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Intensified processes for FAME production from waste cooking oil: a technological review

Alex Mazubert, Martine Poux, Joelle Aubin

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Intensified processes for FAME production from waste cooking oil: A technological review

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H I G H L I G H T S

- Intensified technologies are reviewed to transform waste cooking oil in fatty acid methyl esters.
- Intensified technologies are compared on mass-transfer limited reactions.
- The possible catalysts and the anticipation of the downstream separation steps are discussed.
- A summary table is proposed to compare the different technologies.

A B S T R A C T

This article reviews the intensification of fatty acid methyl esters (FAME) production from waste cooking oil (WCO) using innovative process equipment. In particular, it addresses the intensification of WCO feed-stock transformation by transesterification, esterification and hydrolysis reactions. It also discusses catalyst choice and product separation. FAME production can be intensified via the use of a number of process equipment types, including as cavitation reactors, oscillatory baffled reactors, microwave reactors, reactive distillation, static mixers and microstructured reactors. Furthermore, continuous flow equipment that integrate both reaction and separation steps appear to be the best means for intensifying FAME production. Heterogeneous catalysts have also shown to provide attractive results in terms of reaction performance in certain equipment, such as microwave reactors and reactive distillation.

Keywords:
Process intensification
Biodiesel
Waste cooking oil
Transesterification
Esterification
Hydrolysis

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1. Introduction

1.1. Context and objectives

Biological resources are currently the best alternative to fossil fuels or petrochemical solvents for renewable energy and green chemistry applications. The production of biodiesel, composed of fatty acid methyl esters (FAME), has received much attention in research over the last 15 years as it is an organic, biodegradable and non-toxic fuel source that is made from renewable resources such as vegetable oils and animal fats. Although virgin and food-grade oils have proven to be suitable feedstocks for biodiesel production, the use of edible vegetable oils evokes the 'food versus fuel' debate on the use of widespread farmland areas for biofuel production in detriment of food supply [1]. Furthermore, in addition to increasing food demands the increasing demand for oil for biofuel production could ultimately lead to deforestation and desertification [2]. The use of non-edible crops, such as jatropha or castor oil, avoids the direct competition for food oils but does not resolve the problem of requiring large plantation land areas [3]. This competition explains the high price of edible oils, representing about 60–90% of the process cost [4]. Waste cooking oil (WCO) as a potential renewable feedstock appears to be an economically and environmentally viable solution for FAME production and presents a number of advantages: e.g. WCO are two to three times cheaper than virgin oils [5], the recycling of WCO reduces waste treatment costs [6], and the quality of the FAME is the same as that produced with virgin oils [7]. In France, the release of waste oils in sewage is prohibited and governmental legislations require waste cooking oils from restaurants and food industries to be collected for recycling and disposal (France, article R. 1331-2, public health code [8]). In the UK, the collect of waste cooking oil is strongly supported for reducing costs of waste disposal and for the production of renewable energy (Food standards Agency [9]). In the USA, several companies and communities (e.g. Restaurant Technologies Inc. [10], Shakopee Mdewakanton Dakota Community [11]) provide solutions for waste oil management and recycling.

Although the main use of FAME is biodiesel, many other industrial applications exist [12]. Indeed, FAME possess good solvent properties with low volatility, as well as being biodegradable and non-toxic. As a result, FAME have been used to wash metal pieces [13], printing material, graffiti [14], automobiles and plane parts [15], as well as for cleaning up oil spills [16]. FAME are also used as binders in inks [17], as well as thinning agents for building and civil engineering work [18]. Other applications include the production of pesticides [19] and phytosanitary products [20].

Numerous publications on FAME production are available in the current literature and most of these studies focus on various aspects of the transesterification reaction. Amongst these, a number of reviews have concentrated on the different ways to catalyze the transesterification reaction [21–26] and particularly with calcium oxide [27] or heterogeneous catalysis [28–31]. Some papers have also focused on the different means for pre-treating WCO before

transesterification [6,7,21,23]. Qiu et al. [32] reviewed process intensification technologies for biodiesel production via homogeneous base-catalyzed transesterification. Talebian-Kiakalaieh et al. [33] and Maddikeri et al. [34] reviewed novel biodiesel processes using WCO feedstocks. Emerging processes for biodiesel production are also reviewed by Oh et al. [35]. A number of authors also discuss acoustic cavitation, microwaves [22,24,26,36], membrane reactors and reactive distillation [37] as means to intensify the transesterification reaction for FAME production. Finally, the methods for separation and purification of biodiesel at the outlet of the reactor have been discussed by Leung et al. [21], Enweremadu and Mbarawa [23], and Atadashi et al. [38].

