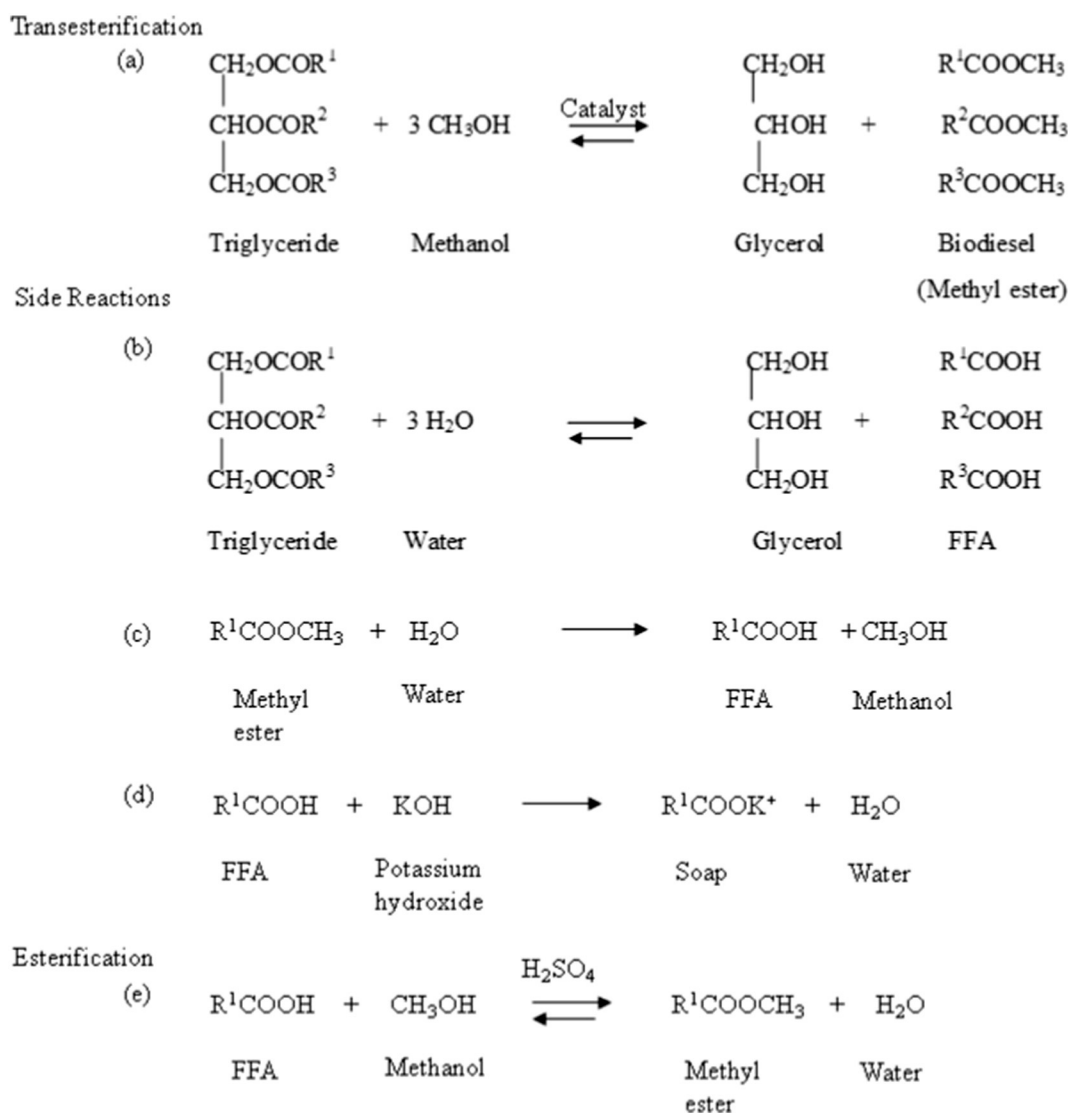FFA   Methanol   Methyl ester   Water

Fig. 1. Various reactions involved in Biodiesel production (a) transesterification; (b) triglyceride hydrolysis; (c) ester hydrolysis; (d) saponification; (e) FFA esterification. R^1, R^2 & R^3 fatty acid chain of triglyceride.

Conventionally, transesterification of vegetable oils with methanol is performed in the presence of homogeneous or heterogeneous alkali/ acid as catalysts (Serdari et al., 1999; Aksoy et al., 1990). Such processes are highly complex in nature due to the downstream separation and purification steps to produce biodiesel of requisite quality. Due to this, pre-treatment of vegetable oil feedstock is highly recommended to overcome the problems associated with downstream processing. Typically, downstream treatments involve separation of reaction product viz. biodiesel and glycerin from contaminants i.e. excess alcohol, soap formed (due to the presence of free fatty acid, FFA, in vegetable oil) and catalyst. Although the removal of the excess alcohol from both phases is achieved by distillation, the removal of catalyst and soap is more complicated, time consuming, and often leads to lower biodiesel yields (Fukuda et al., 2001). Thus, the overall performance of conventional process is mainly governed by impurity levels present in the vegetable oil as well as in the processed product. Therefore, to optimize the product yield and meet desired purity, process advances are made over the period in vegetable oil processing. Such advancement involves the use of pre-treatment steps, modified reactor designs and integration of non-conventional process intensification steps. This has resulted into development of various processing technologies for biodiesel production, which have been widely adopted (Serio et al., 2007; Bournay et al., 2005; Gogate and Kabadi, 2009). In this context, use of supercritical conditions, enzymatic catalyzed, membrane and microwave assisted transesterification have been explored (Saka and Kusdiana, 2001; Du et al., 2004; Refaat et al., 2008; Georgogianni et al., 2009; Cao et al., 2007). In spite of advancement in conventional process technology, the overall economic viability of biodiesel production has been in question due to inferior glycerin quality and its over supply. This in turn demands intense and complex purification steps to upgrade glycerin quality [Hawash et al., 2009; McCoy, 2005, 2006]. Hence, it is utmost important to balance glycerin's availability, quality and demand. Therefore, attempts have been reported either to valorize glycerin stream by converting it to fuel additives (glycerin ethers), speciality chemicals (propane diols) etc. or to eliminate glycerin formation during biodiesel process (Leoneti et al., 2012; Fabbri et al., 2007).

The production of glycerin free biodiesel is conceptualized through two pathways namely hydroprocessing route and replacement of methanol as a reactant. The development hydroprocessing route has added impetus for integration of vegetable oil processing in existing oil refining processes. Such route offers platform for production of diesel and jet fuel fraction namely "Green Diesel" and "Bio-ATF", respectively. The green diesel fuel fraction produced is found to have excellent cetane number vis-à-vis mineral oil based diesel fraction (Choudhary and Phillips, 2011; Lestari et al., 2009). On the other hand, replacement of methanol with dimethyl carbonate (DMC) and methyl acetate (Fabbri

et al., 2007; Huang and Yan, 2008) has led to glycerin free biodiesel formation with enhanced lubricity and combustion properties (Ilham and Saka, 2009, 2010). This is mainly due to miscibility of formed by product, such as triacetin and glycerin carbonates, with biodiesel phase (Tundo and Selva, 2002; Delledonne et al., 2001).

In view of the above, the present review is aimed at understanding of process aspects of various available options for vegetable oil processing to delimit the constrains of the individual processes to develop economically viable option for biofuel production.

Conventional routes for vegetable oil processing for biodiesel production

Transesterification route is the most common method of processing vegetable oil into biodiesel and it is practiced by employing either homogeneous or heterogeneous catalyst. The salient features of this process are discussed below.

Biodiesel through homogeneously catalyzed transesterification of vegetable oil

Transesterification of vegetable oil is performed by employing either acidic or alkaline types of homogeneous catalysts. The selection of alkali or acid catalysts mostly depends on the water content and free fatty acid (FFA) content of the oil which depends on the factors like source of oil, cultivation type and storage mechanism. The alkaline catalysts are preferred for feedstock having FFA content of less than 0.5 wt.% (Helwani et al., 2009). Thus, the use of alkaline homogeneous catalyst such as sodium hydroxide (NaOH), potassium hydroxide (KOH), and sodium methoxide (CH$_3$ONa) has been reported and successfully commercialized for production of biodiesel (Qian et al., 2010; Sharma et al., 2010). A simplified process flow diagram for conventional homogeneous process is depicted in Fig. 2.

The merits of homogeneous alkaline catalyzed biodiesel production process are (1) lower reaction temperature (60–65 °C) and atmospheric pressure; (2) simple operation due to which it is widely preferred for biodiesel production at commercial level (Lotero et al., 2006).

However, alkaline catalyst underperforms when applied over feedstock containing high FFA i.e. >0.5 wt.%. This is mainly due to the neutralization of alkaline catalyst with FFA to produce sodium/potassium soaps (Marchetti and Errazu, 2008) which leads to prolonged reaction time. The formed soaps are miscible in by-product glycerin and subsequently demand their removal through the neutralization in the presence of strong-concentrated inorganic acids (i.e. sulphuric, hydrochloric and phosphoric) or an organic acid (i.e. acetic acid). A brief summary of some studies for biodiesel synthesis using homogeneous alkali catalysts is compiled in Table 1.

On the other hand, acid catalyst has low susceptibility to the FFA in the feedstock, and simultaneously has ability to catalyze reactions both the reaction like FFA esterification and transesterification of vegetable oil (Kulkarni and Dalai, 2006; Canakci and Gerpen, 2003). The summary of few studies for biodiesel synthesis using homogeneous acid catalysts is presented in the Table 2. However, homogeneous acidic catalytic process suffers on the slow kinetics vis-a-vis alkali catalyst thus requiring higher molar ratio of methanol to oil (12:1) and high reaction temperatures (80–100 °C) (Leung and Guo, 2006). Furthermore, the acid catalyzed process is reported to be very sensitive to water content (Leung and Guo, 2006). Among acid catalysts, sulfuric acid (H$_2$SO$_4$) and hydrochloric acid (HCl) are the most-used catalysts in acid catalyzed transesterification processes. In addition, economic analysis has proven that acid catalyzed procedure, being a one-step process, is more economical than the base-catalyzed process which requires an extra step to convert FFA to methyl esters (Zhang et al., 2003a, 2003b). However, acidic catalyst are corrosive in nature, creates handling issue during the operation. Therefore, basic catalytic processes are more commercially acceptable on the industrial scale over acidic catalytic process (Ma et al., 1998).

To overcome the limitations of the individual homogeneous process for both alkali and acid catalysts, two-step processes have been developed for biodiesel production using high FFA content vegetable oils. The two-step process consists of feed preparation (acid
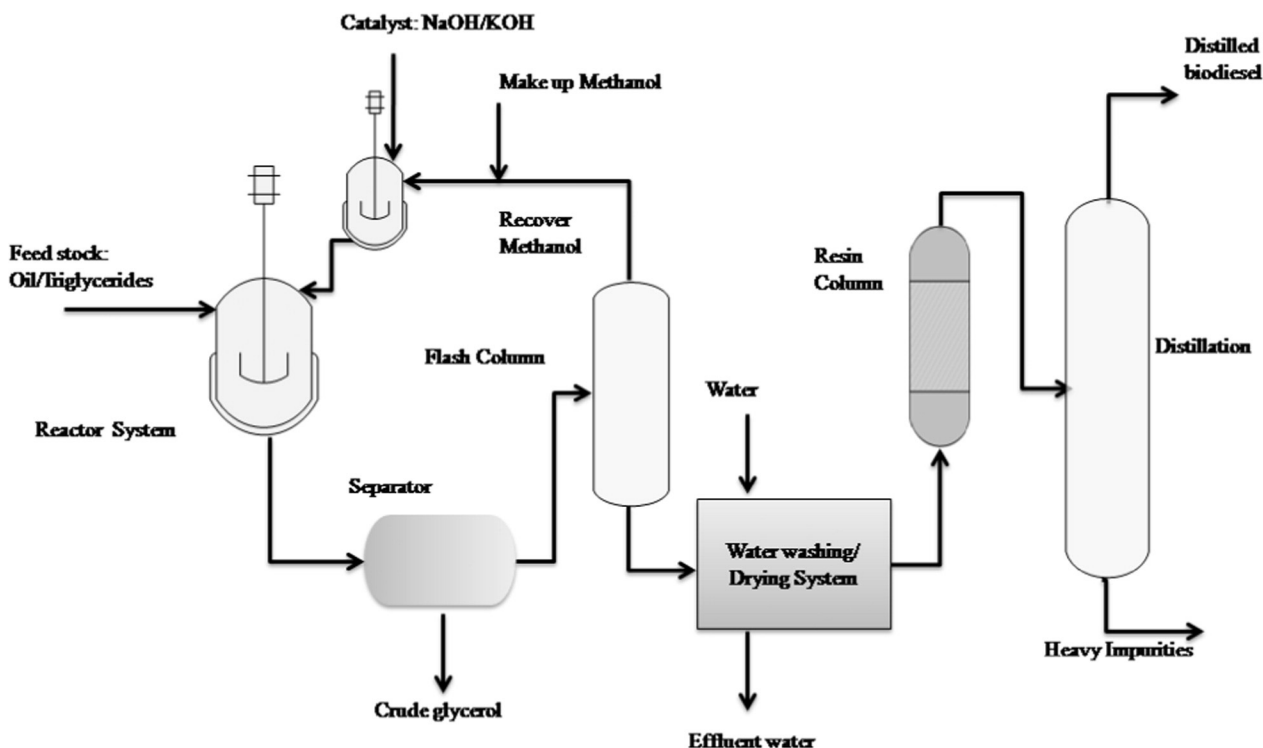

Fig. 2. Simplified process flow diagram for conventional homogeneous process.

Table 1
Summary of some studies for biodiesel synthesis using homogeneous base catalysts.

