

Chapter 2

Biodiesel and Fatty Esters

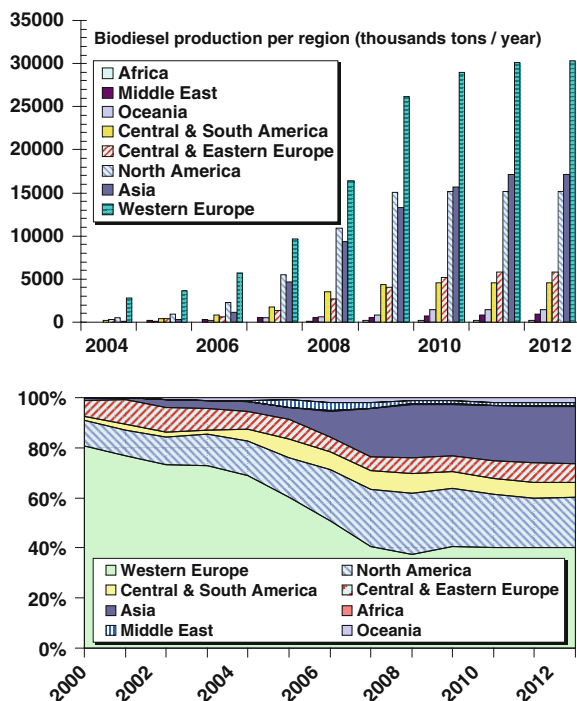
Abstract This chapter provides an overview of biodiesel (basically a mixture of fatty esters) as renewable fuel, covering the market developments and trends, chemical composition and characteristics, properties and performance, complementary use as diesel fuel, main synthesis routes (e.g. esterification or transesterification), various catalysts used for manufacturing (e.g. homogeneous, solid acids and solid base catalysts) and industrial production processes (e.g. batch, continuous, supercritical, enzymatic, multi-step, reactive separations).

Fatty esters are key products of the chemical process industry, involved in various specialty chemicals with applications in the food industry, cosmetics, pharmaceuticals, plasticizers, bio-detergents and biodiesel. However, the main interest has shifted nowadays to the larger scale production of biodiesel—a mixture of fatty acid alkyl esters—hence the current strong market drive for more innovative and efficient processes (Kralova and Sjoblom 2010).

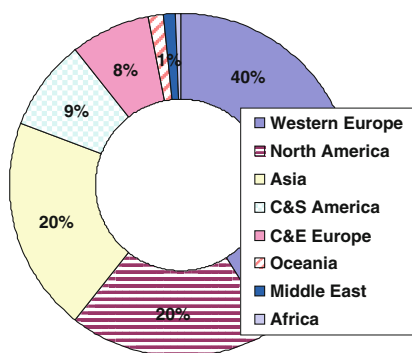
The increasing worldwide interest in biodiesel is illustrated by the tremendous increase of the production, mostly in Western Europe, North America and Asia—as shown in Fig. 2.1 (Blagoev et al. 2008; Kiss 2009). The market potential for biodiesel is actually defined and limited by the market size of the petroleum diesel. Remarkable, there is no major technical limitation on replacing fossil diesel with biodiesel, although a limitation on the feedstock—and the required arable farmland—availability does exist in practice.

The biodiesel market share suffered some changes during the recent decade, being now rather stabilized—as shown in Fig. 2.1 (bottom). An interesting development over the past years is the shift in global biodiesel market share. Europe had over 80 % capacity in 2000, but it is no longer the dominant player of the biodiesel industry, its global share accounting presently about 40 % of global capacity. Other key players emerged—such as Asia, North America, Central and South America—and they have leveled out the global biodiesel market shares. For a complete picture of the current status, Fig. 2.2 shows the biodiesel consumption worldwide and in EU (Kiss 2009). The biodiesel consumption worldwide is actually expected to grow at an average annual rate of over 5 % during 2011–2016 (Blagoev et al. 2008).