The objective of this article is to critically review the different intensified process equipment available and adapted to the global FAME production process and to evaluate their use for the transesterification reaction, as well as the pretreatment reactions (i.e. esterification and hydrolysis) in the case where WCO is used as feedstock. In particular, reaction performance, mass transfer enhancement, ease of separation, possible catalyst types (acid or base, homogeneous or heterogeneous) and energy efficiency of the equipment are discussed. Finally, recommendations on the choice of intensified process equipment for FAME production are given.

In this review the discussion and evaluation of the capacities of various intensified process equipment for FAME production (Sections 2 and 3) is preceded with technical information on the related reactions, catalysis, WCO regeneration, and conventional industrial processes (Sections 1.2–1.4) as introductory material.

1.2. Reactions and catalysis

In the biodiesel industry, vegetable oil is usually transformed into FAME by transesterification. In this reaction, triglyceride reacts with alcohol to give FAME and glycerol, as shown in Fig. 1. Typically, methanol is preferred as the alcohol because of its higher reactivity and low price [21].

This reaction is catalyzed using either homogeneous or heterogeneous, acid or basic catalysts, or enzymes. Various catalysts exist and have been well described in a number of recent reviews [21–26,36]. Table 1 summarizes the strengths and weaknesses of the

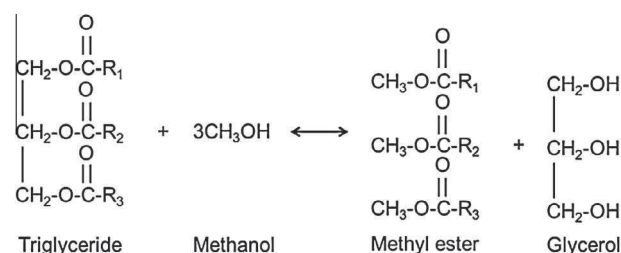


Fig. 1. Transesterification reaction scheme.

Table 1
Comparison of the different types of catalysis of the transesterification reaction [22].

Type of catalyst	Advantages	Disadvantages
Homogenous base	<ul style="list-style-type: none"> – Very fast reaction rate – Mild reaction conditions 	<ul style="list-style-type: none"> – Sensitive to FFA content – Soap formation (causing yield to decrease and increase difficulty for product and catalyst separation)
Heterogeneous base	<ul style="list-style-type: none"> – Inexpensive – Faster than acid-catalyzed reaction – Mild reaction conditions – Easy separation of catalyst – Easy reuse and regeneration of catalyst 	<ul style="list-style-type: none"> – Poisoned at ambient air – Sensitive to FFA content – Soap formation – Leaching of catalyst causing contamination of product – Energy intensive
Homogeneous acid	<ul style="list-style-type: none"> – Insensitive to FFA and water content – Simultaneous esterification and transesterification possible – Mild reaction conditions 	<ul style="list-style-type: none"> – Very slow reaction rate – Corrosive catalysts (e.g. H₂SO₄)
Heterogeneous acid	<ul style="list-style-type: none"> – Insensitive to FFA and water content – Simultaneous esterification and transesterification – Easy separation of catalyst – Easy reuse and regeneration of catalyst 	<ul style="list-style-type: none"> – Separation of catalyst is difficult – Complicated reaction synthesis leading to higher processing costs – High reaction temperature, high alcohol to oil molar ratio, long reaction times – Energy intensive – Leaching of catalyst causing contamination of product
Enzyme	<ul style="list-style-type: none"> – Low reaction temperature (lower than for homogenous base catalysts) – Only one purification step necessary 	<ul style="list-style-type: none"> – Very slow reaction rate – High costs – Sensitive to alcohol (typically methanol, causing deactivation)