Feedstock	Catalyst	Catalyst, wt.%	Molar ratio, Methanol:Oil	Temperature, °C	Reaction time, h	Yield/conversion, %	References
Soybean	KOH	0.8	6:1	40	1	95[a]	Zagonel et al. (2002)
Sunflower	NaOH	1	6:1	60	2	97.1[a]	Dias et al. (2008)
Cottonseed	CH₃ONa	0.75	6:1	65	1.5	96.9[a]	Rashid et al. (2009b)
Rice bran	CH₃ONa	0.88	6:1	55	1	83.3[a]	Rashid et al. (2009a)
Palm	NaOH	1	6:1	60	0.5	95[a]	Lubes and Zakaria (2009)
Palm kernel	KOH	1	6:1	60	1	96[a]	Alamu et al. (2007)
WFO	KOH	1.2	6:1	60	2	95.8[a]	Dias et al. (2008)
Jatropha	NaOH	1	6:1	60	1	98[a]	Chitra et al. (2005)
Jatropha	NaOH	3.3	0.7:1	65	2	55[a]	Berchmans and Hirata (2008)
Jatropha	NaOH	0.8	9:1	45	0.5	96.3[b]	Tapanes et al. (2008)
Jatropha	KOH	1	6:1	50	2	97.1[a]	Berchmans et al. (2010)
Karanja	KOH	1	10:1	60	1.5	92[b]	Karmee and Chadha (2005)
Neem	NaOH	0.7	10:1	60–75	6.5–8	88–94[a]	Nabi et al. (2008)
Castor	NaOH, KOH, CH₃ONa, CH₃OK	0.2 (Molar ratio)	6:1	60	1	85[a]	Meneghetti et al. (2006)
Castor	C₂H₅ONa	1	16:1	30	0.5	93.1[a]	Silva et al. (2009)
Mahua	KOH	1	6:1	45	3	95[a]	Kumar et al. (2011)

[a] Yield.
[b] Conversion.

Table 2
Summary of some studies for biodiesel synthesis using homogeneous acid catalysts.

Feed stock	Catalyst	Catalyst, wt.%	Molar ratio, Methanol:Oil	Temperature, °C	Reaction time, h	Yield/conversion, %	References
Soybean	H₂SO₄	1	6:1–20:1% 30:1	65	69	>90[a][b]	Freedman et al. (1984)
Soybean	HCl	10	20:1	70	45	65[a]	Rachmaniah et al. (2004)
Rice bran	HCl	10	20:1	70	6	>90[a]	Rachmaniah et al. (2004)
Corn	p-TsOHa	4		80	2	97.1[a]	Guan et al. (2009)
Canola	AlCl₃	5	24:1	110	18	98[a]	Soriano et al. (2009)
Mahua	H₂SO₄	6	9:1	65–70	5	92[a]	Saravanan et al. (2010)
Castor	H₂SO₄	0.2[c]	6:1	60	8	85[a]	Meneghetti et al. (2006)
	HCL	0.2[c]	6:1	60	4	75[a]	Meneghetti et al. (2006)

[a] Yield.
[b] Conversion.
[c] Molar ratio.

catalyzed FFA esterification) followed by transesterification (base catalyzed transesterification) to reduce the FFAs (below 1%) for achieving high biodiesel yield within a short reaction time at mild reaction conditions (Canakci and Gerpen, 2003). By using an acid catalyst (mainly sulfuric acid) in the first step of the process, the soap formation is eliminated which improves the product yield and reduces the complexities involved in the downstream purification steps. However, higher amount of acid catalyst is required in the first step due to slow rate of FFA esterification reaction (Jain and Sharma, 2010; Lakshmi et al.,

2011). A summary of some studies for biodiesel synthesis using two step homogeneous acid–base catalysts is presented in Table 3.

The sustainability of the aforementioned processes is mainly governed by the quality of the feedstock and by product i.e. glycerin formed during the process. Typically, both the acid as well as alkali catalyzed transesterification routes of vegetable oil lead to poor quality of glycerin formation, which in turn demand complex purification steps leading to economic off balance of the process on sustainable basis. This has added a quest for development alternate routes to process

Table 3
Summary of some studies for biodiesel synthesis using two step homogeneous acid/base catalysts.

Feed stock	Catalyst	Catalyst, wt.%	Molar ratio, Methanol:Oil	Temperature, °C	Reaction time, h	Yield/conversion, %	References
Jatropha	H₂SO₄	0.5	6:1	45	2	93[b]	Patil et al. (2009)
	KOH	2	9:1	60	2	95[a]	
Jatropha	H₂SO₄	1	3:7[c]	65	3	95[b]	Jain and Sharma (2010)
	NaOH	1	3:7[c]	50	3	90.1[a]	
Jatropha	H₂SO₄	0.4	8:1	60	0.5	92[b]	Wang et al. (2006)
	KOH	1	6:1	60	0.5	86.2[a]	
Karanja	H₂SO₄	1	6:1	50	0.75	94[b]	Patil et al. (2009)
	KOH	0.5	9:1	50	0.5	80[a]	
Karanja	H₂SO₄	1	0.1–0.5:1[d]	60	–	95[b]	Lakshmi et al. (2011)
	KOH	1	0.1–0.5:1[d]	60	1	97[b]	

[a] Yield.
[b] Conversion.
[c] v/v.
[d] w/w.

vegetable oil for biodiesel production. The efforts made in this regard are listed below.

Biodiesel through heterogeneously catalyzed transesterification of vegetable oil

The use of solid heterogeneous catalyst offers eco-friendly option for biodiesel synthesis due to its ease of regeneration and reusability (Dossin et al., 2006; Mbaraka and Shanks, 2006). In addition, solid catalysts also offer ease of operation and efficiencies to handle high FFA (>0.5%) as well as low quality feed stocks for production of biodiesel (Leung et al., 2010). Moreover, heterogeneous catalyzed biodiesel production does not face the obstacle of soap formation and as a result offers platform for easier separation and purification steps in downstream processing. This in turn often leads to ease formation of better quality of glycerin during the process (Nakagaki et al., 2008).

Typically, literature reports the investigation on both acidic and basic heterogeneous catalysts and their combination for processing of vegetable oil for biodiesel production. The most commonly used basic catalysts are alkaline metal carbonates (Na_2CO_3, K_2CO_3), alkaline earth metal carbonates ($CaCO_3$), alkaline earth metal oxides (CaO, MgO, SrO, BaO) and transition metal oxides (ZnO) (Dossin et al., 2006; Fukuda et al., 2001; Liu et al., 2007; Lotero et al., 2005; Ma and Hanna, 1999; Verziu et al., 2008). On the other hand, heterogeneous acid catalysts such as Nafion-NR50 (perfluorinated alkane sulfonic acid resin), sulfated zirconia-alumina (SZA), and tungstated zirconia–alumina (WZA), have been investigated for biodiesel production (Lopez et al., 2007; Chai et al., 2007). In addition, solid acids such as tungstated zirconia and sulfated zirconia can significantly promote the transesterification of vegetable oils as well as the esterification of FFAs (Kouzu et al.,

2008; Furuta et al., 2004). A typical overview of different solid catalysts employed for vegetable oil processing to produce biodiesel is given in Table 4.

Interestingly, the combination of homogeneous and heterogeneous catalyst system has also been investigated for biodiesel synthesis (Corro et al., 2010; Deng et al., 2011; Sharma et al., 2010). The summary of few studies reported on biodiesel synthesis using two-step homogeneous and heterogeneous catalysts is compiled in Table 5 wherein heterogeneous catalysts are used either to catalyze FFA esterification or transesterification of vegetable oil.

Owing to the aforementioned distinct advantages of heterogeneous catalyst systems, M/s Axens, France, using proprietary solid catalyst (Zn/Al_2O_3), has developed a continuous biodiesel production process viz. Esterfip-H. The Esterfip-H process consists of two fixed bed catalytic reactors producing biodiesel by transesterification of oils such as sunflower, soybean and rapeseed with methanol in the temperature range of (170–250 °C) and pressure (30–50 bar) conditions (Bournay et al., 2005). The first reactor targets conversion of triglyceride moiety to monoglyceride and two moles of biodiesel whereas second reactor converts monoglyceride to biodiesel and glycerine. The excess methanol is removed after each of the two reactors by a partial flash vaporization. The salient features of this process include production of biodiesel with minimum purification steps along with high quality glycerin. However, such process demands utmost control on moisture level during the feedstock processing to avoid hydrolysis of formed biodiesel phase under mentioned reaction conditions. On similar lines, a process viz. ENSEL™ based on solid acid catalyst viz. double metal cyanide complex has been developed wherein esterification of FFA present in vegetable oil and transesterification of vegetable oil is performed at elevated temperature (150–200 °C) and autogenous pressure to produce biodiesel

Table 4
Summary of some studies for biodiesel synthesis using heterogeneous catalysts.

Feed stock	Catalysts	Catalyst, wt.%	Molar ratio, Methanol:Oil	Reaction time, h	Temperature, °C	Yield/conversion, %	References
Soybean	MgO, ZnO, Al_2O_3	5	55:1	7	70, 100, 130	82[b]	Antunes et al. (2008)
Soybean	Nano MgO	5	36:1	0.16	260	>99[b]	Wang et al. (2007)
Soybean	WO_3/ZrO_2, zirconia–alumina and sulfated tin oxide	6.7	40:1	20	200–300	90[b]	Furuta et al. (2004)
Soybean	Calcined LDH (Li–Al)	1–3	15:1	1–6	65	71.9[b]	Shumaker et al. (2008)
Soybean	La/zeolite beta	1.1	14.5:1	4	160	48.9[b]	Shu et al. (2007)
Soybean	MgO $MgAl_2O_4$	30[d]	3:1	10	65	57[b]	Wang et al. (2008)
Soybean	CaO, SrO	8	12:1	0.5–3	65	95[b]	Liu et al. (2008)/Liu et al. (2007)
Soybean	ETS-10	60	6:1	24	120	94.6[b]	Suppes et al. (2004)
Sunflower	CaO/SBA-14	14	12:1	5	160	95[b]	Albuquerque et al. (2008)
Jatropha Curcas	CaO	1.5	9:1	2.5	70	93[b]	Huaping et al. (2006)
VO	Cs-heteropoly acid, SO_4^{2-}/ZrO_2, $SO_4^{2-}/Al2O3$, SO_4^{2-}/SiO_2, WO_3/ZrO_2	0.2[e]	19.4:1	1	75	70[b]	Park et al. (2008)
Rape seed	Mg–Al HT	1.5	6:1	4	65	90.5[b]	Zeng et al. (2008)
Sunflower	NaOH/alumina	0.4	6–48:1	1	50	99[b]	Arzamendi et al. (2007)
Palm	Mg–Al–CO_3 (hydrotalcite), Mg/Al ratio, 3	7.5	30:1	6	100	86.6[b]	Xie et al. (2006)/Trakarnpruk and Porntangjitlikit (2008)
Cotton seed	Mg–Al–CO_3 HT	1	6:1	12	180–210	87[b]	Barakos et al. (2008)
Blended VO	Mesoporous silica loaded with MgO	3.5	8:1	5	220	96[b]	Li and Rudolph (2008)
Jatropha	Montmorillonite KSF	4.8	12:1	6	160	68[a]	Zanette et al. (2011)
Jatropha	Amberlyst 15	1–20	16:1	3	65	59[a]	Supamathanon et al. (2011)
	K/NaY zeolite	12	16:1	6	65	73[a]	
Jatropha	CaMgO	4	15:1	3	65	83[b]	Taufiq-Yap et al. (2011)
Jatropha	CaO $Fe_2(SO_4)_3$	1.5	9:1	3	70	100[a]	Endalew et al. (2011)
	Li–CaO + $Fe_2(SO_4)$	1.5	9:1	3	70	100[a]	
Karanja	Li/CaO	1.75	12:1	1	65	>99[a]	Kaur and Ali (2011)
Karanja	ZnO	0.1	10:1	24	120	83[a]	Karmee and Chadha (2005)
Castor	$Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$	5	29:1	3	60	20[a]	Zieba et al. (2010)
Castor	TiO_2/SO_4^{2-}	5[c]	6:1	1	120	25[a]	Almeida and Noda (2008)
Cottonseed	TiO_2/SO_4^{2-}	2	12:1	8	230	>90[a]	Chen et al. (2007)
Cottonseed	KF–Al_2O_3	3	12:1	3	65	>90[a]	Lingfeng et al. (2007)

[a] Yield.
[b] Conversion.
[c] mol% of catalyst to the oil.
[d] MgO content in catalyst.
[e] *w/v*.

Table 5
Summary of some studies for biodiesel synthesis using two step homogeneous and heterogeneous catalysts.

Feed stock	Catalysts	Catalyst, wt.%	Molar ratio, MeOH:Oil	Temperature, °C	Reaction time, h	Yield/FFA conversion, %	References
Jatropha	SiO$_2$·HF	2–15	12:1	60	1	96[b]	Corro et al. (2010)
	NaOH	1	6:1	60	2	99.6[a]	
Jatropha	H$_2$SO$_4$	4[c]	40(methanol to FFA)	60	1	88[b]	Deng et al. (2011)
	Hydrotalcite with Mg/Al molar ratio, (3/1)	0.5–1.25	4:1	45	1.5	95[b]	
Mahua	H$_2$SO$_4$	0.5–2[d]	6:1	55	1	91[b]	Singh et al. (2011)
	CaO	1.5–3	8:1	65	2.5	95[a]	
Karanja	H$_2$SO$_4$	1.5[d]	6:1	65	1	91[b]	Sharma et al. (2010)
	CaO	1–3.5	8:1	65	2.5	95[a]	
Neem	SO$_4^{2-}$/ZrO$_2$	0.5–1.5	9:1	65	2	94[b]	Muthu et al. (2010)
	KOH	1	6:1	60	2	95y	

[a] Yield.
[b] Conversion.
[c] vol.% of H$_2$SO$_4$ w.r.t. oil.
[d] v/v.