Fig. 2.1 Biodiesel production per region and the global biodiesel market share



Biodiesel consumption worldwide



Biodiesel consumption in EU

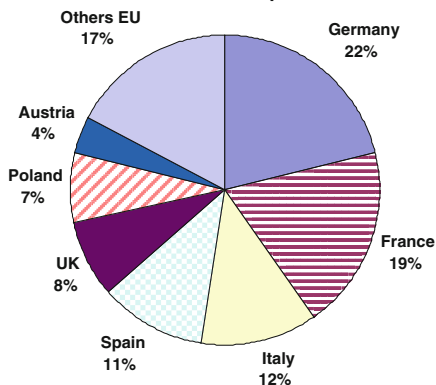


Fig. 2.2 Biodiesel consumption worldwide (*left*) and in EU (*right*)

Biodiesel is an alternative renewable and biodegradable fuel with properties similar to petroleum diesel (Bowman et al. 2006; Balat et al. 2008; Knothe 2010). Actually it has several advantages over petroleum diesel: it is safe, renewable, non-toxic and biodegradable; it contains no sulfur and is a better lubricant. Despite the chemical differences these two fuels have similar properties and performance

Table 2.1 Properties of petroleum diesel versus biodiesel

Fuel property	Diesel	Biodiesel
Fuel standard	ASTM D975	ASTM D6751
Fuel composition	C ₁₀ –C ₂₁ HC ^a	C ₁₂ –C ₂₂ FAME ^a
Kinetic viscosity, mm ² /s (at 40 °C)	1.3–4.1	1.9–6.0
Specific gravity, kg/l	0.85	0.88
Boiling point, °C	188–343	182–338
Flash point, °C	60–80	100–170
Cloud point, °C	–15 to 5	–3 to 12
Pour point, °C	–35 to –15	–15 to 10
Cetane number (ignition quality)	40–55	48–65
Stoichiometric Air/Fuel Ratio (AFR)	15	13.8
Life-cycle energy balance (energy units produced per unit energy consumed)	0.83/1	3.2/1

^a HC hydrocarbons, FAME fatty acid methyl esters

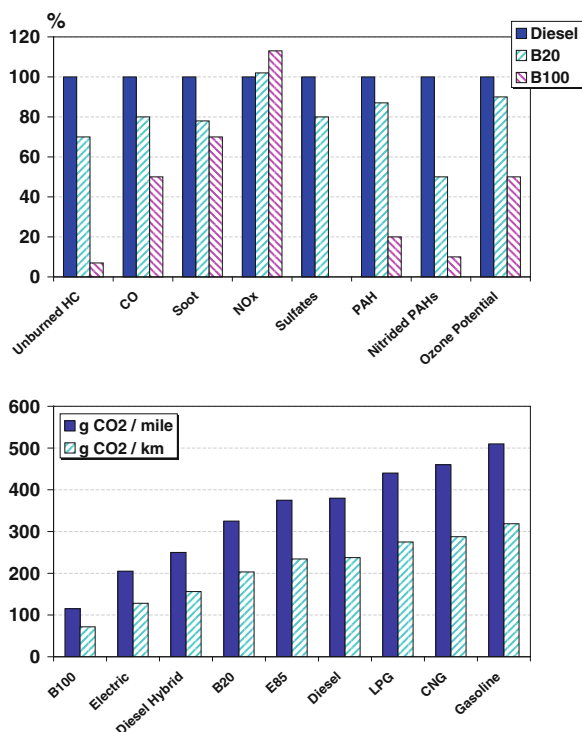
parameters—as shown in Table 2.1 (Kiss et al. 2008). Along with its technical advantages over petroleum diesel, biodiesel brings several additional benefits to the society: rural revitalization, creation of new jobs, and less global warming.

An important characteristic of diesel fuels is the ability to auto-ignite, quantified by the cetane number (cetane index). Biodiesel not only has a higher cetane number than petroleum diesel, but also a higher flash point meaning better and safer performance. Blends of biodiesel and petroleum diesel are designated by a ‘B’ followed by the vol. % of biodiesel. B5 and B20—the most common blends—can be used in unmodified diesel engines. The presence of oxygen in biodiesel (~ 10 %) improves combustion and reduces CO, soot and hydrocarbon emissions, while slightly increasing the NO_x emissions. Figure 2.3 shows the biodiesel versus petroleum diesel emissions, as well as the amount of CO₂ per distance produced by various fuels (Kiss et al. 2008). Remarkable, using B20 in trucks and buses would completely eliminate the black smoke released during acceleration and thus contribute to a cleaner air in urban areas.