different catalyst types. In industrial FAME processes, homogeneous alkali catalysts (e.g. KOH, NaOH) are the most often used. These inexpensive catalysts lead to short reaction times and are easy to handle in terms of transportation and storage [36]. However, base-catalyzed transesterification is very sensitive to the presence of free fatty acids (FFA) in the oil, which leads to undesired soap formation. Soap formation decreases the reaction yield and facilitates the formation of emulsions, thereby causing difficulties in the downstream separation process [3,39]. Consequently, it is generally recommended that the acidity of the oil must be less than 1 mg KOH/g oil [6,23]. Alkali catalysis is also sensitive to presence of water, forming inactive alkaline soaps [40]. Water content is therefore limited to 0.05 vol.% (ASTM D6751 standard) [21]. It is important to point out that the FFA content is very different in unused vegetable oils compared with WCO. Cooking processes and the presence of water cause the hydrolysis of triglycerides, which increases the FFA content in the oil [3,41]. The absence of oxygen at high temperatures causes thermolytic reactions whereas oxidative reactions occur if air is dissolved [22], thereby changing the composition of the oil. Polymerization and saponification can also occur [7]. Furthermore, the viscosity, surface tension and color of virgin oils change after the cooking processes [42]. Unlike base-catalyzed transesterification, acid-catalyzed transesterification is insensitive to FFA content. However, it is associated with a number of disadvantages, for example the need of higher reaction temperatures and alcohol to oil molar ratios, the difficulty of catalyst separation, as well as serious environmental and corrosion issues [22]. Most importantly, the reaction rate of acid-catalyzed transesterification has been reported to be 4000 times slower than that using alkalis [43]. This has been proven in a number of studies: e.g. a base-catalyzed transesterification carried out at 65 °C, a methanol to oil molar ratio of 6:1, and 1% w/w of KOH has shown to give a 96.15% yield in 1 h [44] whereas an acid-catalyzed transesterification carried out at 65 °C, a methanol to oil molar ratio of 30:1% and 1% w/w of sulfuric acid has shown to give 90% yield in 69 h [45].

As summarized in Table 1, heterogeneous catalysis offers a number of advantages over homogenous catalysis and in particular, the ease of catalyst separation and the possibility to reuse and regenerate it. However, in industrial practice, heterogeneous catalysts are less widely used due to the high temperatures required, the problems related to catalyst leaching, and their sensi-

tivity to FFA and water content [46]. Nevertheless, recently studies show that a novel heterogeneous catalyst, strontium oxide (SrO), gives faster reaction rates than the usual homogenous catalyst types, such as potassium hydroxide [46,47]. The yield is greater than 95% at 65 °C in 30 min of reaction time in presence of 3 wt.% of SrO and the activity is retained for 10 cycles [47]. A SrO/SiO₂ catalyst leads to a 95% conversion in 10 min and even with about 3 wt.% of FFA and water, the conversion is still greater than 90% in 20 min [46]. One of the main advantages of this novel alkali heterogeneous catalyst is that it allows WCO treatment with less strict requirements: indeed, SrO can catalyze the transesterification of WCO even if the FFA and water content are greater than the limits required for conventional homogeneous base-catalysts (3 wt.%).

1.3. Regeneration of waste cooking oil

Since the interest in WCO for biofuel production has increased in recent years, there is an increased need for the reduction of FFA in WCO. Indeed, if the FFA content of WCO is too high (superior to 1 mg KOH/g oil), the transesterification conversion rate is insufficient and too much soap is produced, hindering the separation of glycerol and ester. In such cases, a pretreatment step is required to regenerate the WCO, thereby improving its quality in terms of FFA and water content in detriment of increased processing costs [23]. As described in a recent review [36], many physical methods for reducing FFA, moisture and solids content in WCO exist. Moisture can be removed by drying (with MgSO₄, calcium chloride, ion exchange resins), by filtration (under vacuum, through a chromatography column, silica gel or cellulose fiber, under microwave irradiation), with steam injection and sedimentation treatment, as well as by distillation. FFA content can be reduced by the neutralization and the separation of soaps in a decanter, membrane filtration [48], and solvent extraction (particularly with anhydrous methanol or ethanol) [49]. Filtration is typically used for the removal of suspended solids and water washing is employed for the separation of soluble salts from the WCO [6].

Chemical pretreatment methods are another way to reduce FFA content. Three alternatives exist for FAME production. The first is acid-catalyzed esterification shown in Fig. 2. The esterification of

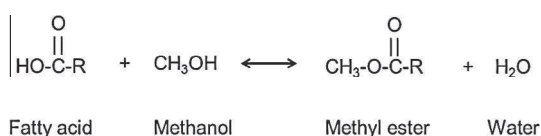


Fig. 2. Reaction scheme for the esterification of fatty acids with methanol to methyl esters and water.

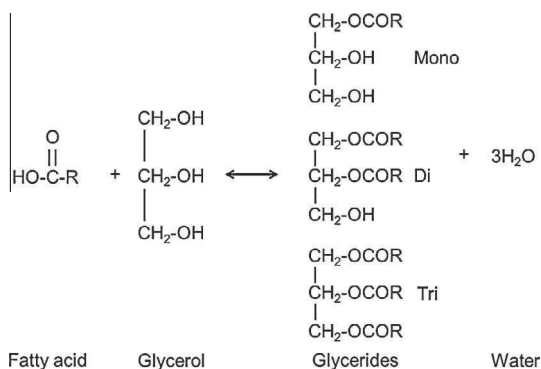


Fig. 3. Reaction scheme of the esterification of fatty acids with glycerol to glycerides and water.