(Srinivas et al., 2009). Such processes are envisaged to offer better overall economics for biodiesel production in view of the superior quality of glycerin produced compared to homogeneous catalyzed processes.

On similar lines, efforts are also been made to improve the cost benefit for homogeneous route by applying non-conventional approaches for vegetable oil processing to develop rapid, energy efficient and cost effective processes keeping in view of the enhancement of the quality of by-product. The efforts made in this context are discussed in the following section.

Non-conventional routes for vegetable oil processing for biodiesel production

Enzyme-catalyzed transesterification

In recent years, enzymes have gained importance due to their ability to catalyze reactions for biofuel production by offering ease of separation while comparing with conventional method of production. Typically, enzymes are biocatalyst, principally naturally occurring lipases which are isolated from a number of bacterial species such as *Candida antarctica*, *Pseudomonas cepacia*, *Rhizopus oryzae*, *Candida rugosa*, *Rhizomucor miehei*, *Thermomyces lanuginosus*, and *Pseudomonas fluorescens* (Moreira et al., 2007). The enzymes are typically employed in immobilized form for biodiesel production to enable the stability and reusability of enzyme in the process of transesterification. Immobilization can be provided by several methods viz. adsorption, covalent bonding, entrapment, encapsulation, and cross-linking, by embedding the enzyme on solid support. These methods provide the stability and option of recycling the enzyme in the process of transesterification, and reduce the overall cost of the enzyme which is considered to be the biggest hurdle in commercialization.

Several researchers have investigated the transesterification reaction of vegetable oils with methanol by employing immobilized Novozym 435 (commercially available *C. antarctica* lipase) (Shimada et al., 1999). This immobilized enzyme found to slightly economically viable for transesterification of vegetable oil (Ranganathan et al., 2008).

Typically, enzymatic catalysis proceeds at mild reaction conditions viz. near to stoichiometry molar ratio of alcohol to vegetable oil (3:1), mild temperature (40–50 °C), stirring speed of about 200 rpm, enzyme concentrations in the range of 12.5–25%, with reaction time of 4–8 h. Furthermore, it offers high quality products and by-product (glycerin), ease of product recovery, and also insensitive to FFA content present in oil (Kulkarni and Dalai, 2006). Hence, these facts prove that enzyme catalyzed biodiesel production has immense potential to be an eco-friendly and a promising alternative to the chemical process. Thus, attempts have been made to investigate the potential of various enzymes for transesterification reaction of vegetable oils using methanol (Table 6).

However, it is also reported that enzyme activity suffers significantly by addition of methanol (0.5 M equivalent) in the beginning of the reaction and also with generation of byproducts viz. glycerin (Marchetti and Errazu, 2008). Therefore, researches have suggested the stepwise addition of methanol, substitution of acyl acceptor (viz. methyl acetate, acetate ethyl) to avoid formation of glycerin and addition of high concentration of chemical co-solvent (viz. t-butanol, 1,4-dioxane, ionic liquid) to improve the enzyme activity (Ha et al., 2007; Chen et al., 2006). Nevertheless, additions of chemical solvents are being discouraged due to

Table 6
Summary of some studies for enzymatic biodiesel synthesis.

Feed stock	Catalyst	Catalyst, wt.%	Molar Ratio, Methanol:Oil	Reaction time, h	Temperature, °C	Yield/conversion, %	References
Soybean	*Candida antarctica*	4	1:1[d]	30	48	93.8[a][b]	Van Gerpen et al. (2004)
Soybean	Lipozyme RMIM	7	3:1	50	4	60[a]	Lv et al. (2008)
Olive pomace	*Thermomyces lanuginosus* lipase	5	6:1	25	24	93[a]	Yücel (2011)
Jatropha	*Burkholderia cepacia* lipase	5	3.3–3.5:1	40	12	95[a]	Kawakami et al. (2011)
Rapeseed	*Candida antarctica*	5	3:1	40	24	76.1[a]	Watanabe et al. (2002)
Jatropha	*Pseudomonas cepacia*	5	4:1	50	8	98[a]	Shao et al. (2008)
WCO	Novozym 435	15	3.8:1	44.5	12	100[a]	Azócar et al. (2010a)
Castor	Novozym 435/lipozyme IM	20	10:1/3:1[c]	65	6	81.4/98.0[a]	Oliveira et al. (2004)
Grease	*Pseudomonas cepacia* (PS30)	13.7	6.6:1[c]	38.4	2.47	96[a]	Wu et al. (1999)
WCO	Novozym 435	4	3:1	30	50	90.9[a]	Watanabe et al. (2001)
	Rhizopus oryzae	30	4:1	40	30	88–90[a]	Chen et al. (2006)

[a] Yield.
[b] Conversion.
[c] Ethanol:oil.
[d] Stepwise addition of methanol in three steps.

Table 7
Summary of some studies for enzymatic biodiesel synthesis in supercritical carbon dioxide.

Feed stock	Catalyst and reaction condition	Catalyst, wt.%	Molar ratio, Methanol:Oil	Temperature, °C	Pressure, bar	Reaction time, h	Conversion, %	References
Sunflower	Novozym 435, methanol/ethanol in supercritical CO_2	30	5:1	45	68[c]/>73.8[d]	12	23[a], 27[b]	Giridhar et al. (2004)
Sesame	Novozym 435 Candida, methanol/ethanol in supercritical CO_2	10	3:1	50	100[c]/>73.8[d]	24	60[a], 51[b]	Varma et al. (2010)
Mustard	Novozym 435 Candida, methanol/ethanol in supercritical CO_2	10	3:1	50	100[c]/>73.8[d]	24	71[a], 71[b]	Varma et al. (2010)
Castor	Novozym 435, methanol/ethanol in supercritical CO_2	10	5:1	50	68[c]/>73.8[d]	12	45[a], 38[b]	Varma and Madras (2007)
Soybean		20	4:1	45	130[d]	6	58[a]	Lee et al. (2009)
Olive	*Candida antartica* lipase, methanol in supercritical CO_2						65.8[a]	
Sunflower							50[a]	
Rapeseed							60[a]	
Palm							59[a]	
Groundnut		30	5:1	45	68[c]/>73.8[d]	15	~65[a], 75[b]	Rathore and Madras (2007)
Palm	Novozym 435, methanol/ethanol in supercritical CO_2	30	5:1	45		15	~65[a], 75[b]	
Pongamia pinnata		30	5:1	45		24	~47[a], 52[b]	
Jatropha curcas		30	5:1	45		24	~47[a], 56[b]	

[a] Conversion into methyl ester.
[b] Conversion into ethyl ester.
[c] Initial pressure at room temperature.
[d] Reaction pressure at specified temperature.

involvement of separation cost of solvent after the reaction and associated environmental concerns for handling chemical solvents in the process.

To overcome this aspect, enzymatic transesterification of vegetable oil has been attempted under supercritical carbon dioxide ($SCCO_2$) conditions. The use of supercritical carbon dioxide phase offers distinct advantages in enhancing solubility of non-polar organics (vegetable oil) in polar phase (methanol) with extremely high diffusivities. A simultaneous use of $SCCO_2$ and enzymatic catalysis is reported to favor eco-friendly transformation of vegetable oil into biodiesel (Table 7). However, owing to the slow reaction kinetics, this route is not preferred at industrial scale.

Transesterification under supercritical methanol phase

Transesterification of vegetable oil in supercritical methanol phase is one of the non-catalytic methods for biodiesel production (Saka and Kusdiana, 2001). It is well known that the supercritical fluids (SCFs) are fluids above their critical temperature and pressure with gas like diffusivities and a liquid like viscosities. Thus, high solubility of vegetable oil in supercritical methanol phase leads to form a single phase, thus allowing rapid formation of biodiesel phase with highly pure glycerin phase. Unlike, conventional catalytic process, such reaction approach is found to be insensitive to moisture content as well as FFA content of vegetable oil and offers ease of separation and purification of biodiesel phase (Bunyakiat et al., 2006; Saka and Kusdiana, 2001). Conversely, the supercritical method simultaneous promotes the hydrolysis of triglyceride (TG) in the presence of moisture, esterification in the presence of FFA and largely transesterification which in sum turns into a positive effect on fatty acid methyl ester yield (Saka and Kusdiana, 2001; Kusdiana and Saka, 2001 and 2004). In contrast, the moisture and presence of FFA are unacceptable in conventional industrial method of biodiesel production due to formation of soap and deactivation of the catalyst. Furthermore, reaction is supercritical alcohol is much faster due to reduction in diverse polarity behaviors of TG and alcohol, which provide high conversion and high yield. Reported studies claim that the complete conversion is achieved within 10 min of reaction at high molar ratio of alcohol to oil (40:1), high pressure (20–40 MPa), high temperature (250–400 °C) (Saka and Kusdiana, 2001; Kawashima et al., 2009).

The literature reports the investigation on effect of the process parameters like reaction temperature, pressure, alcohol to oil molar ratio, and reaction time on supercritical transesterification (Demirbas,

2009a, 2009b; Hawash et al., 2009; Rathore and Madras, 2007; Valle et al., 2010). Typically, an increase in the reaction temperature and pressure is reported to have favorable effect on the conversion and biodiesel yield, which attributes to the supercritical properties of alcohol (Campanelli et al., 2010; Rathore and Madras, 2007). In addition, a very high molar ratio (40:1) is also reported to drive the reaction equilibrium in the forward direction for achieving almost complete conversion (Campanelli et al., 2010). The yield of fatty acid methyl esters is found to be increased with increasing the molar ratio of methanol to oil, perhaps due to the increased contact area between alcohol and triglycerides (Hawash et al., 2009; Rathore and Madras, 2007). The optimal condition is zeroed at temperature (300 °C), pressure (9 MPa) and reaction time (15 min) in which biodiesel yield is reported to be more than 97% (Saka and Kusdiana, 2001). The studies pertaining to aforementioned reaction parameters on biodiesel synthesis under supercritical methanol medium are compiled (Table 8).

However, the use of supercritical approach suffers major disadvantage due to requirement of very high pressure and temperature, excessive molar ratio of alcohol/methanol to oil and probable degradation of biodiesel at an extremely high temperature with exposure of time (Juan et al., 2011). Thus, their applicative potential at commercial level is yet to be established.

Microwave assisted transesterification

The microwave-assisted transesterification is an energy efficient route for rapid biodiesel production. Microwaves assisted transesterification have gain research interest for their direct mode of energy transfer to the reactant molecules (Lertsathapornsuk et al., 2008). This non-ionizing radiation influences the molecular motions such as ion migration or dipole moment, and does not affect the molecular structure (Fini and Breccia, 1999; Refaat et al., 2008). Typically, induced molecular friction generates in situ heat for the reaction by employing continuous magnetic field on polar molecules and ions (Azcan and Danisman, 2007; Saifuddin and Chua, 2004). It employs microwave frequency of 2.45 GHz and 900 MHz, which are permissible for use at domestic and industrial level, respectively. Such route encompasses the advantage of volumetric heating of polar reaction mass (methanol) under the influence of microwaves (Lertsathapornsuk et al., 2008). Therefore, transesterification is efficiently accelerated in a short reaction time due to instantaneous localized superheating thereby enhancing the reaction kinetics (Refaat et al., 2008; Azcan and Danisman, 2007). Such

Table 8
Summary of some studies for biodiesel synthesis in supercritical condition.

Feed stock	Alcohol	Molar ratio, Alcohol:oil	Temperature, pressure	Reaction time, min	Yield/ conversion, %	References
Rapeseed	Supercritical methanol	42:1	350 °C, 19 MPa	4	95[a]	Kusdiana and Saka (2001)
Rapeseed	Supercritical methanol	42:1	350 °C, 30 MPa	4	95[b]	Saka and Kusdiana (2001)
Rapeseed	Supercritical methanol	42:1	350 °C, 35 MPa	4	98.5[b]	Saka and Kusdiana (2002)
Rapeseed	Supercritical methanol	42:1	350 °C,14 MPa	4	35[a]	Kusdiana and Saka (2001)
Rapeseed	Subcritical acetic acid	54:1	300 °C, 20 MPa	30	92[a]	Saka et al. (2010)
	Supercritical methanol	14:1	270 °C, 17 MPa	15	97[a]	
Rapeseed	Supercritical methanol + metal oxide catalysts (ZnO)	40:1% 1 (wt.) ZnO	250 °C, 10.5 MPa	10	95.2[a]	Yoo et al. (2010)
Rapeseed	Subcritical water + Two-step	1:1[c]	270 °C, 20 MPa	60	90[a]	Minami and Saka (2006)
	supercritical methanol	1.8:1[c]	320 °C, 20 MPa	10		
	Supercritical methanol	1.8:1[c]	380 °C, 20 MPa	15	80[a]	
Purified palm	Supercritical methanol	40:1	372 °C, 29.7 MPa	16	81.5[a]	Tan et al. (2010c)
	Supercritical ethanol	33:1	349 °C, 26.2 MPa	29	79.2[a]	
Palm	Supercritical methanol	30:1	360 °C, 22 MPa	20	72[a]	Tan et al. (2010a, 2010b)
Refined, bleached and deodorized palm	Supercritical methanol	45:1	350 °C, 40 MPa	5	90[a]	Song et al. (2008)
Soybean	Supercritical methanol	40:1	310 °C, 35 MPa	25	96[a]	He et al. (2007)
Refined soybean	Supercritical methanol	42:1	350 °C, 20 MPa	10	95[a]	Yin et al.(2008)
	Supercritical methanol + hexane (co-solvent)		300 °C	30	85.5[a]	
	Supercritical methanol + CO_2 (co-solvent)		300 °C	30	90.6[a]	
	Supercritical methanol + KOH		160 °C, 10 MPa	30	98[a]	
Sunflower	Supercritical methanol + calcium oxide (3 wt. %)	41:1	251.8 °C, 24 MPa	6	100[a]	Demirbaş (2007)
Jatropha	Supercritical methanol	40:1	350 °C, 20 MPa	40	>90[b]	Rathore and Madras (2007)
Jatropha	Supercritical methanol	5:1	289.8 °C, 11 MPa	15	100[b]	Chen et al. (2010)
Jatropha	Supercritical methanol + propane	43:1	319.8 °C, 8.4 MPa	4	100[a]	Hawash et al. (2009)
Wet algae	Supercritical methanol	9:1	255 °C, 8.3 MPa	25	90[a]	Patil et al. (2010b)
Cottonseed	Supercritical methanol	41:1	249.8 °C	8	98[a]	Demirbas (2008)
	Supercritical ethanol	41:1	229.8 °C	8	70[a]	
Rice bran	Supercritical methanol	27:1	300 °C, 30 MPa	5	51.28[a]	Kasim et al. (2009)
Dewaxed/degummed rice bran					94.84[a]	
WCO	Supercritical methanol	10:1–50:1	300 °C, 8.7 MPa	10–30	80[a]	Patil et al. (2010a)
WCO	Supercritical methanol	41:1	286.8 °C	30	100[a]	Demirbas (2009a, 2009b)
Chicken fat	Supercritical methanol	6:1	400 °C, 41.1 MPa	6	88[a]	Marulanda et al. (2010)
Linseed	Supercritical methanol	41:1	249.8 °C	8	98[a]	Demirbas (2009a, 2009b)
	Supercritical ethanol	41:1	249.8 °C	8	89[a]	
	Supercritical methanol	41:1	229.8 °C	8	70[a]	
	Supercritical ethanol	41:1	229.8 °C	8	65[a]	
Hazelnut kernel	Supercritical methanol	41:1	350 °C	5	95[b]	Demirbaş (2002)
Coconut and palm kernel	Supercritical methanol	42:1	350 °C, 19 MPa	6.7	95–96[b]	Bunyakiat et al. (2006)
R. sativus L.	Supercritical ethanol	42:1	317.4 °C, 12.5 MPa	29	95.5[a]	Valle et al. (2010)
	Supercritical methanol	39:1	316.8 °C, 14.1 MPa	27	99.8[a]	