2.1 Biodiesel Production Routes

Biodiesel is a mixture of fatty acid alkyl esters, produced mainly from green sources such as vegetable oils, animal fat or even waste cooking-oils from the food industry (Encinar et al. 2005; Kulkarni and Dalai 2006; Kulkarni et al. 2006; Knothe 2010; Lam et al. 2010; Maddikeri et al. 2012;). Remarkable, waste cooking-oils are much less expensive than virgin vegetable oil, and a total of over 25 million tons of waste cooking oil is generated annually, mainly in United States, China, Europe, Malaysia, Japan, Canada (Maddikeri et al. 2012). Moreover, the controversial ‘food versus fuel’ competition (Knothe 2010) can be completely avoided when the raw materials used are waste vegetable oils (wvo)

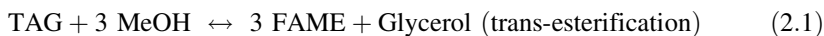
Fig. 2.3 Biodiesel versus petroleum diesel emissions (*top*). Comparison of CO₂ emissions for most common fuels (*bottom*)



with high free fatty acids (FFA) content, non-food crops such as *Jatropha* (Kumar and Sharma 2005; de Oliveira et al. 2009; Kaul et al. 2010) and *Mahua* (Puhan et al. 2005; Kapilan and Reddy 2008; Jena et al. 2010), or even castor oil (da Silva et al. 2009; Canoira et al. 2010).

At present, employing waste and non-edible raw materials is mandatory to comply with the ecological and ethical requirements for biofuels (Feofilova et al. 2010; Nigam and Singh 2011). However, waste raw materials can contain a substantial amount of free fatty acids (Demirbas 2009; Maddikeri et al. 2012). Accordingly, the development of very efficient processes (e.g. based on reactive separation technologies) is required for the fatty esters manufacturing, in which the use of a solid catalyst is especially wanted in order to suppress the costly chemical processing steps and waste treatment (Sharma et al. 2011a, b).

As a non-petroleum-based diesel fuel, biodiesel consists of fatty acid methyl esters (FAME), currently produced by the trans-esterification of tri-alkyl glycerides (TAG) with methanol leading to glycerol by-product, or the esterification of free fatty acids (FFA) with methanol leading to water by-product. The main equilibrium reactions can be summarized as follows:



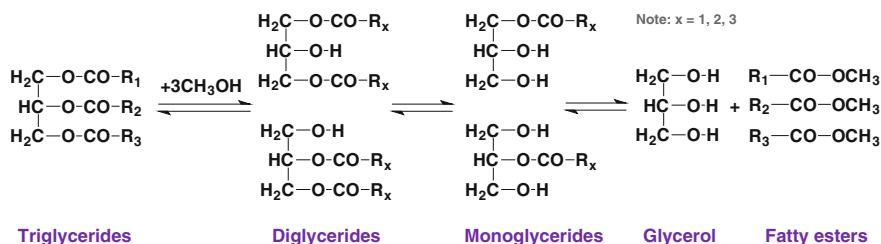
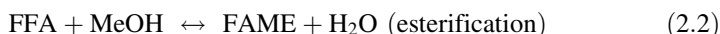


Fig. 2.4 Trans-esterification reaction of triglycerides with methanol



The esterification reaction is typically acid catalyzed and it is rather simple. However, the trans-esterification reaction is actually more complex, proceeding with the formation of di-glycerides and mono-glycerides as intermediates, as illustrated in Fig. 2.4 (Abdullah et al. 2007). Glycerol is obtained as a by-product of the trans-esterification, typically about 10 %wt of the total amount of FAME. An excess of glycerol is therefore available on the market and it is urgent to find new convenient uses for glycerol, thus reducing also the cost of biodiesel production. Several options can be used to consume the large amount of glycerol deriving from biodiesel (Santacesaria et al. 2012), such as the use of glycerol for making commodities (e.g. glycerol hydrochlorination to chlorohydrins, or glycerol dehydration to acrolein) and for producing oxygenated additives for fuels (e.g. ethers, esters, acetals, and ketals).