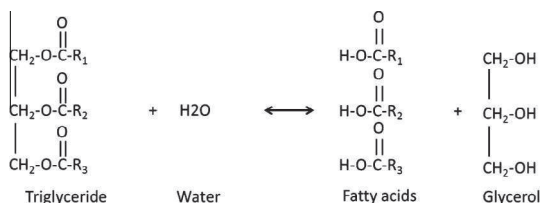


Fig. 4. Reaction scheme of the hydrolysis of triglycerides to fatty acids and glycerol.

FFA in WCO is a solution to reduce the level of FFA in the oil before performing the transesterification.

Esterification typically uses methanol (or ethanol) but glycerol may also be employed [50] as shown by the reaction scheme, given in Fig. 3. This direct esterification of fatty acids with glycerol is of particular interest since the WCO is not only regenerated but the FFA levels are also reduced using glycerol, which is the side-product of the biodiesel reaction. Another industrial application of this reaction is production of monoglycerides [51]. A number of recent studies have focused on the development of various heterogeneous catalysts for this reaction including zinc [50], Fe-Zn double-metal cyanide catalyst [52], and solid superacid $\text{SO}_4^{2-}/\text{ZrO}_2 - \text{Al}_2\text{O}_3$ [53] leading to acceptable conversion at 200 °C and under atmospheric pressure after 3–4 h reaction time. Enzymatic catalysis has also been explored and has shown to give about 90% conversion in about 80 h with immobilized lipase (*Rhizomucor miehei*) [54] and a 96.5% yield is obtained in 72 h with Novozym 435 [55].

Another chemical route for the regeneration of WCO and the production of FAME is hydroesterification. In this reaction the, FFA are first concentrated via hydrolysis as shown in Fig. 4, and then transformed to FAME via esterification. Continuous hydrolysis processes have existed in industry for many years (e.g. Colgate-Emery, Foster-Wheeler). They are typically conducted at high temperature (260 °C) due to the absence of catalyst and at high pressures (50 bar) to maintain the reactants in a liquid state, enabling thus 98% conversion [56,57]. More recently, Satyarathi et al. [58] obtained 80% of FFA at 190 °C with a solid catalyst (Fe-Zn) in 12 h. Hydroesterification thus combines the well-known hydrolysis process with fatty acid esterification. It is currently used in commercial biodiesel plants in Brazil [59].

It is interesting to point out that all three reactions related to FAME production (i.e. transesterification, esterification and hydrolysis) involve a reaction between two immiscible reactants and are mass-transfer limited. Further, a numbers of similarities can be found between these three reaction types. A comparison of performance of these different reactions in conventional processes is given in the next section.

1.4. Conventional processes

Before entering the discussion on the various intensified process equipment for FAME production, it is important to highlight the characteristics of existing FAME production or related processes using conventional equipment, such as stirred tank reactors, packed beds and columns.

Table 2 gives typical examples of process characteristics of transesterification and esterification reactions performed in laboratory-scale stirred tank reactors. The most important features of these reactions are the immiscibility (or partial miscibility) of the reactants and products, and the reaction time for acceptable conversion, which is of the order of a couple of hours in these small scale reactors.

At the level of industrial production, the French Institute of Petroleum (IFP) has developed both a discontinuous and a continuous process for transesterification using a homogenous alkali catalyst [62]. The discontinuous reactor operates at temperatures between 45 and 85 °C with a maximum pressure of 2.5 bar and produces 80,000 tons of FAME per year. The time required to reach thermodynamic equilibrium is on the scale of 1 h and the yield is between 98.5% and 99.4%. The continuous process leads to similar yields and the production capacity is superior to 100,000 tons per year. A continuous heterogeneous base-catalyzed transesterification process named ESTERFIP-H™ has also been developed by IFP [62]. The catalyst is a zinc aluminate spinel ($\text{Zn Al}_2 \text{O}_4$), the operating temperature and pressure ranges between 180–220 °C and 40–60 bar, respectively. The yields achieved are greater than 98%. In Brazil, there are a significant number of biodiesel plants in operation. One example is the biodiesel plant in Belém-PA-Brazil that started up in April 2005. This plant produces 12,000 ton/year using a heterogeneous catalytic esterification of fatty acids in a fixed bed reactor and involves several steps of chemical reaction and product separation [59].