[a] Yield.
[b] Conversion.
[c] v/v.

energy efficient approach has been employed for processing of various vegetable oil feedstocks (Table 9).

In sum, microwaves induced transesterification reaction offer high yield of purified product, and minimize the separation and purification time (Nuechter et al., 2000; Hernando et al., 2007). Therefore, microwave heating is environmentally benign, more energy-efficient and favorably method over conventional methods, where heating is relatively slow and inefficient as heat transfer depends on convection currents, thermal conductivity, specific heat and density of the reaction mixture (Refaat et al., 2008; Groisman and Gedanken, 2008).

Although, microwave processing is well established route in ceramic industry, its integration with vegetable oil processing route is yet to be carefully examined at commercial level for biodiesel production.

Cavitation/Ultrasonic irradiation assisted transesterification

Cavitation has been recognized as an effective method to enhance mass transfer rate between immiscible liquid–liquid phases within a heterogeneous liquid reaction system. Such concept has been applied for biodiesel production (Gogate and Kabadi, 2009; Pal et al., 2010; Qiu et al., 2010). Typically, cavitation is broadly classified into two types: hydrodynamic cavitation and acoustic cavitation (Qiu et al., 2010). It aids in achieving high local energy densities, temperature and pressure within the reaction mass through generation of cavities followed by their growth and subsequently violent collapsing of cavities, thereby delimiting the mass transfer and enhancing the reaction kinetics (Gogate and Kabadi, 2009; Qiu et al., 2010).

Hydrodynamic cavitation can be generated by using an orifice plate/ throttling valve/venture across the direction of a liquid flow (Gogate and Kabadi, 2009). The mixing efficiency of a hydrodynamic cavitation is reported to be 160–400 times higher which consumes half of the energy compared to the conventional mixing method especially in case of immiscible liquids (Pal et al., 2010; Qiu et al., 2010). On the other hand, acoustic cavitation is induced by means of ultrasound to achieve the similar features as to hydrodynamic cavitation (Qiu et al., 2010).

Ultrasonic waves are energy application of sound waves, which lies between 20 kHz and 100 MHz, are beyond human hearing limits (16 and 18 kHz) (Vyas et al., 2010). Ultrasonic irradiations are generated through piezoelectric material with the help of power converter (transducer). This high frequency sound wave compresses and stretches the

Table 9

Summary of some studies for biodiesel synthesis in microwave.

Feed stock	Catalyst	Catalyst amount, wt.%	Molar ratio, Alcohol/oil	Microwave conditions	Reaction time, min	Temperature, °C	Yield/conversion, %	References
Soybean	NaOH	1	6:1	900 W	1	30	97.7[b]	Hsiao et al. (2011)
Soybean	NaOH	1	6:1	600 W (Ultrasonic) 900 W(Microwave)	1 2	60	97.7[b]	Hsiao et al. (2010)
Soybean	Nano CaO (heterogeneous catalyst)	3	7:1	0–900 W	60	65	96.6[b]	Hsiao et al. (2011)
Soybean	NaOH	0.6	5:1[c]	NR[d]	10	73	99.25[b]	Terigar et al. (2010)
Soybean	NaOH	1.30	18:1	300 W	1	60	97[a], 95[a]	Hernando et al. (2007)
Soybean and oleic acid	Sulfated zirconia	5	20:1	1600 W	20	60	90[b]	Kim et al. (2011)
Soybean Corn	Diphenyl ammonium salts: DPAMs (Mesylate) DPABs (Benzenesulfonate) DPATs (Tosylate) DPAMs DPABs	2.5 (w/w)	20 10 10 10 9	NR[d]	20	150	100[b], 96[b], 100[b] 92[b], 97[b]	Majewski et al. (2009)
Neat vegetable virgin sunflower	KOH	1	6:1	500 W		65	96.15[a]	Refaat et al. (2008)
Safflower seed	NaOH	1	10:1	300 W	6	60	98.4[b]	Düz et al. (2011)
Crude palm	KOH	1.50	8.5:1[c]	70 W	5	70	85[a], 98.1[b]	Suppalakpanya et al. (2010)
Cotton seed	KOH	1.5	6:1	21% of 1200	7	60	92.4[a]	Azcan and Danisman (2007)
Rice bran	NaOH	0.6	5:1[c]	–	10	73	99.34[a]	Terigar et al. (2010)
Rapeseed	KOH NaOH	1	6:1	67% of 1200 W	5 3	50 40	93.7[a] 92.7[a]	Azcan and Danisman (2008)
Rapeseed	Catalyst free	–	2.5:1	NR[d]	240 (80 bar)	310	91[b]	Geuens et al. (2008)
Maize	NaOH	1.5	10:1	NR[d]	5	NR[d]	98[b]	Öztürk et al. (2010)
Canola	ZnO/La$_2$O·2CO$_3$ (heterogeneous catalyst)	<1	1:1 (w/w)	NR[d]	<5	<100	>95[a]	Jin et al. (2011)
Camelina sativa	Heterogeneous metal oxide catalysts (BaO, SiO)	1.5 2	9:1	800 W	4–5	60–64	94[a], 80[a]	Patil et al. (2009)
Macauba	Novozyme 435 Lipozyme IM	2.5 5	9:1[c] 9:1	NR[d]	15 5	30 40	45.2[b] 35.8[b]	Nogueira et al. (2010)
Castor	H$_2$SO$_4$/C	5	12:1	200 W	60	65	94[a]	Yuan et al. (2009)
Castor	Al$_2$O$_3$/50% KOH SiO$_2$/50% H$_2$SO$_4$ SiO$_2$/30% H$_2$SO$_4$	1 1 1	6:1	40 W 40 W 220 W	5 30 25	60	95[b] 95[b] 95[b]	Perin et al. (2008)
Jatropha	KOH	1.50	7.5:1	1200 W	2	65	97.4[b]	Shakinaz et al. (2010)
Jatropha curcas	NaOH	4	30:1	NR[d]	7	55	86.3[b]	Yaakob et al. (2008)
Crude karanja	KOH	1.33	33.4:1 (w/w)	180 W	2.5	NR[d]	89.9[b]	Venkatesh et al. (2011)
Dry micro algae	KOH	2	9:1	800 W	6	60–64	80.13[b]	Patil et al. (2011)
WFO	NaOH	3	12:1[c]	800 W	0.5	78	97[b]	Lertsathapornsuk et al. (2008)
WFO	NaOH	1	6:1	600 W	5	64	93.36[a]	Yücel (2010)
FO	NaOH	0.5	6:1	50% of 750 W	4	60	87[b]	Saifuddin and Chua (2004)
Domestic WCO	KOH	1	6:1	500 W	60	65	95.79[a]	Refaat et al. (2008)
Restaurant WCO	KOH	1	6:1	500 W	60	65	94.51[a]	Refaat et al. (2008)
Triolein	KOH, NaOH	5	6:1	25 W	1	50	98[b]	Leadbeater and Stencel (2006)
Yellow horn	Heteropol yacid (HPA)	1	12:1	500 W	10	60	96.22[a]	Zhang et al. (2010b)

[a] Yield.
[b] Conversion.
[c] Ethanol to oil.
[d] Not reported.

molecular spacing of a medium in which it passes through to create localized high energy densities within reaction mass.

Ultrasonic irradiation holds three major effects; (1) variation of sonic pressure, (2) cavitation, and (3) acoustic stream mixing which causes solvent compression and rarefaction cycle, liquid will break down and cavities/bubble formation followed by disrupting the interfacial boundary layers respectively (Colucci et al., 2005; Kumar et al., 2010b). In total, these effects improve mass transfer, create high local pressure (up to 1000 atm) and temperatures (~5000 K), increased catalytic surface areas, and thus finally accelerate the rate of reaction (Gogate and Kabadi, 2009; Pal et al., 2010; Qiu et al., 2010). Accordingly, the use of ultrasound during transesterification of vegetable oil leads to improvement in the heat and mass transfer by generating small cavities and vigorous mixing between immiscible reactants (Oil and methanol). Thus, provides sufficient activation energy to initiate the reaction which improves upon the reaction rate and yields, and thereby shorter the reaction time and energy consumption (Singh et al., 2007; Ji et al., 2006). Attempts have studies the effect of catalyst, type of alcohol, ultrasonic power and frequency on ultrasonic assisted biodiesel production (Refaat and El Sheltawy, 2008; Wang et al., 2007). A brief summary of few studies for biodiesel synthesis in the presence of Cavitation/Ultrasonic irradiation is presented in Table 10.

Owing to the advantages of cavitation in influencing the degree of reactant mixing and reaction kinetics, a commercial scale process for transesterification of vegetable oil using homogeneous catalyst system has been developed (Gordon et al., 2011). Recently, various cavitation based technologies for biodiesel production have been reviewed (Oh et al., 2012). In this context, the patented hydrodynamic cavitation reactor i.e. Bioforce 9000 Nano for commercial biodiesel production is developed by Cavitation Technologies Inc. (CTI) (Gordon et al., 2011; Voegele, 2009). Major plant, engineering and equipment supplier in the field of oil and fats, M/s Desmet Ballestra in Brazil is adopting this technology, where biodiesel production is envisaged to grow enormously (Cavitation Technologies Inc., 2013). On similar lines, M/s SRS Engineering installed 10 MMgpy turnkey biodiesel plant using hydrodynamic cavitation technologies at Moberly, Missouri, USA. The facility is targeted to process multiple feedstocks like soybean oil, waste vegetable oil and animal fats with an option of high FFA feedstocks (Cavitation Technologies Inc., 2013). Furthermore, M/s SRS Engineering has claimed substantial savings in capital and production costs with cavitation based technology while comparing with existing conventional technologies. On the other hand, ultrasonic based cavitation approach is yet to be exploited at commercial level due to possible erosion of ultrasonic source due to the high surface energy intensity (Gogate and Kabadi, 2009; Qiu et al., 2010).

Membrane assisted transesterification

Membrane assisted transesterification provides platform for clean, energy efficient and cost effective continuous biodiesel production (Sanchez Marcano and Tsotsis, 2002). Typically, membrane reactor simultaneously offers shifting equilibrium to reversible transesterification reaction towards product formation and selective separation, which improves the quality of biodiesel (Cao et al., 2007). The transesterification of vegetable oil is performed in membrane reactor by exploiting the immiscibility of the oil and methanol, which posed the major mass transfer limitation to conventional biodiesel production. Typically, membrane process integrate reaction and separation steps into a single step, thereby reducing separation costs and recycle requirements, and an enhancement of thermodynamically limited or product inhibited reactions resulting in higher conversions per pass (Dubé et al., 2007). Therefore, the application of membrane in biodiesel production has received attention in recent years (Reyes et al., 2012; Cao et al., 2008b; Dubé et al., 2007). This process is a unique combination for simultaneous steps viz.

Table 10
Summary of some studies for biodiesel synthesis in Cavitation/Ultrasonic irradiation.