In general, the trans-esterification is base catalyzed while the esterification is catalyzed by acids—although alternative acid/base catalysts could be used but at prohibitive reaction rates. The reaction time can be dramatically shortened by increasing the liquid–liquid interfacial area by various process intensification techniques (e.g. static mixers, micro-channels reactors, microwaves assisted reactors, ultrasound assisted reactors, rotating/spinning tube reactors and centrifugal contactors) or by integrating the reaction and separations steps to pull the equilibrium to full conversions (e.g. catalytic reactive distillation). After the FAME synthesis stage, there are several down-stream processing steps required for catalysts neutralization and salt removal, alcohol recovery and recycle, as well as glycerol and biodiesel purification (Hanna et al. 2005; Meher et al. 2006; Narasimharao et al. 2007; Santacesaria et al. 2012).

2.2 Catalysts for Fatty Esters Synthesis

The conventional biodiesel production is still dominated by the use of homogeneous alkaline catalysts (e.g. NaOH, KOH, K/NaOMe), leading to severe economical and environmental penalties due to the problems associated with their use

(Shahid and Jamal 2011; Atadashi et al. 2013). Development of heterogeneous catalyst such as solid and enzymes catalysts could overcome most of the problems associated with homogeneous catalysts. Presently, there is a tremendous interest in using solid (heterogeneous) catalysts instead of the conventional homogeneous ones for biodiesel production. A solid catalyst can be used in a (rotating) packed bed continuous reactors having better performance as compared to CSTRs (Chen et al. 2010). Moreover, the costly catalyst separation operations can be greatly reduced. Solid catalysts are also essential to the development of reactive-separation units for biodiesel production. Lotero et al. (2005), Helwani et al. (2009), Lee and Saka (2010), Singh and Sarma (2011), Sharma et al. (2011a, b), published recently specialized reviews about using solid catalysts in the biodiesel synthesis, while Refaat (2011) focused on using solid metal oxide catalysts such as: alkali earth metal oxides, transition metal oxides, mixed metal oxides and supported metal oxides. Clearly, these solid catalysts create new opportunities for the biodiesel production by reactive separation processes, such as catalytic reactive distillation.

The trans-esterification of tri-alkyl glycerides could be carried on in the presence of aluminosilicates as showed by Mittelbach et al. (1995) who compared the activity of layered aluminosilicates with sulfuric acid. However, the activity of the solid catalysts was lower and dependent on the operating conditions. The impregnation with sulfuric acid increased the performance of the catalysts, complete tryglicerides conversion being achieved after 4 h, at 220 °C and 52 bar. Nonetheless, leaching compromised the reusability of these catalysts. Kaita et al. (2002) used aluminium phosphate with various ratios of metal to phosphoric acid. The authors claim good activity and selectivity, while the catalyst appears to be stable. However, high temperatures (200 °C) and a large excess of methanol were still necessary.

The literature concerning the use of solid catalyst for esterification of fatty acids is much more abundant. Ion exchange resins such as Amberlyst and Nafion were proved to be effective (Chen et al. 1999; Heidekum et al. 1999), but swelling was the main problem associated with use of organic resins because it controls the accessibility of the acidic sites and therefore the reactivity. Moreover, most ion-exchange resins are not thermally-stable at high temperatures (Steinigeweg and Gmehling 2003; Kiss et al. 2006a, b), providing only limited reaction rates. Zeolites allow tailoring the catalytic properties by choosing the appropriate crystal structure, pore size, Si/Al ratio and acidic strength (Kiss et al. 2006a, b). Nevertheless, the mass transfer might impose limitations on the overall rate of the process. As a consequence, only the large-pore zeolites proved to be successful (Corma et al. 1994). Heteropoly acids supported on silica molecular sieves such as MCM41, were effective for gas-phase esterification (Verhoef et al. 1999; Mbaraka et al. 2003) under mild operating conditions (110 °C) leading to 95 % alcohol conversion. Recently, sulfated zirconia proved its activity for several acid-catalysed reactions (Yadav and Nair 1999; Omota et al. 2003a, b; Kiss et al. 2006a, b, 2008).