Examination of the literature data on the performance of laboratory and industrial processes highlights that transesterification, esterification and hydrolysis are all limited by mass transfer. In the case of transesterification, the mass transfer limitation [63] results in reaction times of the order of a couple of hours for desired conversion (up to 96.5%) [60,64]. Indeed, the reaction rate is limited by the immiscibility of triglycerides and methanol at the beginning of the reaction and then because the glycerol phase separates out taking most of the catalyst with it as the reaction proceeds [66]. This latter point is confirmed by kinetics, which show that the reaction rate is sigmoidal, i.e. slow at both the beginning and end of the reaction but fast at an intermediate stage [67]. Indeed, the initial immiscibility between reactants rapidly disappears because of the formation of diglycerides and monoglycerides, which play the role of emulsifier [68]. As the mono and diglycerides appear, the size of the dispersed phase droplets decreases and then increases as glycerol is formed [67]. The size of droplets (and consequently the interfacial area) therefore directly influences the reaction rate [69]. Esterification with both methanol and glycerol is limited by mass transfer due to the low solubility between the reactants [70,71]. Partial miscibility is observed with short-chain fatty acids and equilibrium can be shifted with an excess of reactant or the removal of the product. In hydrolysis, high temperatures allow higher oil solubility in

Table 2
Comparison of the characteristics of the different reactions in conventional processes [50,60,61].

Reaction	Catalyst	Reactor	Miscibility			Operation conditions		Reaction time and conversion		Reference
			Reactants	During the reaction	Products	T (°C)	P (atm)	t (h)	c (%)	
Transesterification	Base/ Homogenous	1.5 L glass cylindrical reactor	No	Yes	No	60	1	1	88	[60]
Esterification (with Methanol)	Acid/ Homogenous	0.5 L three neck round bottom flask	Low	Low	Low	60	1	1.5	96.6	[61]
Esterification(with Glycerol)	Acid/ Heterogeneous	Lab scale stirred reactor	No	Partial (increased with high temperatures)	No	200	1	3	90	[50]

water and a better electrolytic dissociation of water, both of which improve mass transfer. Equilibrium can also be shifted using an excess in water [56] or by removing product.

The use of process intensification equipment for FAME production provides a means to reduce the mass transfer limitations related to transesterification, esterification and hydrolysis with less energy consumption, as well as under safer and cleaner conditions. A step towards integrating process intensification in biofuel plants is illustrated by the Biobrax plant (Bahia, Brazil), which produces 60,000 tons of biodiesel per year by hydroesterification [72]. The process is based on a combination of a counter current splitting column and reactive distillation with a heterogeneous catalyst operated at 260 °C. Although distillation is an energy demanding operation, the reactive distillation step has the advantage of combining the reaction and separation steps of the esterification, providing thus a more efficient and cleaner process. Indeed, it has been shown under batch conditions, where the reaction and separation steps are carried out consecutively, that the time required to separate the ester product from the glycerol is sixteen times greater than the time required reach 95% conversion [44].

2. Process equipment for the intensification of FAME production

A number of means to intensify processes exist and these involve a range of equipment types and methods, including microreaction technology, multifunctional reactors and novel activation techniques like microwaves and ultrasounds [73,74]. In this section, the use of process intensification techniques that are adapted to liquid–liquid mass transfer limited reactions, such as transesterification, esterification and hydrolysis are reviewed and assessed. In the following sections, yield is defined by the relation:

$$y = n_{\text{FAME}}/3n_{\text{TG}} \quad (1)$$

y is the yield, n_{FAME} is the number of moles of FAME and n_{TG} is the initial number of moles of triglycerides.

Conversion is defined by the relation:

$$c = (n_{\text{TG initial}} - n_{\text{TG final}})/n_{\text{TG initial}} \quad (2)$$

c is the conversion (%), $n_{\text{TG initial}}$ is the initial number of moles of triglycerides and $n_{\text{TG final}}$ is the final number of moles of triglycerides.

2.1. Microreactors

Microreaction technology for chemical and biological applications has undergone major technical and scientific development since the mid-1990s and these miniaturized reaction systems have now proven, through both research and industrial practice, to provide innovative and sustainable solutions for the chemical and process industries [75,76]. Due to the small characteristic dimensions and the extremely high surface to volume ratio of these reactors, heat and mass transfer are remarkably intensified

and the temperature within can be tightly controlled. These features make microreactors particularly adapted to mixing limited, highly exo/endermotic and/or mass transfer limited reactions.