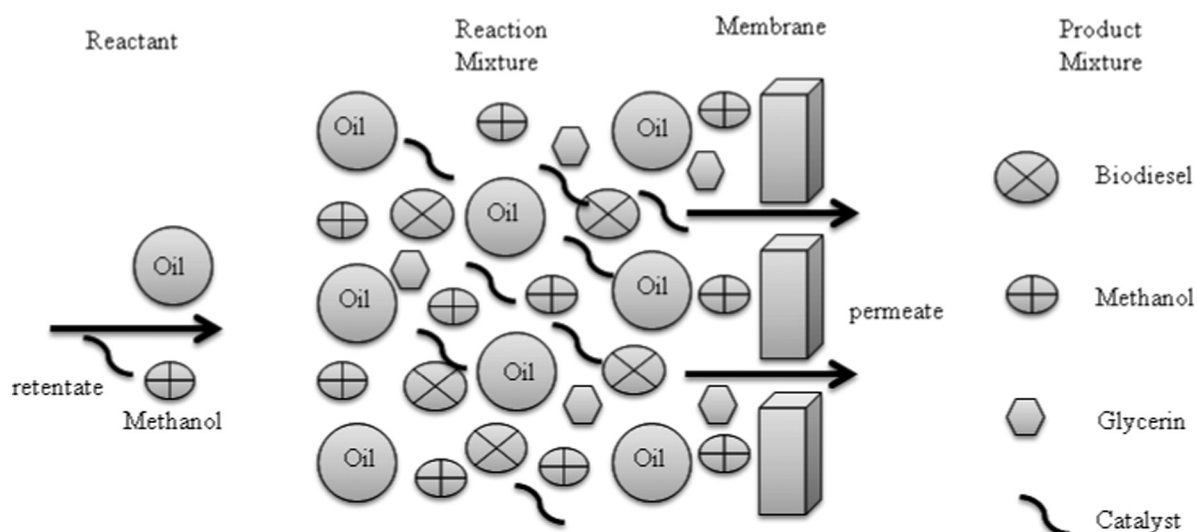| Feed stock	Catalyst	Catalyst Amount, wt.%	Alcohol	Molar ratio, Alcohol/oil	Reaction temperature, °C	Reaction time, min	Reaction condition	Yield/conversion, %	References
Refined soybean oil	KOH	1.5	Methanol	6:1	40	15	20 kHz, 14.49 W	>99.4[b]	Colucci et al. (2005)
Soybean	NaOH	1	Methanol	6:1	45	10	197 kHz, 150 W	99[a]	Ji et al. (2006)
Soybean	KOH	0.5	Methanol	6:1	26–45	30<	611 kHz, 139 W	>90[b]	Mahamuni and Adewuyi (2009)
Soybean	Na or K methoxide	0.15	Methanol	6:1	45	60	21.5 kHz, 600 W	100[b]	Cintas et al. (2010)
Soybean	Ti(Pr)4 Al(Pr)3	3	Methanol	6:1	60	120	–	64[a]	Ye et al. (2007)
Soybean	Novozym 435	6	Methanol	6:1	40	240	40 kHz, 500 W	96[a]	Yu et al. (2010a, 2010b)
Palm	KOH	–	Methanol	6:1	38–40	20	45 kHz, 600 W	95[a]	Stavarache et al. (2007)
Palm	CaO SrO BaO	3	Methanol	9:1	65	60	30 kHz	77.3[a] 95[a] 95[a]	Mootabadi et al. (2010)
Palm	BaO SrO	2.8	Methanol	9:1	65	50<	20 kHz, 200 W	>92[a]	Salamatinia et al. (2010)
Canola	KOH	0.7	Methanol	5:1	25	50	20 kHz, 1000 W	>95[b]	Thanh et al. (2010a)
Canola Soybean Corn	KOH	1	Methanol	6:1	55	30	450 W	95[a] 95[a]	Lee et al. (2011)
Neat vegetable oil	NaOH	0.5	Methanol	6:1	25	20	Ultrasonic cleaner 20 kHz 40 kHz 1200 W	98[a]	Starvarache et al. (2005)
	KOH							96[a]	
Coconut	KOH	0.75	Ethanol	6:1	–	7	24 kHz, 200 W	>92[a]	Kumar et al. (2010a)
WCO	KOH	1	Methanol	6:1	45	40	20 kHz, 200 W	89[b]	Hingu et al. (2010)
WCO	KOH	0.7	Methanol	2.5:1 (mol)	20–25	10	20 kHz, 1000 W (at each step)	81[a]	Thanh et al. (2010b)
		0.3		1.5:1		20		99[a]	
Triolein	KOH	1	Methanol	6:1	25	30	Ultrasonic cleaner 40 kHz, 1200 W	~99[a]	Hanh et al. (2008)
Triolein	NaOH KOH	1	Methanol Ethanol	6:1	25	25	Ultrasonic Cleaner 40 kHz, 1200 W	>95[b]	Hanh et al. (2009)
Beef Tallow	KOH	0.5	Methanol	6:1	60	1.16	40 kHz, 1200 W	>92[b]	Teixeira et al. (2009)

[a] Yield.
[b] Conversion.

Fig. 3. Schematic of membrane assisted reaction and separation mechanism for biodiesel production.

phase solubility, oil droplet separation and product separation at lower reaction temperatures (Saleh et al., 2010; Baroutian et al., 2011; Cao et al., 2008a; Dubé et al., 2007; Böddeker, 2008). The process uses cross-flow filtration through micro-porous inorganic membranes for selective removal of biodiesel, methanol and glycerin during transesterification. The schematic of membrane assisted simultaneous reaction and separation is presented in Fig. 3. Typically, membrane restricts the flow of large oil droplets and promotes mixing of reactants thereby reducing mass transfer. Additionally, the presence of two phases in the reactor also ensures product quality by creating a barrier, which prevents the movement of un-reacted oil into the product stream (Böddeker, 2008). This phenomenon is remarkable, keeping in view of

the reversible nature of transesterification, to shift the reaction equilibrium towards product side, which yields high purity and quality biodiesel (Dubé et al., 2007; Cao et al., 2008b). The employed membranes are either organic in nature (i.e. polymeric) or inorganic where the thermal stability of the latter is better than the former. The pore size of the membrane is the crucial parameter and the effects of the pore size have been investigated for the biodiesel production (Cao et al., 2007). The membrane assisted biodiesel synthesis requires higher molar ratios of methanol to oil and ultralow catalyst concentration compared to conventional synthesis (Cao et al., 2008a; Cheng et al., 2010). A summary of reported studies for biodiesel synthesis using membrane reactor is presented in Table 11.

Table 11
Summary of some studies for biodiesel synthesis using membrane.

Feed stock	Catalyst	Mixture	Membrane	Temperature, °C	System Pressure, kPa	Trans-membrane pressure, kPa	FAME content in permeate	References
Palm	KOH	Crude biodiesel from KOH-trans-esterification of refined palm oil	Ceramic tube	60	NR[a]	150	>90	Wang et al. (2009)
Palm	KOH (heterogeneous)	Crude biodiesel from heterogeneous KOH-trans-esterification of refined palm oil	Ceramic tube	70	100	NR[a]	95	Baroutian et al. (2011)
Canola	H_2SO_4	Emulsion (commercial Canola oil/methanol/H_2SO_4 FAME, glycerin)	Carbon tube	65	138	NR[a]	96	Dubé et al. (2007)
Canola	H_2SO_4	Emulsion (commercial canola oil/methanol/H_2SO_4 FAME, glycerin mixture) with recirculation of phase methanol/H_2SO_4	Ceramic tube	65	275.8	173.4	93	Cao et al. (2008b)
Canola	NaOH	Crude Biodiesel from NaOH-transesterification of canola oil	Ceramic tube	55	41	NR[a]	79	Reyes et al. (2012)
Canola	NaOH	Biodiesel from NaOH-transesterification of canola oil	Ceramic disc	40	NR[a]	66.7	60	Cheng et al. (2009)
Soybean	PTSA/MCM-41	Mixture of soyabean oil, methanol	Ceramic membrane tube	80		80	84.1	Xu et al. (2014)
Soybean	KF/Ca — Mg — Al hydrotalcite solid base	Mixture of soyabean oil, methanol	Membrane tube	70		50	91	Xu et al. (2013)
Palm	KOH	Mixture of palm oil, methanol, KOH	Ceramic membrane	40	NR[a]	2 00	98.32	Atadashi et al. (2012)

[a] NR.

Table 12
Summary of some studies for biodiesel synthesis using static mixer.

Feed stock	Type of mixing element	Catalyst, wt.%	Molar ratio, MeOH/oil	Temperature, °C	Residence time, s	Yield, %	References
Canola	Helical mixing element	KOH, 1.5	6	60	1800	97.6[a][b]	Thompson and He (2007)
Soybean	Metal foam	KOH, 1	6	60	196	95.2[a]	Yu et al. (2010a, 2010b)
Soybean	Stainless steel wool	KOH, 2	6	60	180	97[a]	Santacesaria et al. (2011a); Santacesaria et al. (2012a, 2012b)
Soybean	Stainless steel sphere						Santacesaria et al. (2011a)
	Uniform spheres $\Phi = 2.5$ mm, Channels ≈ 1000 μm	KOH, 1	6	60	80	82[a]	
	Two sizes spheres $\Phi_1 = 2.5$ mm, $\Phi_2 = 1$ mm, Channels ≈ 500 μm	KOH, 2	6	60	60	98.2[a]	
	Two sizes spheres $\Phi_1 = 2.5$ mm, $\Phi_2 = 0.39$ mm, Channels ≈ 300 μm	KOH, 1	6	60	20	80.5[a]	

[a] Yield.
[b] Conversion.

Static mixer assisted transesterification

Static mixers are known to promote radial mixing in the mass transfer limited chemical reactions for immiscible liquids (Thompson and He, 2007). This special type of reactor system consists of specially designed motionless helical mixing elements within a hollow cylindrical geometry and offers intense agitation with minimal energy consumption compared to conventional mechanical agitation. The advantages of such reactor are mainly, no moving parts, low space requirement, and low maintenance and operating cost. The continuous biodiesel production in the presence of homogenous sodium hydroxide as catalyst is reported using static mixer reactor systems which are in integration with other equipments (Peterson et al., 2002; Thompson and He, 2007). This type of reactor system is also reported for efficient biodiesel separation from emulsified reactants (Boucher et al., 2009). Table 12 summarizes some studies for biodiesel synthesis using static mixer. The reaction condition is zeroed for 99% conversion and simultaneous removal of 70–99% of the glycerol at 60 °C temperature, 1.5% sodium hydroxide catalyst concentration and 30 min reaction time (Thompson and He, 2007).

The utilization of static mixer/plug flow reactor in commercial scale has been demonstrated by M/s ENERGEA, Austria and M/s Spec Engineers India, for the production of biodiesel (SPEC, 2010). The reactor dimensions are reported to be 1500 mm × 700 mm × 2000 mm for 50 ton/day capacity with less reaction time (20 s), maximum yield and conversion using minimal energy have been achieved (SPEC, 2010).

Features of commercial process for transesterification of vegetable oil

Owing to the aforementioned developments, the commercial turnkey plant is reported to offer by M/s Lurgi, M/s Desmet Ballestra and M/s Pacific Biodiesel based on the homogeneous catalytic process (Pacific Biodiesel, 1996; GmbHL, 1996; Desmet Ballestra, 2008; Oh et al., 2012). The offered commercial technology claims multi-feedstock flexibility with FFA content up to 15% using pre-treatment steps prior to main transesterification reaction. Typically, M/s Lurgi and Desmet Ballestra offer simultaneous separation of products/by-products to drive the reversible transesterification reaction towards forward direction. The two and three stage rector cum separator type of system is offered by both the process licensors whereas M/s Pacific biodiesel uses the batch operation for easy of handling feed stock, chemicals and manages the quality (Pacific Biodiesel, 1996; GmbHL, 1996; Desmet Ballestra, 2008; Oh et al., 2012). The produced biodiesel has been claimed to meet desired fuel specifications with glycerin purity up to 90% depending on the purification steps involved in the process. On the other hand, the commercial plant based on heterogeneous catalyst process, Esterfip-H offers ease of product separation, high quality of biodiesel

and glycerin, but suffers on battery limit of the FFA and water content which cannot tolerate impurities above the 0.25% and 1000 ppm, respectively (Melero et al., 2009). This continuous process consists of two fixed bed reactors, which sequentially handle oil and methanol (Bournay et al., 2005). The complete conversion is reached within two successive fixed-bed stages with glycerin separation in each stage to shift the equilibrium towards the product formation (Ondrey, 2004). The produced biodiesel claimed to have a higher purity (>99%) with production yield (~100%) without involving purification steps. In addition, the directly produced by-product glycerin is claimed to have purity level of at least 98% without any contaminants. These aspects eliminate the product purification and refining steps, and ultimately, reduce the total production costs. Nevertheless, this process still have drawbacks such as close window for feedstock selection, higher methanol to oil ratio, higher temperature and pressure compared to conventional homogeneous alkali catalytic process.

An alternative: glycerin free routes

Hydroprocessing

The search for diesel fuel, from renewable source, with excellent oxidation stability and fuel quality in terms of improved cetane number has led to development of vegetable oil glycerin free hydroprocessing route. The hydroprocessing of vegetable oil or its blend with petroleum feedstock involves hydrodeoxygenation of triglycerides and hydrofining of derived products in the presence of catalyst and hydrogen environment. This process leads to formation of a liquid hydrocarbon mixture specially C_{15}–C_{18} n-paraffins within the boiling range of mineral oil based diesel, which is commonly called "green diesel", "renewable diesel", "bio-hydrogenated diesel", and second-generation biodiesel and ATF (Choudhary and Phillips, 2011).