Table 2.2 presents an overview of the available solid acid and base catalysts for the fatty esters production by (trans-)esterification (Kiss 2010). These solid

Table 2.2 Benefits and drawbacks of acid and base catalysts tested for (trans-)esterification

Catalyst type	Benefits	Drawbacks
Ion-exchange resins (Nafion, Amberlyst)	Very high activity Easy regeneration	Low thermal stability Possible leeching
TungstoPhosphoric Acid ($H_3PW_{12}O_{40}$)	Very high activity	Soluble in water
TPA-Cs salt ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$)	Super acid sites	Low activity per weight
Zeolites (H-ZSM-5, Y and Beta)	Controllable acidity and hydrophobicity	Small pore size Low activity
Sulfated metal oxides (zirconia, titania, tin oxide)	High activity Thermally stable Water tolerant	Deactivates in water, but not in organic phase Average activity
Niobic oxide (Nb_2O_5)	Low temperatures	Long reaction times
Calcium oxide/CaO	High yield, reusable	High reactants ratio
Calcium methoxide/ $Ca(OMe)_2$	High yield, short times	High reactants ratio
Calcium ethoxide/ $Ca(OEt)_2$	Low temperatures	Long reaction times
Li-doped zinc oxide/ZnO	Good initial performance	Incomplete yields
KF, KI, K_2CO_3	Short reaction times	Subject to leeching
KF-Eu $_2O_3$, KNO $_3$ -Al $_2O_3$	High or moderate activity: $La_2O_3 > MgO \gg ZnO \sim CeO_2$	Basic strength of the active sites on surface
Single metal oxides (La_2O_3 , MgO, ZnO, CeO_2)	Increased surface basicity	Incomplete yields
Mixed/supported metal oxides(Al_2O_3 -SnO $_2$, Al_2O_3 -ZnO, MgO- La_2O_3)	Resistance to FFA/moisture	
Mg-Al hydrotalcites	High activity, no leeching Resistance to FFA/moisture	Slow deactivation (fouling)
Stearates of Cd, Mn and Pb	Good yield, short times	High temperatures

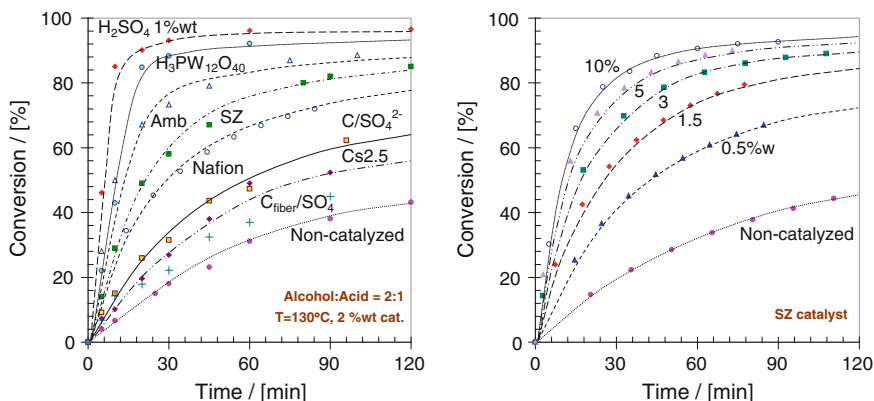


Fig. 2.5 Conversion profiles for the esterification of dodecanoic acid with 2-ethylhexanol, using various acid catalysts (*left*), and catalyzed by SZ (*right*)

catalysts are described at large in several reviews and research papers (Kiss et al. 2006a, b; Narasimharao et al. 2007; Di Serio et al. 2008; Helwani et al. 2009; Jothiramalingam and Wang 2009; Melero et al. 2009; Lee et al. 2009; Lee and Saka 2010; Refaat 2011; Semwal et al. 2011; Sharma et al. 2011a, b; Endalew et al. 2011; Singh and Sarma 2011; Santacesaria et al. 2012; Atadashi et al. 2013).