Microreactors are of particular interest for performing immiscible liquid–liquid reactions because they potentially offer very high interfacial area between phases, thereby improving the rate of mass transfer [77]. Indeed, mass transfer enhancement is highly dependent on the liquid–liquid flow regime and droplet size, which depend not only on the physical properties of the fluids (viscosity, density, interfacial tension. . .) but also the operating conditions, the reactor geometry, as well as the properties of the construction material (e.g. wettability, roughness) [76]. In liquid–liquid flow, two types of flow regimes typically occur, namely slug-flow and parallel flow as depicted in Fig. 5 [77,78]. The slug-flow pattern is characterized by drops of uniform size, separated by uniform lengths of the continuous phase. Two mechanisms contribute to the mass transfer process: convection within the dispersed drops and the continuous phase slugs due to the creation of recirculation flow patterns [77,79] and diffusion between adjacent slugs of dispersed and continuous phases. Mass transfer can be enhanced by increasing the interfacial area and the intensity of recirculation in the slugs, which depend on operating conditions. Parallel flow consists of two continuous streams of the dispersed and continuous phases flowing parallel to one another, without convective mixing. Here, the rate of mass transfer is governed by the diffusive mechanism and depends directly on the characteristic size of the fluid streams and therefore the microreactor geometry. The fact that no droplets are formed means that phase separation at the reactor outlet is relatively easy [80]. It is worthwhile point out that the interfacial area and intensity of internal recirculation in slug flow can be modified by changing the flow rate in a given microreactor, whereas in parallel flow the interfacial area is determined by the characteristic dimension of the microreactor geometry or microchannel.

For the transesterification reaction, a microreactor may be a viable choice because the reaction is limited by mass transfer and the

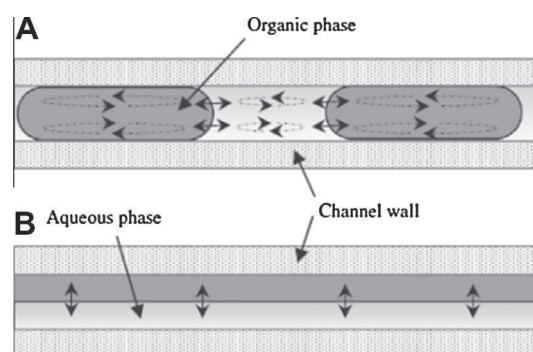


Fig. 5. Types of liquid–liquid flow patterns in microreactors: (A) slug flow; and (B) parallel flow [78].

small characteristic size of microreactors allows high interfacial areas between phases to be obtained. In transesterification, the reactants (e.g. methanol and glycerides) are immiscible at the beginning of the reaction, an emulsion of fine droplets (or pseudo-homogenous phase) is obtained during the reaction, and then at the end of the reaction the products (esters and glycerol) form two distinct and immiscible phases again [69]. The emulsion of fine droplets formed during the course of the reaction (depicted in Fig. 6) is specific to transesterification and due to the formation of mono and diglycerides [68]. Table 3 shows a typical advantage of microreactors over batch reactors in the fact that a smaller emulsion droplet size is achieved in a shorter processing time [81], which means that higher conversion in a shorter time can be achieved in microreactors.

A number of studies in the literature have demonstrated the feasibility of using microreactors for improving the performance of transesterification reactions. Table 4 compares the different data available for a homogeneous base-catalysed transesterification reaction in terms of reaction and flow conditions, microreactor characteristics and reaction performance.

From the ensemble of these data, it can be seen that it is very difficult to correlate reaction conditions, flow conditions and microreactor characteristics. However, a general observation for all results can be made being that very high yields and conversions can be obtained for the transesterification within just a few minutes in the microreactor, compared with a reaction time of the order of an hour in conventional batch conditions [81]. This can be attributed to the small droplet size and large interfacial area obtained almost immediately in the microreactor.

Although it is not directly clear from the results in Table 4, the characteristic dimension of the microreactor (typically the diameter of the microchannel) has an important effect on the reaction

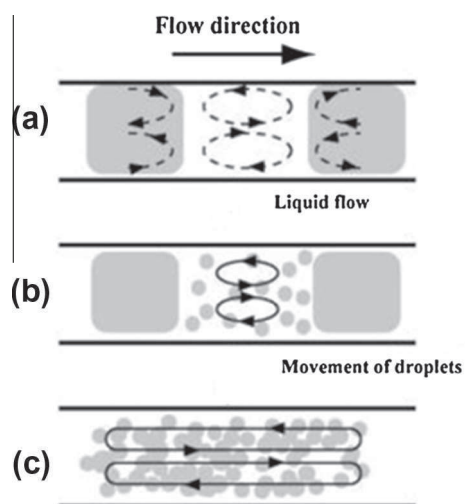


Fig. 6. Evolution of liquid-liquid flow patterns over the course of a transesterification reaction in a microreactor. (a) Slug flow whereby the reactants form two distinct phases; (b) Beginning of emulsion formation in the continuous phase due to the production of mono- and di-glycerides; and (c) Emulsion during the course of the reaction, before phase separation of products. [82].