Typically, hydrodeoxygenation process is performed over Ni/Co–Mo–Al_2O_3 type of catalyst to produce long chain n-paraffins whereas hydroisomerization step is carried out using proprietary catalyst to tailor the cold flow properties by converting n-paraffins to iso-paraffins. The hydroisomerization step is reported to be the most critical step because cold flow properties of green diesel produced needs to be improved to meet cold flow plugging point (CFPP) without much compromise on cetane number whereas pour point for bio-ATF fraction needs to be achieved ≤47 °C as per the aviation industry norms (IS, 2008). It may be noted that n-paraffins have higher cetane number than corresponding branched isomers whereas increase in degree of branching improves cold flow properties. Hydrotreatment process that is robust in nature can handle varieties of feed stock ranging from edible vegetable oil (soybean, rapeseed, palm), non-edible vegetable oil (Jatropha and algal), acid oil/waste cooking oil (WCO) and extremely lower-cost stock such as tallow oil and waste greases. The hydrogen requirement during the process is found to be highly dependent on the nature of feedstocks. For example, the less unsaturated feedstock, such

as palm and tallow oils requires lower hydrogen consumption vis-à-vis feedstock with higher olefin content, such as soybean and rapeseed oils. Similar to conventional process, pre-treatment of feedstock is mandatory for employing hydroprocessing route as the presence of gum and metal content in the feedstock severely hampers the activity of the hydrotreating catalysts. Furthermore, the type of catalyst and temperature are the most important factors to determine the yield and composition of liquid products, such as green naphtha (C_5–C_{10}), green jet fuel (C_{11}–C_{13}), and green diesel (C_{14}–C_{20}), and even green liquid petroleum gas (LPG) (Bezergianni et al., 2009, Table 13). Here, the severity of process depends on the quality of feedstock and operating conditions. The salient features of this route include, flexibility, ease of optimization to accommodate changes in feedstock, and integration with refinery operation.

In recent years, several refiners have had an increasing interest in producing renewable liquid fuels from the hydroprocessing of various triglyceride feedstocks. This has led to successful development of commercial processes, which are now offered by M/s UOP and M/s Halder Topse (Kalnes et al., 2008; Egeberg et al., 2010). A simplified process sketch is shown in Fig. 4.

In this process, hydrogen is mixed with feedstock at predefined pressure (~ up to 100 bar) and processed over a multi-stage adiabatic reactors at each stage. In the first catalytic hydrodeoxygenation reactor, alkanes generate along with by-products like carbon dioxide, water and propane from fatty acid chain. This first stage process produces diesel boiling-range paraffins, and also has shown complete conversion with very high selectivity towards desired products. The deoxygenated product can be separated by distillation, and the heavier fractions are further hydrotreatment. The obtained hydrodeoxygenated n-paraffin rich diesel (is mainly composed of C_{15} and C_{18} n-paraffins) has high cetane number (>70) but poor cold flow properties (freezing point in between 20 and 28 °C). Therefore, additional mixing of hydrogen is required through an integrated catalytic hydro-isomerisation process which produces branched paraffin rich diesel to meet the cold flow properties.

Implementation of the above process scheme does not required additional facilities for refiners and can easily integrate with the existing infrastructure at refinery. Even, vegetable oils can be mixed with straight run gas oil (VO) and/or vacuum gas oil (VGO) for hydroprocessing in existing conventional hydrotreaters (diesel hydrodesulfurization units) used in refineries (Corma et al., 2007; Huber and Corma, 2007; Stern and Hillion, 2000). By doing this, operation costs can be reduced by using the existing installations and also would offer flexibility in the production scheme and a very good alternative to the production of mixed petro-biofuel. In this setup, two main reactions would occur, e.g. hydrodeoxygenation of triglycerides and hydrodesulfurization of gas oil. Both reactions are carried out over the same hydrotreating catalyst. The deoxygenated products are stable in nature and completely compatible with petro-diesel fuels, and exhibit high cetane number (Senol et al., 2005; Ferrari et al., 2001; Kubickova et al., 2001; Snåre et al., 2008). Literature summary of such work with oil sources and their blend with mineral oil diesel, reactor type, reaction conditions, catalysts, and main products are shown in Table 13.

Recently, several petroleum related companies such as UOP/ENI (Ecofining process) (UOP, n.d.), The Neste Oil Co. (NExBTL process) (Neste Oil, 2014), Tyson Foods Inc. and Syntroleum Corporation (Environmental Leader and Tyson Foods, 2014), Valero Energy Corporation (New Orleans Net, 2014), ConocoPhillips (Conocophillips renewable diesel, 2014), Nippon Oil Corporation.(Second Generation Renewable Diesel, 2014), have shown their interest in producing renewable green liquid fuels based on hydroprocessing of various types of triglyceride feedstocks.

Substitution of methanol

The need for biodiesel process economic improvement w.r.t. glycerin glut, has led to development of methanol free route of transesterification for biodiesel production. Therefore, to alter the reaction pathways for avoiding the formation of glycerin, alternatives of alcohol/methanol as methyl acetate and dimethyl carbonate (DMC) have been explored (Huang and Yan, 2008; Fabbri et al., 2007; Su et al., 2009).

The difference in reaction pathway for transesterification of vegetable oil with methanol vis-à-vis DMC as reported elsewhere (Fabbri et al.,
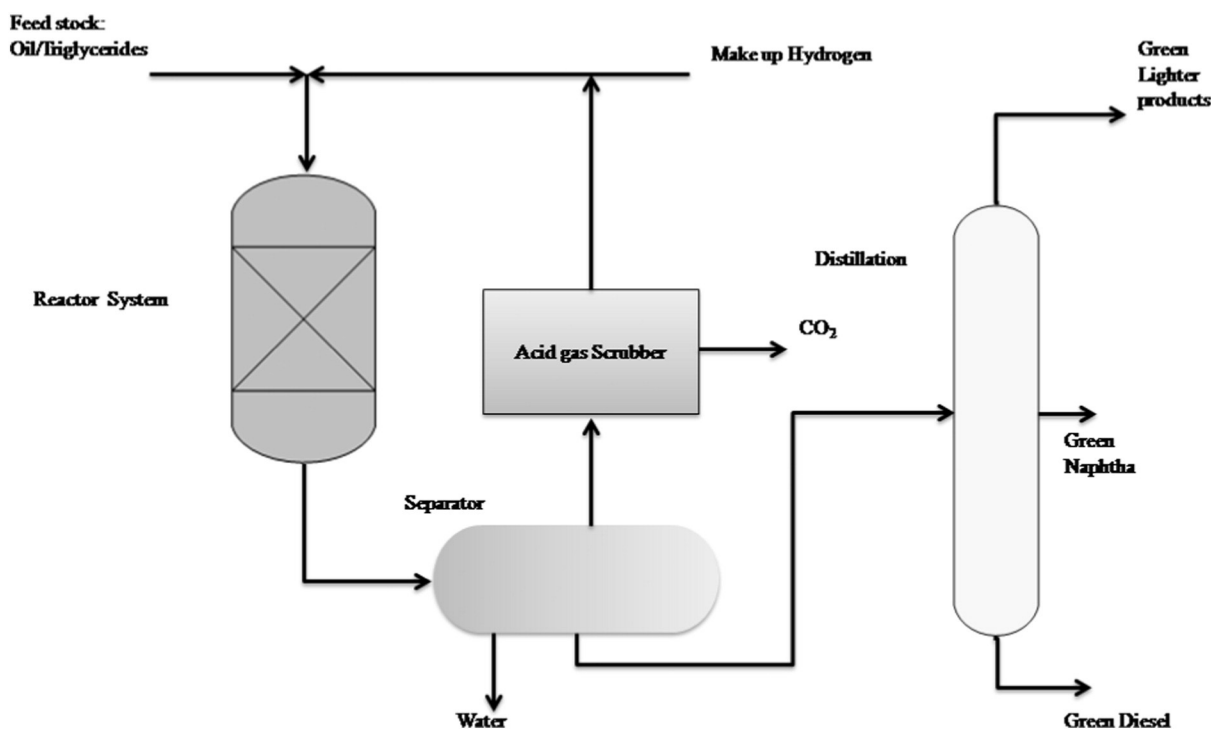

Fig. 4. Process for hydrotreatment of vegetable oil for Green diesel production.

Table 13
Summary of some studies for green diesel synthesis through hydro treatment.

Feed Stock	Reactor type	Reaction conditions	Catalyst	Main products	Conversion/yield, wt.%	References
Neat oil as feedstock						
Jatropha	Fixed bed	$T = 350\ ^\circ C$ $P = 4\ MPa$ LHSV = $7.6\ h^{-1}$ H_2/oil ratio = $800\ Nm^3/m^3$	$NiMo/Al_2O_3\text{-}SiO_2$ $NiMo/SiO_2$ $NiMo/\gamma\text{-}Al_2O_3$ $NiMo/H\text{-}Y$ $NiMo/H\text{-}ZSM\text{-}5$	LPG C_{15}–$C1_8$ n-paraffins C_{11}–C_{20} C_{11}–C_{20} C_{11}–C_{20} C_5–C_{10}	100^b/83.5^a	Liu et al. (2011)
Jatropha	Batch	$T = 270\ ^\circ C$ $P = 6.5\ MPa$ $t = 12\ h$ Catalyst/oil wt. ratio = 1	$Pt/H\text{-}ZSM\text{-}5$ Pt/USY	C_{10}–C_{20} n-paraffins C_{10}–C_{20} n-paraffins	83.8^b/67.7^a 100^b/90^a	Murata et al. (2010)
Soybean	Batch	$T = 400\ ^\circ C$ $P = 9.2\ MPa$ $t = 1\ h$ Catalyst/oil wt. ratio = 0.044, 0.088	$NiMo/\gamma\text{-}Al_2O_3$ $Pd/\gamma\text{-}Al_2O_3$ $CoMo/\gamma\text{-}Al_2O_3$ $Ni/Al_2O_3\text{-}SiO_2$ $Pt/\gamma\text{-}Al_2O_3$ $Ru/\gamma\text{-}Al_2O_3$	C_{15}–C_{18} n-paraffins C_{15}–C_{17} n-paraffins C_{15}–C_{17} n-paraffins C_{15}–C_{17} n-paraffins C_{15}–C_{17} n-paraffins C_{15}–C_{17} n-paraffins	92.9^b/64.5^a 91.9^b/79.2^a 78.9^b/33.7^a 60.8^b/39.2^a 50.8^b/37.7^a 39.7^b/32.0^a	Veriansyah et al. (2011)
Soybean	Batch	$T = 350\ ^\circ C$ $P = 0.7\ MPa\ N_2$ $t = 4\ h$ Stirring rate = 1000 rpm	Ni/Al_2O_3 $NiAl/LDH$ $MgAl/LDH$	$\geq C_{18}$ C_8–C_{17} C_8–C_{17}	68^b/51.2^a 74^b/52.9^a 72^b/47.8^a	Morgan et al. (2012)
Rapeseed	Fixed bed	$T = 340\ ^\circ C$ $P = 4.0\ MPa$ LHSV = $1\ h^{-1}$ H_2/oil ratio = 500–$1000\ Nm^3/m^3$	$NiMo/\gamma\text{-}Al_2O_3$ NiW/TiO_2 $NiMo/TiO_2$ NiW/ZrO_2 NiW/NaY	C_{15}–C_{18} n-paraffins	93^b/54.5^a	Mikulec et al. (2010)
Rapeseed	Batch	$T = 300$–$400\ ^\circ C$ $P = 5$–$11\ MPa$ $t = 3\ h$	$NiMo/Al_2O_3$ $Pt/H\text{-}Y\ Pt/H\text{-}ZSM\text{-}5$	C_7–C_{18} n-paraffins C_5–C_{22} n- and iso-paraffins	70–80^a 20–40^a	Sotelo-Boyás et al. (2011)
Sunflower	Fixed bed	$T = 360$–$420\ ^\circ C$ $P = 18\ MPa$ Oil flow = 49 g/h H_2 flow = $0.049\ Nm^3/h$	Sulfided catalyst (not specified)	C_{15}–C_{20} n- and iso-paraffins	64.7^a (360 °C)	Simacek et al. (2011)
Sunflower	Fixed bed	$T = 360$–$380\ ^\circ C$ $P = 6$–$8\ MPa$ LHSV = 1.0–$1.2\ h^{-1}$ H_2/oil ratio = $450\ Nm^3/m^3$	$CoMo/Al_2O_3$ $NiMo/Al_2O_3$ NiW/Al_2O_3	Gases C_5–C_{10} n-paraffins C_{11}–C_{19} n-and iso-paraffins	94–99.8^b/63.1–71.5^a 81.8–97.4^b/42–51.9^a 86.7–95.6^b/9.4–49.3^a	Hancsók et al. (2012)
Sunflower	Fixed bed	$T = 350$–$370\ ^\circ C$ $P = 2$–$4\ MPa$ LHSV = $1.0\ h^{-1}$ H_2/oil ratio = $500\ Nm^3/m^3$	$NiMo/Al_2O_3\text{-}F$	C_{15}–C_{18} n-paraffins	73.2–75.6^a	Kovacs et al. (2011)
Sunflower	Fixed bed	$T = 380\ ^\circ C$ $P = 4$–$6\ MPa$ LHSV = $1.0\ h^{-1}$	$CoMo/Al_2O_3$	C_{14}–C_{19} n-paraffins	100^b/73.7–73.9^a	Krár et al. (2010)

Table 13 (*continued*)