Figure 2.5 (left) provides the conversion profiles for several acid catalysts tested for the fatty esters production by esterification, such as: tungstophosphoric acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) and its cesium salt (Cs2.5), Amberlyst-15, a styrene-based sulfonic acid, Nafion-NR50, a copolymer of tetrafluoroethene and perfluoro-2-(fluorosulfonylethoxy)-propyl vinyl ether, sulfated carbon-based catalysts (carbon fiber, mesoporous carbon), sulfated zirconia and other metal oxides (Kiss et al. 2006a, b, 2008). Sulfated zirconia (SZ) is well known for its industrial applications in a variety of processes and it can be modified with sulfate ions to form a superacidic catalyst, depending on the treatment conditions. By increasing the amount of SZ catalyst used the reaction rate, hence conversion after a certain time, can be further increased—as shown by Fig. 2.5, right (Kiss et al. 2006a, b)—making this catalyst suitable for reactive separations applications where high activity is required in a rather short time. Moreover, SZ is also very selective, thermally stable, and the re-calcination of the used catalyst can restore its original activity (Kiss et al. 2006a, b, 2008).

Although the reaction mechanism for the heterogeneous acid-catalysed esterification was shown to be in principle similar to the homogeneously catalysed one, there is an important difference that concerns the relationship between the surface hydrophobicity and the catalysts activity. This is especially true when both reactants (fatty acid and alcohol) are very lipophilic compounds. Three cases are possible, as illustrated in Fig. 2.6 (Kiss et al. 2006a, b). First, in case of one isolated Brønsted acid site surrounded by a hydrophobic environment, it is likely that the hydrophobic tail of the fatty acid would be adsorbed parallel to the

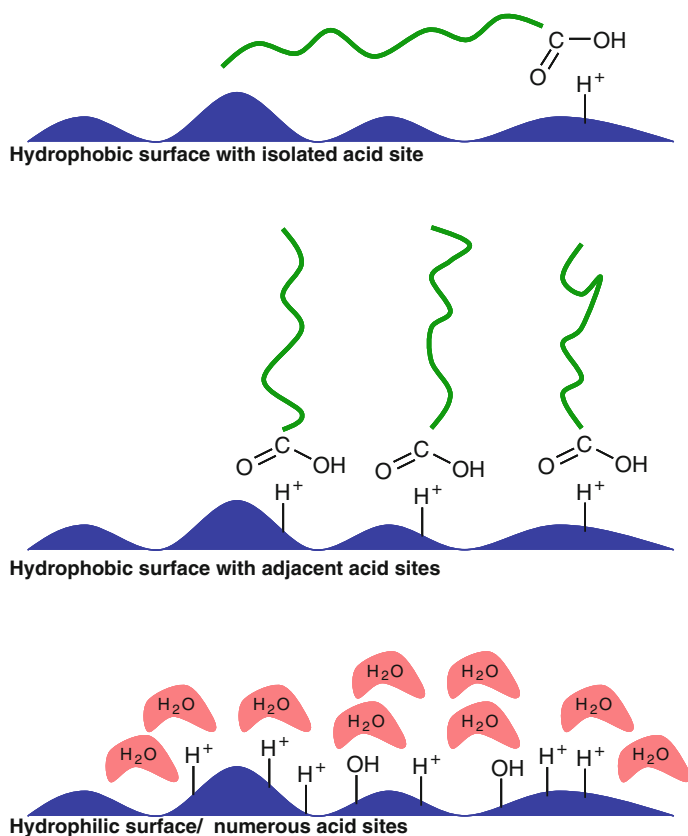


Fig. 2.6 Cartoon of the influence of the surface hydrophobicity on the catalytic activity

hydrophobic surface. Second, if there are a few acid sites in the vicinity, the fatty acid molecules could adsorb perpendicular to the surface, with the tails forming a local hydrophobic environment. Finally, in the case of a very acidic and/or hydrophilic material (many adjacent acid sites and/or hydroxy groups), the by-product water from the esterification would adsorb on the surface, and the catalyst would lose its activity since the water layer would prevent the access of fatty acid and alcohol to the catalyst (Kiss et al. 2006a, b).