Table 3
Influence of the type of reactor on the droplets mean diameter (dm) for the transesterification reaction [94,81].

Type of reactor	Operating time (min)	dm (μm)
Batch (250 mL)	3	12.9
(two flat-blade paddle agitator)	60	5.1
Microreactor ($d = 140 \mu\text{m}$)	0.5	1.9

performance as it directly influences drop size and interfacial area. This effect of miniaturisation is clearly illustrated in Table 5. As the microreactor diameter decreases from 2 mm to 250 μm , the interfacial area increases 8-fold. Further, the yield increases whilst the residence time remains fixed, which shows that the increased reaction performance is directly due to the effects of miniaturisation.

Although reaction performance improves with decreasing drop size, the downside is that phase separation at the outlet of the reactor becomes more difficult if an emulsion is formed. Indeed, smaller drop size typically signifies a more stable dispersion [86]. Nevertheless, it has been shown that the separation of transesterification products is almost instantaneous for slug and parallel flow [83,84] in continuous microreactors due to the relatively large size of the slugs/streams compared with droplets in an emulsion formed in batch tanks.

In addition to transesterification reactions, microreactors have also shown to be effective for use in the pretreatment step of WCO via acid-catalyzed esterification for the reduction of FFA. Table 6 [87] summarizes the reaction performance of an esterification and a transesterification both carried out with an acid catalyst in a microreactor. The novelty of this work is that the same acid catalyst is employed for both the esterification and the transesterification, which means that the final catalyst neutralization and separation steps are not required. The results show that in the first step of acid-catalyzed esterification, the FFA present in the oil is esterified in 7 min. The second step is the acid-catalyzed transesterification, which has very slow reaction rate in conventional systems (e.g. 90% conversion in 69 h with 1%w sulfuric acid), but demonstrates a dramatic decrease in reaction time in the miniaturized system, with a 99.9% yield obtained in only 5 min [87].

There are no studies on the esterification of fatty acids with glycerol in microreactors reported in the literature. Indeed, operating temperatures above 200 $^{\circ}\text{C}$ are conventionally employed to increase solubility between the reactants. Microreaction technology may therefore be an attractive alternative to current processes since the high interfacial area and the excellent heat transfer characteristics of microreactors could provide mass transfer enhancement with reduced energy consumption. The hydrolysis of triglycerides has however been demonstrated in a microreactor (0.65 mm diameter) using immobilized enzymes at 25 $^{\circ}\text{C}$. Although the reaction yield is particularly low at this temperature – only 16.8% – it is ten times greater than that obtained in a batch reactor [88]. It can therefore be inferred from these results that the improved reaction performance in the microreactor is due to the miniaturization effects and increased interfacial area between phases.

Table 7 presents the advantages and drawbacks of microreactors for the different reactions involved in FAME production. In summary, the literature data show that the miniaturization of reactors clearly has a positive effect on mass transfer limited reactions principally due to an increase in the interfacial area between phases. For the best performance of these reactors, it appears important that process parameters be controlled such that an emulsion (i.e. small drop sizes) is formed during the reaction for the enhancement of reaction rates and that slug or parallel flow patterns are formed before the reactor outlet to facilitate the separation of products. The combination of parallel flow and the continuous extraction of one of the products (e.g. glycerol or water, depending on the reaction) also appears as an attractive means to shift reaction equilibrium, as shown by Jachuck et al. [84] for base-catalyzed transesterification. The effects of miniaturization have also shown to provide new ways to perform the reactions, e.g. the use of a common catalyst and reactor for the both the pretreatment of high FFA content feedstock via esterification and FAME production via an acid-catalyzed transesterification, which takes only 5 min compared with tens of hours in conventional

Table 4

Results obtained for homogeneous base-catalyzed transesterification in microreactors. *y*: yield (%), *c*: conversion (%), *R*: molar ratio methanol:oil, *t*: residence time (min), *w*: weight fraction of catalyst (%), *T*: temperature (°C), ϕ : reactor dimension (mm), *F*: flow-rate (mL/h). I: beginning of the reaction, II: during the reaction, III: end of the reaction, s-f: slug-flow, e: emulsion, p: parallel flow [81–85].