Feed Stock	Reactor type	Reaction conditions	Catalyst	Main products	Conversion/yield, wt.%	References
Sunflower	Fixed bed	H_2/oil ratio = 500–600 Nm^3/m^3 T = 310–360 °C P = 2 MPa LHSV = 0.9–1.2 h^{-1} H_2/oil ratio = 1000 Nm^3/m^3	Pd/SAPO-31	C_{16}–C_{18} n- and iso-paraffins	89.3–73.4[a]	Kikhtyanin et al. (2010)
Safflower	Batch	T = 340 °C P = 0.98 MPa H_2–N_2 H_2–N_2 ratio: 1:4 Cat./oil wt. ratio = 0.0025 t = 3 h	Pt/SBA-15 NiMoC/SBA-15 CoMoC/SBA-15 Triflic acid/SBA-15	Gases C_5–C_9 n-paraffins C_{10}–C_{14} n-paraffins C_{15}–C_{23} n-paraffins	25[b] 99[b]	Barrón et al. (2011)
Palm	Fixed bed (pilot plant)	T = 350 °C P = 4–9 MPa LHSV = 2 h^{-1} TOS = 0–14 days	NiMo/Al_2O_3	C_{16}–C_{18} n-paraffins	100[a], molar	Guzman et al. (2010)
Palm	Batch	T = 300–320 °C Atm. pressure t = 1–2 h Catalyst/oil wt. ratio = 0.0133	NiMo/zeolite (klinoptilolite type)	C_8–C_{19} n-paraffins	11.93[a], vol.	Nasikin et al. (2009a)
Palm	Fixed bed	T = 450 °C WHSV = 2.5 h^{-1}	HZSM-5 MCM-41	Naphtha, kerosene, and diesel-range paraffins		Sang et al. (2003)
Waste cooking oil	Fixed bed	T = 350 °C P = 2 MPa LHSV = 15.2 h^{-1} H_2/oil ratio = 400 Nm^3/m^3	Ru/Al13-montmorillonite	C_{15}–C_{18} n-paraffins	100[b]/82.1–84[a]	Liu et al. (2012)
WCO	Batch	T = 380–430 °C P = 1–2 MPa Catalyst/oil wt. ratio = 0.0028 t = 0.75–1.5 h	HZSM-5 sulfated zirconia	Naphtha, kerosene, and diesel-range paraffins	79.2[a]	Charusiri et al. (2006)
Blend of mineral–gas oil + vegetable oil as feedstock						
Rapeseed	Fixed bed	T = 300 °C P = 4.5 MPa LHSV = 1.5 h^{-1} H_2/oil ratio = 250 Nm^3/m^3	NiMo/Al_2O_3	C_{15}–C_{20} n-paraffins	97[b]	Donnis et al. (2009)
Rapeseed	Fixed bed	T = 400–420 °C P = 18 MPa WHSV = 1 h^{-1} H_2/oil ratio = 1000 Nm^3/m^3	NiMo/Al_2O_3	C_{15}–C_{20} n-paraffins	55.4[a] (420 °C)	Simacek and Kubicka (2010)
Palm	Fixed	T = 310–350 °C P = 3.3 MPa WHSV = 0.7–1.4 h^{-1}	CoMo/Al_2O_3	Diesel-range paraffins	100[b]	Templis et al. (2011)

Feedstock	Reactor	Conditions	Catalyst	Product	Yield/Conversion	Reference
Palm	Fixed	H_2/oil ratio = 1500 Nm^3/m^3 T = 300–320 °C P = 1 atm	NiMo/zeolite klinoptilolite type	Diesel-range paraffins	11.9[a]	Nasikin et al. (2009a,b)
Sunflower	Fixed	T = 360–380 °C P = 8 MPa LHSV = 1 h^{-1} H_2/oil ratio = 600 Nm^3/m^3	NiMo/Al2O3	C_{11}–C_{22} n-paraffins	82–90[a]	Tóth et al. (2011)
Sunflower	Fixed bed	T = 350 °C P = 13.8 MPa LHSV = 1.5 h^{-1} H_2/oil ratio = 1060 Nm^3/m^3	Hydrotreating catalyst (not specified)	Diesel-range paraffins	85[b]/42[a]	Lappas et al. (2009)
Sunflower	Fixed bed	T = 350 °C P = 6.9 MPa LHSV = 1.5 h^{-1} H_2/oil ratio = 1068 Nm^3/m^3	Hydrocracking commercial catalysts (not specified)	Naphtha, kerosene, and diesel-range paraffins	64[b] (catalyst B) 37.5[b] (catalyst C)	Bezergianni et al. (2009)
Sunflower	Fixed bed	T = 300–450 °C P = 5 MPa LHSV = 4.97 h^{-1} H_2/oil ratio = 1600 Nm^3/m^3	NiMo/Al_2O_3	C_{15}–C_{18} n-paraffins	54–75[a]	Huber et al. (2007)
Sunflower	Fixed bed	T = 320–350 °C P = 3–6 MPa LHSV = 1.4 h^{-1} H_2/oil ratio = 1068 Nm^3/m^3	NiMo/Al_2O_3-β-zeolite	C_{17}–C_{18} n-paraffins	/>90[b]	Sankaranarayanan et al. (2011)
Soybean	Fixed bed	T = 340–380 °C P = 5 MPa LHSV = 2.4 h^{-1} H_2/oil ratio = 1500 Nm^3/m^3	NiW/Al_2O_3–SiO2 NiMo/Al_2O_3	C_{15}–C_{20} n-paraffins	85–95[a]	Tiwari et al. (2011)
WCO	Batch	T = 325 ° P = 2 MPa Stirring = 900 rpm t = 1, 2, 5, 20 h	Pt/γ-Al_2O_3 Ni/γ-Al_2O_3 Pt/γ-Al_2O_3		100[b]/60[a] 76.8[b] 100[b]	Madsen et al. (2011)
WCO	Fixed bed	T = 330–398 °C P = 8.3 MPa LHSV = 1 h^{-1} H_2/oil ratio = 710 Nm^3/m^3	Hydrotreating catalyst (not specified)	C_8–C_{29}n- and iso-paraffins	72.62[b]/71[a] (at 350 °C)	Bezergianni et al. (2010)

LHSV, Liquid hour space velocity.
WHSV, Weight hour space velocity.
TOS, Time on-stream.
[a] Yield.
[b] Conversion.

Table 14

Summary of some studies for glycerin free synthesis of biodiesel through substituting methanol.

Feed stock	Reactant	Catalyst	Molar ratio, reactant/oil	Temperature, pressure	Reaction time, min	Yield/conversion, %	References
Palm	DMC	KOH as heterogeneous catalyst, 8.5 wt.% of oil	9:1	60–75 °C, 1 atm	480	96.2[a]	Zhang et al. (2010a)
Soybean	DMC	Heterogeneous: 5 wt.% of oil, Homogeneous: 5 mol% of oil	2042 g oil, 782 g DMC and 632 g DMC with cat.	90 °C, 1 atm	300		Fabbri et al. (2007)
		Sodium methoxide (30% in methanol)				>99.5[b]	
		Na₂PEG (300)				>98[b]	
		Sodium hydride				<5[b]	
		1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD)				>99.5[b]	
		1,8-Diazabicyclo [5.4.0] undec-7-ene (DBU)				<5[b]	
		1,4-Diazabicyclo[2.2.2]octane (DABCO)				<5[b]	
		4-Dimethylaminopyridine				<5[b]	
		Hydrotalcite Pural Mg70				<5[b]	
		13X Zeolite				<10[b]	
		Titanosilicate ETS 10				<5[b]	
Rapeseed	Supercritical DMC	No catalyst	42:1	300 °C, 20 MPa	20	97.4[a]	Ilham and Saka (2012)
Palm	Supercritical DMC	No catalyst	39:1	380 °C	30	91[a]	Tan et al. (2010b)
Canola	DMC	TBD, 2.5 wt.% oil	3:1	60 °C, 1 atm	360	99.92[b], 99.45[a]	Kurle et al. (2013)
Pongamia pinnata	DMC	KOH catalyst, 4 wt.%	3:1	60 °C, 1 atm	360	96[a]	Panchal et al. (2013)
Soybean/Waste soybean/Sunflower/Jatropha curcas	Supercritical methyl acetate	No catalyst	42:1/42:1/42:1/42:1	345 °C, 20 MPa/345 °C, 20 MPa/345 °C, 20 MPa/345 °C, 20 MPa	50/50/50/50	100[a]/100[a]/100[a]/100[a]	Campanelli et al. (2010)
Rapeseed Oleic acid	Supercritical methyl acetate	No catalyst	42:1	350 °C, 20 MPa	45	91[a]	Saka and Isayama (2009)
Purified palm	Supercritical methyl acetate	No catalyst	30:1	399 °C	59	97.6[a]	Tan et al. (2010a)
Jatropha curcas	Sub-critical water + supercritical DMC	No catalyst	217:1/14:1	270 °C, 27 MPa/300 °C, 9 MPa	25/15	>97[a]	Ilham and Saka (2010)
Rapeseed/Oleic acid	Supercritical DMC/Supercritical DMC	No catalyst	42:1/42:1	350 °C, 20 MPa/300 °C,9 MPa	12/9	94[a]/90[a]	Ilham and Saka (2009)

[a] Yield.
[b] Conversion.

2007) in which glycerin-adduct, glycerin dicarbonate (GDC), is co-produced with DMC-biodiesel instead of low value glycerin. Interestingly, DMC based biodiesel is reported to have better lubricating properties vis-à-vis conventional biodiesel due to miscibility of formed by-product GDC in the DMC-biodiesel phase. In addition, the characteristics of produced DMC-biodiesel have been reported to be in good agreement with conventional methanol based biodiesel (Fabbri et al., 2007). In this method, the mutual solubility of oil and DMC does not require any solvent, and act as a solvent to overcome the mass transfer limitation between oil and alcohol as in the conventional method. However, DMC based transesterification synthesis is reported to have prolonged reaction time and high amount of catalyst owing to polarity difference between reactant and catalyst (Fabbri et al., 2007). Therefore, non-catalytic supercritical DMC process using vegetable oil as a feedstock has been attempted (Ilham and Saka, 2009, 2010). It is worthwhile to note that the reported process is a non-catalytic process, which offers the elimination of several cumbersome separation and purification steps as compared to conventional process. In addition, the by-products in supercritical synthesis such as glycerine carbonate (GC), glycerin di-carbonate (GDC), citramalic acid, and glyoxal (if FFA is present), obtained in this process are highly valuable adducts for biodiesel and diesel fuel instead low value glycerin in the conventional process (Ilham and Saka, 2009). A brief summary of the efforts made on glycerin free biodiesel synthesis via transesterification route is listed in Table 14.

On similar lines, the lipase-catalyzed transesterification has been reported using vegetable oil and DMC in presence of immobilized lipase Novozym 435 (Su et al. 2007). However, the high cost of the enzyme has limited the commercial exploitation of the process. Furthermore, supercritical methyl acetate method has been investigated to produce glycerin free biodiesel and triacetin (Saka and Isayama, 2009). As a result, the mixture of biodiesel and triacetin can be used entirely as a kind of biofuel due to their miscibility and similar improved fuel properties like DMC-biodiesel (Saka and Isayama, 2009). The two step biodiesel production process has also been investigated based on the hydrolysis of triglycerides in sub-critical water and followed by esterification of fatty acids in supercritical dimethyl carbonate in catalyst free route (Ilham and Saka, 2010). Although, these methods could produce the by-products with higher values, the severe reaction conditions may become a major concern in commercial application.

Energy consumption

Energy requirement for various operations and processes is essential for selection of any particular process. Very limited studies are available in literature pertaining to energy requirement for biodiesel production process. The comparative energy consumption of various processes is shown in Table 15.

Typically, overall biodiesel synthesis is endothermic reaction where heat is supplied by heating media to reaction mass and subsequently recovered through outlet stream. Energy requirement of the process varies with reaction condition, separation strategies for product/byproduct and number of operations involved. For this purpose, biodiesel processes are optimized with pinch analysis and heat integration to reduce the overall energy usage. In fact, it is a challenge to identify the optimal heat load, which needs to be removed and added from the hot and cold streams in the process, respectively. Therefore, heat integration options are prevailing for estimation of minimal energy requirements. Some of the studies have reported comparison of catalytic and non catalytic process.

Challenges & opportunities — biodiesel sustainability, GHG emission and economic viability

Biodiesel has bio-origin, which drives from vegetable oil (edible or non-edible) through chemical substitution using low molecular alcohol. In addition, it is eco-friendly, renewable and sustainable fuel which offer carbon neutral cycle by utilization emitting CO_2 in the growth of oil crops. Even, low molecular weight alcohols such as ethanol, can be derived from biomass via processes such as gasification of biomass and lingo cellulosic conversion of biomass to alcohol to complete the sustainability cycle.

India has over 300 different species of trees, which produces oil-bearing seeds and can manage WCO (waste cooking oil) by implementing policy (Subramanian et al., 2005; Azam et al. 2005). Thus, there is a

Table 15
Comparative energy consumption study for biodiesel production.

Feedstock	Mode	Molar ratio, methanol to oil	Catalyst, wt.% of oil	Operating condition	Conversion/yield, %	Total heat utility, (kWh kg^{-1} biodiesel) based on ASPEN simulation	Reference
Refined palm oil	Batch	5:1[a]	NaOH, 5%[b]	50–60 °C, 8 h	95	0.03[#]	Pleanjai and Gheewala (2009)
Soybean oil	Batch	6:1	NaOH, 1%	60 °C	97	4.01	Myint and El-Halwagi (2009)
Soybean oil	Two stage stirred tank	4.3:1	NaOH, 1.78%[c][d]	60 °C, 1 h	99	0.029	Haas et al. (2006)
Soybean oil	Microwave, Batch	–	–	80 °C, 20 min	98.64	0.049	Kanitkar (2010)
Rapeseed oil	Two reactors in series	6:1	NaOH, 1%	60 °C, 101.3 kPa, 1 h	99	0.419	Apostolakou et al. (2009)
Animal fat and soybean oil (50:50 v/v)	Batch	6:1/7.1:1 (esterification and transesterification)	HCl, 0.35–2.00% NaOH, 1%	60 °C, stirring rate: 600 rpm	71%[y] (dry wash) 81%[y] (wet wash)	0.224	Canoira et al. (2008)
Rapeseed oil	Supercritical, continuous reactor	40:1	Catalyst free	300 °C, 35 MPa, 30 min	95.1%[y]	0.91–1.05	Lim et al. (2009)
Triolein	Supercritical, reactive distillation	3.2:1	Catalyst free	270 °C, 7 MPa	99	0.152	Gomez-Castroa et al. (2010)
Refined canola oil	Batch	3:1[d]	Triazabicyclodecene, 2.5%	60 °C 101.3 kPa, 6 h	99.92, 99.45[y]	0.202	Kurle et al. (2013)
Oleic acid	Supercritical, Microwave, Batch	3–20:1	Catalyst free	150–225 °C, 3.7 min	60	0.06	Melo-Junior et al. (2009)

[a] v/v.
[b] w/v, NaOH:MeOH.
[c] w/w, NaOH:MeOH.
[d] DMC:oil.
[y] Yield.
[#] Case study data.

significant potential for non-edible oil and WCO for biodiesel production as an alternative to fossils fuel. In fact, Indian approach towards the development of biodiesel program is different than the other parts of world and depends exclusively on non-food feedstocks. These feed stocks to be raised on degraded/marginal or wastelands either that are not suited to agriculture, or diverted from stock, are banned for human consumption. Thus, it avoids a possible conflict of fuel vs. food debate (Kumar and Sharma, 2011).