Recently, Patel et al. (2013) reported the synthesis of sulfated zirconia and its characterization by various physico-chemical techniques such as energy-dispersive X-ray spectroscopy (EDS), thermal analysis using thermo-gravimetric analysis (TGA) and derivative thermo-gravimetry (DTG), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction analysis (XRD), Brunauer-Emmett-Teller (BET) surface area measurement, scanning electron microscope (SEM) and n-butyl amine acidity determination. The use of SZ catalyst was explored for the biodiesel production by esterification of oleic acid with methanol. Moreover, the

influence of various reaction parameters—such as catalyst concentration, acid/alcohol molar ratio, catalyst amount, reaction temperature and reaction time—on the catalytic performance was studied to optimize the conditions for maximum yield of 90 % methyl oleate. Remarkable, it was also possible to regenerate and reuse the catalyst.

Based on the brief literature review, it can be concluded that many solid acids and solid base catalysts are available for the biodiesel production by esterification and trans-esterification.

2.3 Industrial Biodiesel Processes

As vegetable oil is currently still too expensive, the current trend is to use less expensive raw materials. However, the use of new feedstock containing large amounts of fatty acids requires novel or improved processes for obtaining FAME through esterification of FFA and trans-esterification of tri-glycerides. At present, the most common biodiesel technologies employ homogeneous catalysts (Vicente et al. 2004; Narasimharao et al. 2007), in either batch or continuous processes where both the reaction and separation steps can create bottlenecks.

The literature overview reveals several key biodiesel processes, currently in use either at pilot and/or industrial scale (Kiss 2010, 2011; Santacesaria et al. 2012). For convenience, we provide here a brief summary of these processes, based on the catalyst type (such as homogeneous, heterogeneous, dual function, enzymatic catalysts, and catalyst-free) and the biodiesel production process type (e.g. batch, continuous, integrated):

1. *Batch processes* are conventionally used for the trans-esterification of triglycerides, using an acid or base catalyst. High quality virgin oil is required as raw material (<1 % FFA), otherwise a pre-treatment step is compulsory to remove the free fatty acids (Santacesaria et al. 2012). A key advantage of the batch processes is the good flexibility with respect to composition of the feedstock, but the equipment productivity is rather low and the operating costs are quite high (Hanna et al. 2005; Lotero et al. 2005). While rather simple and useful, requiring mild operating conditions (ambient pressure and temperatures lower than 100 °C), these batch processes are practically not suitable for the large-scale production of biodiesel.
2. *Continuous processes* combine both esterification and trans-esterification steps, allowing higher productivity. Nonetheless, most of these processes are still plagued by the drawbacks of using homogeneous catalysts although solid catalysts emerged in the last decade (Dale 2003; Kiss et al. 2006a, b; Yan et al. 2010; Sharma et al. 2011a, b). Several reactive distillation processes were also reported (He et al. 2005, 2006; Kiss et al. 2006a, b, 2008; Dimian et al. 2009)—as clearly illustrated in Fig. 2.7 (www.yellowdiesel.com). A commercial alternative is the ESTERFIP-H process developed by the French Institute of

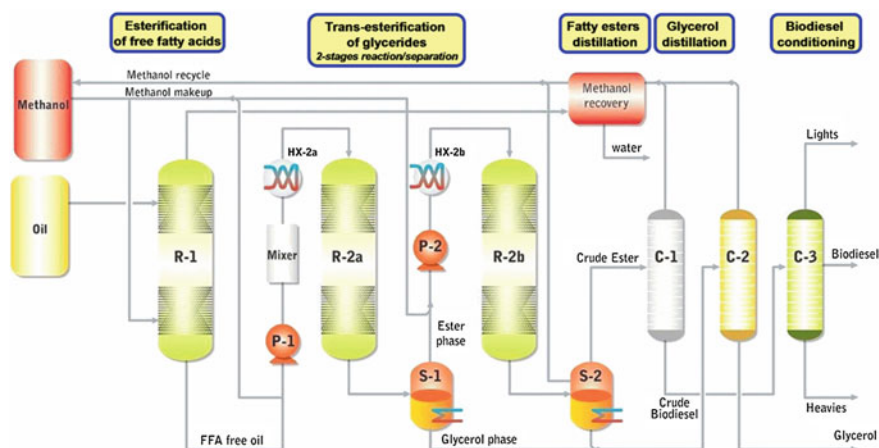
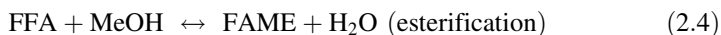
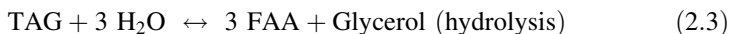