Biodiesel can also provide support to farmers by providing an additional income for non-edible oil bearing seed crops, particularly those grown primarily for animal feed and other applications. Farmers can grow non-edible oilseed as energy crops annually with food crops such as wheat, rice and soybean. The practice of growing energy crops on marginal lands has become an important area of research, especially as concerns about fuel vs. food security and biodiversity mounts. Rural biodiesel production facilities may supply jobs and other sources of income to the surrounding and supplies local energy needs which could be a viable solution to energy needs. Moreover, in the future, second generation biofuels and biodiesel could use agricultural residues and other feedstocks that are not used as food.

In view of environmental perspective, the combustion of biodiesel has reported to emit less CO_2 or green house gas (GHG) and other pollutants (Gomaa et al., 2011). This indicates that the engine exhaust contains no SO_2, and shows decreasing emissions of PAH, CO, HC, soot and aromatics. The NOx emission is reported to be in less as compared to diesel depending on engines combustion characteristics. Hence, to understand utilization of bio-origin feed stock or biomass on greenhouse gas emissions, several researches have reported Life cycle assessment (LCA) of biodiesel for assessing the environmental impacts associated with biodiesel production using various feed stock (Siregar et al., 2014). The total environmental impact is 74% less in case of using WCO as raw material compared to non-edible Jatropha oil whereas total environmental impact for biodiesel production from palm oil is higher than that of Jatropha oil (Sajid et al.,, 2016; Siregar et al., 2014). Thus, research results of LCA may differ even for apparently similar biomass and bioenergy systems. Variations are due to several reasons: type and management of raw materials, conversion technologies, end-use technologies, system boundaries and reference energy system with which the bioenergy chain is compared. Furthermore, many key issues that can affect the outcome, such as carbon cycle of the feed stock and soil variation with time, nitrous oxide and methane emissions from agricultural activities; selection of the appropriate fossil reference system; homogeneity of the input parameters in Life Cycle Inventories; influence of the allocation procedure when multiple products are involved; future trends in bioenergy (i.e. second-generation biofuels and biorefineries) are also needed to take in account to draw any conclusion based on LCA study (Cherubini et al., 2009).

Despite the wide range of LCA results, it has been possible to draw some important conclusions and devise recommendations concerning the existing bioenergy systems, and some emerging implications about the future deployment and trends of bioenergy products.

Based on the aforementioned biodiesel production approaches, it is imperative that alternative process and technologies has better implementation potential owing to ease of separation and recycling of stream and catalyst, hassle less separation and purification of product/byproduct, high valued byproduct instead of low valued glycerin, simple downstream treatment procedures where less or no waste water generation and handling various stream through environmentally aspects. Furthermore, the cost of instruments and processing seems to be cheaper and less energy intensive in the discussed options than the conventional process considering treatment modules, separation and purification of generated derivatives.

Previously, economic studies have been performed for biodiesel production, incorporating various factors such as capital cost, manufacturing cost and biodiesel break-even price. The economic performance of a biodiesel plant (e.g., fixed capital cost, total manufacturing cost, and the break-even price of bio-diesel) can be determined once certain factors are identified, such as plant capacity, process technology, raw material cost and chemical costs (Zhang et al., 2003a, b; Rathore et al., 2015). However, biodiesel price majorly driven by feed stock cost, which is about 80% of the total operating cost. Other important costs are labor, methanol and catalyst, which must be added to the feedstock (Demirbas, 2009a,b). Out of various feed stocks available for biodiesel production, palm oil is the potential option which is traded internationally and available for import in the short term contract (Dene and Hole, 2006). The costs for biodiesel production from various feedstocks by manufactures are shown in Table 16.

Future perspective

Owing to stringent environmental norms, the implementation of biofuel programs is expected to increase worldwide, which is expected to add fuel growth of energy efficient and cost effective new commercial processes for vegetable oil processing from varied sourced options. Till date, the developed routes based on transesterification of vegetable oil for biodiesel production offer limitation w.r.t. feedstock impurity (i.e. FFA and gum) level and hence demand pre-treatment steps to counter impurity levels. Such steps coupled with glycerin purification steps are expected to lead to expensive proposition for vegetable oil processing for production of biodiesel. In view of this, glycerin free synthesis of biofuel production through vegetable oil could offer better option from commercial point of view. Thus, glycerin free biodiesel production through transesterification of vegetable oil can be integrated with non conventional options such as supercritical/microwave/cavitation/static mixture assisted processing to enhance the kinetics of reaction. For example, microwave coupled with static mixture approach assisted DMC-glycerin process can significantly enhance the reaction kinetic. This is mainly because of localized heating

Table 16
Summary of economic viability by commercial biodiesel producers.

Feed stock	Technology	Price range of feed stock, Rs/ton[b]	Price range of derived biodiesel, Rs/ton[b]	Producer details	Reference
WCO/UCO[a]	Multiple feed stock	49,600–52,700	62,000–65,100	Bio Max Fuels Limited, Hyderabad, India	Bio Max Fuels Limited
Palm fatty acid distillates		39,000–42,000	52,000–54,000		
Palm acid oil		34,000–36,000	49,000–52,000		
Palm oil stearin	–	38,000–40,000	48,000–51,000	Ruchi Bio Fuels Pvt. Ltd., Indore, India	Ruchi Biofuels Fuels Pvt. Ltd.
Palm oil stearin	–	38,000–40,000	48,000–51,000	Emami Agrotech Limited, Kolkata, India	Emami Agrotech Limited
Palm oil stearin	–	38,000–40,000	48,000–51,000	Kaleesuwari Refinery Pvt. Limited, Chennai, India/Naturol Bio-Chemicals &Foods Limited, Hyderabad, India	Kaleesuwari Refinery Pvt. Limited/Naturol Bio-Chemicals &Foods Limited
WCO	–	35,000–42,000	54,000–60,000	Eco Green Fuels Pvt. Ltd., Bangalore, India	Eco Green Fuels Limited

[a] Waste cooking oil/used cooking oil.
[b] Indicative price based on last two year (2013–2015) data. Conversion Rate, 1 USD = 65.06 Rs. as on 14.08.2015.
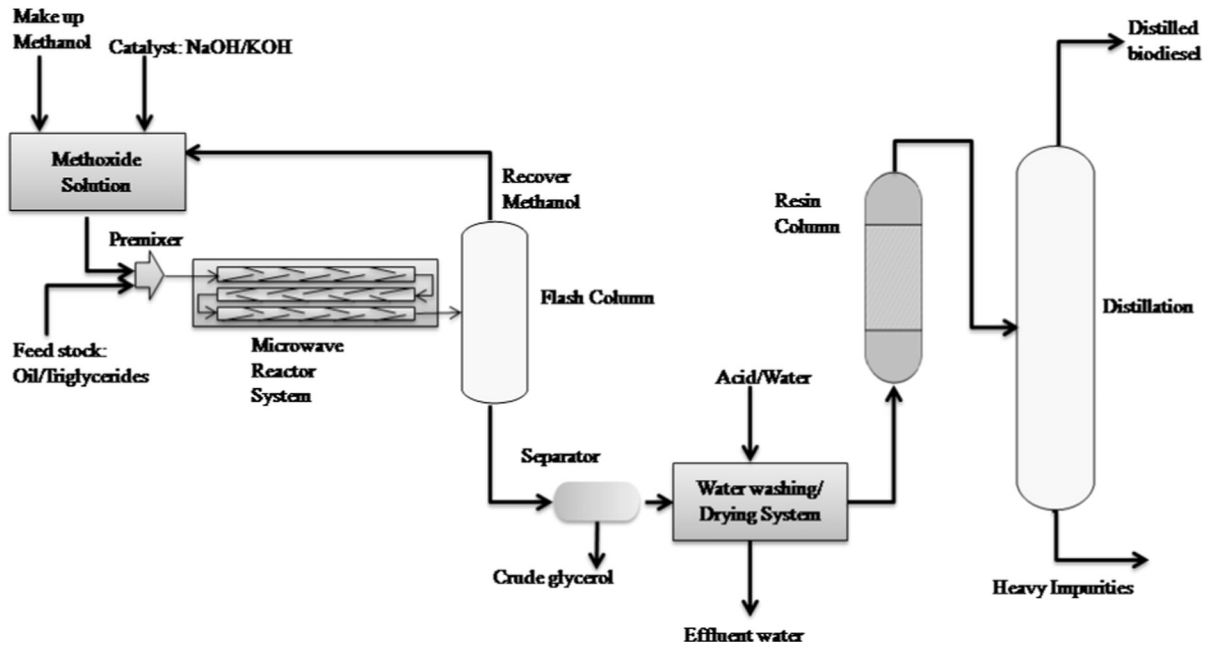
Fig. 5. Conceptualized process for microwave method.

of microwaves can favor better dissolution of catalyst which coupled with increased efficiency of reactant mixing in the presence of static mixture is expected to reduce the reaction time significantly. A conceptualize process is depicted in Fig. 5.

In this proposed process, combination of microwave heating system is coupled static mixer with for simultaneously getting the benefit of localized heating and intense mixing to propagate the fast reaction kinetics. The design of proposed reaction system required to have multiple static mixer element in series, made of microwave non absorber material where thickness of the holding concentric pipe is specially designed to avoid the loss of microwave penetration. The optimum frequency

needs to be zeroed in for safety purpose and optimal performance of the process. The pre-mixer, acid neutralization, washing and resin column are essential part of the process for overall plant efficiency.

Likewise, supercritical process coupled with static mixture feature for continuous production of dimethyl carbonate/diethyl carbonate (DMC/DEC)-biodiesel from commercial point of view can be envisaged (Fig. 6). The salient features of the proposed process are listed below:

• Simultaneously utilization of process intensification method viz. supercritical condition and static mixers
• Fast reaction kinetics thereby less reaction time

Fig. 6. Conceptualized process for non-catalytic glycerin free supercritical DMC/DEC method.

- No catalyst recovery, treatment owing to non-catalytic process
- Low space requirement due to size of reactor
- Less maintenance in the absence of mechanical moving assemblies

Typically, feed preparation unit is proposed prior to reaction to avoid downstream operational problems associated to gums and unsaponified matter presented in crude vegetable oil. The proposed process scheme consists of three sections i.e. feed preparation section, reaction section and product separation cum purification section. Thus, degummed oil can be subjected to supercritical attained reaction section where TGs enter with DMC in pre-determined molar ratio obtained from this study. The reactor section is proposed to consist of multiple continuous plug flow type reactor, having static mixer element to promote vigorous mixing where supercritical pressure can be achieved through high pressure pump and under vigorous stirred conditions by static mixer elements. The pre-determined reactant ratio at optimized reaction conditions can be utilized for production of glycerin free biodiesel in supercritical condition. The excess DMC recovery can be achieved via flash column operation for its recycle from the formed product. Subsequently, reacted mass can be left for settlement in a decanter where two layers of reaction mass will be formed where upper layer consists of biodiesel as well as GDC and lower layer consists of un-reacted oil, if any. The separated biodiesel can be used directly or further purified through reduced pressure distillation. The recovery of lighter component such as GDC from biodiesel can be envisaged based on the economic feasibility of the process. In the proposed process, proposed reactor design which is capable of coping the higher production capacity and lower operating costs can ensure the long term supply of biodiesel and overall economy. Though, the supercritical fluid technology requires high temperature and high pressure, it can provide the distinct advantage in comparison to conventional process. In fact, the key operating parameters such as oil concentration and the density of the mixture (depending on temperature, pressure and composition) in the supercritical phase, can be easily controlled and optimized under flow conditions.

The key features of the proposed process are envisaged in terms of recovery of (a) excess DMC/DEC using flash column and its recycling into the process without any treatment, (b) non-catalytic and no discrete operation viz. catalyst neutralization and separation is required, (c) no production of low valued glycerin and, (d) optional recovery of valuable by-product, GDC based on market demand for its derivatives.

On the other hand, hydroprocessing route for biofuel production is expected to demand development of new generation catalyst systems, which can either operate at less severe conditions especially from hydrogen management point of view as the hydrogen cost is expected to govern the overall process economics. Furthermore, catalyst formulation development with better hydrothermal stability and cycle life are highly essential for sustainability of hydroprocessing route.

In sum, glycerin free biofuel generation via vegetable oil processing can be integrated with either non-conventional routes or novel hydroprocessing catalyst developmental approach for economic competitiveness as the demand for biofuel increases in coming years.

Conclusion

Ever increasing demand for transportation fuel, depleting oil reserves and stringent emission norms have added impetus for development of processes for biofuel production. Among the targeted biofuels, biodiesel production processes have been well developed and commercialized. However, process economics of biodiesel production is often reported to be dependent on quality of by-product (glycerin) as well as process efficiency. The poor quality of by-product is reported to off-balance the entire value chain of biodiesel production. Therefore, based on detailed review, it is worthwhile to look at glycerin free production processes for biodiesel production as described in the present review. On the other hand, stand alone/Co-hydroprocessing routes are attractive but are energy intensive. Therefore, it is utmost important to address optimum balance between by-product quality and process intensity for selection of available routes for biodiesel production on sustainable basis.

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