Fig. 2.7 Biodiesel production process combining esterification and trans-esterification

Petroleum (Bournay et al. 2005). This is a gas-phase process that uses a solid catalyst based on Zn and Al oxides, requiring temperatures of 210–250 °C and high pressures of 30–50 bar. As major drawbacks, the ESTERFIP-H process requires high quality refined oil and high reaction temperatures.

3. *Supercritical processes* were developed to solve the problem of oil-alcohol miscibility that hinders the kinetics of trans-esterification, as well as to take advantage of not using a catalyst at all. The operating conditions are quite severe ($T > 240$ °C, $p > 80$ bar) and therefore require special equipment (He et al. 2007; Gomez-Castro et al. 2011). However, at high temperatures, the esterification and trans-esterification reactions occur together without any problems, and the reaction rate is not affected by the presence of water by-product. The recent study of Lee and Saka (2010) emphasized the potential of non-catalytic supercritical processes and review the current status and challenging issues. Future process developments could further reduce the reaction time, by operating in the presence of a catalyst, at lower temperature and pressure—in order to render this technology more economically attractive.
4. *Enzymatic processes* have low energy requirements, as the reaction is carried out at mild conditions—ambient pressure and temperatures of 50–55 °C (Lai et al. 2005; Su et al. 2007, 2009; Chen et al. 2008; Dussan et al. 2010). However, due to the lower yields and long reaction times the enzymatic processes can not compete yet with other industrial processes (van Gerpen 2005; Demirbas 2008). In addition, research efforts are also carried out on using algae or microbial mass as raw materials (Liu and Zao 2007; Francisco et al. 2010).
5. *Multi-step processes* are somewhat simpler, as the tri-glycerides are hydrolyzed first to fatty acids that are subsequently esterified to their corresponding fatty esters in a second step (Kusdiana and Saka 2004; Minami and Saka 2006):



These processes are now very attractive and gain market share due to obvious advantages: high purity glycerol is obtained as by-product of the hydrolysis step, and the esterification step can be performed in conventional reactors or using solid acid catalysts in various integrated reactive-separation units (Kiss et al. 2008; Kiss 2009, 2011). Also, the use of solid catalysts avoids the neutralization and washing steps, leading to an overall simpler and more efficient process. Note that in the case when the raw materials consist mainly of FFA, only the esterification step is actually required.

6. *Reactive-separation processes* are based on esterification or trans-esterification reactions, carried out in the presence of liquid or solid catalysts, in integrated units such as: reactive distillation, reactive absorption, reactive extraction, membrane reactors or centrifugal contact separators (Kiss 2011, 2013a, b; Kiss and Bildea 2012). These integrated processes offer high conversion and selectivity, as well as increased energy efficiency. Reactive separations are the main object of this work, and therefore described in details over the next chapters.
7. *Hydro-pyrolysis processes* employ a fundamentally different chemical route as compared to the previously described manufacturing methods. Tri-glycerides are converted to fuel by hydrogenation followed by pyrolysis. The key difference is that the fuel product (second-generation biodiesel) is a mixture of long-chain hydrocarbons instead of the conventional fatty esters (Snare et al. 2009). Considering this difference of chemical composition, the correct name for this fuel product should be green-diesel and not biodiesel. The process is known as NExBTL (biomass to liquid) and it was invented by the Finnish company Neste Oil (Maki-Arvela et al. 2008; Snare et al. 2009). While it has clear advantages, this process requires more complex equipment and implies the availability of a low-cost hydrogen source.

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