Oil	Catalyst	Performance		Reaction conditions				Type of reactor	Flow-pattern			Material	ϕ	<i>F</i>	Reference
		<i>y</i>	<i>c</i>	<i>R</i>	<i>t</i>	<i>w</i>	<i>T</i>		I	II	III				
Cottonseed (0.8% FFA)	KOH	99.4	–	6	6	1	60	Micromixer + Tube	s-f	–	s-f	Quartz	0.25	14.7	[83]
Soybean	NaOH	99.5	–	9	0.47	1.2	56	Zigzag microchannel	e	e	e	Stainless steel	0.24	8.1	[81]
Canola	NaOH	–	99.8	6	3	1	60	T-mixer + Tube	–	s-f	p	Teflon	1.5	231	[84]
Sunflower	KOH	–	100	23.9	1	4.5	60	T-joint + tube	s-f	e	e	FEP	0.8	8.2	[82]
		–	59.3	4.6	3.7	4.5	60	T-joint + tube	s-f	e	s-f	FEP	0.8	8.2	[82]
		–	100	23.9	1.6	4.5	40	T-joint + tube	s-f	e	s-f	FEP	0.8	8.2	[82]
		–	97	11.3	0.83	4.5	60	T-joint + tube	–	–	–	FEP	0.8	8.2	[82]
Soybean	KOH	–	100	6	1.5	3.32	60	T-joint + Slit-channel	s-f	s-f	s-f	Nylon	2 × 152.4 × 1	12.2	[85]

Table 5

Influence of the characteristic dimension of the microreactor on interfacial area, *a*, and on reaction yield. ϕ : reactor dimension (mm), *F*: flow-rate (mL/h), *a*: interfacial area, *y*: yield (%) [83].

ϕ (mm)	<i>F</i> (mL/h)	<i>t</i> (min)	<i>a</i> (m ² /m ²)	<i>y</i> (%)	Reference
2	706.7	8	2000	78.6	[83]
0.53	48.4	8.2	7547	96.7	
0.25	14.7	6	16,000	98.8	

equipment. The use of microreactors for mass transfer enhancement in hydrolysis reactions has also been demonstrated and is certainly a means for improving the performance of the esterification of glycerol.

The drawback of the use of microchannels and capillary tubes is the low flow rate capacity, which typically ranges from about 10–200 mL/h. However, commercial microreaction technology equipment exist (e.g. reactors by Corning Inc. [89], Chart® [90], Ehrfeld® [91], IMM® [92]) and allow high flow rate capacities up to 10 L/h, which may be more suitable to FAME production at an industrial scale. Indeed, the performance of these reactors for FAME production has rarely been studied and the enhancement of reaction rates and mass transfer due to miniaturization, as well as the ease of product separation are still yet to be demonstrated.

2.2. Cavitation reactors

Cavitation is the generation, growth and collapse of gaseous cavities, which causes the release of large levels of energy in very small volumes, thereby resulting in very high energy densities. The phenomena can occur at millions of locations in the reactor simultaneously, thereby generating conditions of very high local temperature and pressures at overall ambient conditions. The generation of cavities is caused by pressure variations and occurs when the local pressure is less than the saturation pressure. Four techniques exist for the generation of cavitation: acoustic, hydrodynamic, optical and particle. Acoustic and hydrodynamic cavitation are the most commonly employed techniques since the intensity of optic and particle cavitation is insufficient for FAME production. In acoustic cavitation, ultrasounds produce pressure variations in the liquid. Hydrodynamic cavitation, on the other hand, is generated by creating a sudden variation in velocity due

to a change in the geometry of the system (e.g. an orifice or venturi). For detailed general information on cavitation and existing technologies, the reader is referred to reviews by Gogate et al. [93–95].

When using cavitation to activate liquid phase reactions, two mechanistic steps can be identified. Firstly, the cavity, which contains vapor from the liquid phase or dissolved volatile gases, collapses. The collapsing of the cavity induces extreme temperatures and pressures causing molecules to fragment and generate highly reactive radical species. These species react either within the collapsing bubble or in the bulk liquid. Secondly, the sudden collapse results in an inrush of the liquid, which fills the void and produces shear forces in the surrounding bulk liquid that are capable of breaking the chemical bounds of any molecules. For liquid–liquid reactions, such as transesterification, the cavitation collapse near the liquid–liquid interface causes the rupture of the interface and enhances mixing. This results in very fine emulsions that are typically more stable than those obtained in conventional reactors [93]. Indeed, the creation of such fine emulsions, and therefore high interfacial area between reacting phases, enables mass-transfer limited reactions such as transesterification, esterification or hydrolysis to be greatly enhanced.

Tables 8, 9 and 10 present the performance of esterification, transesterification and hydrolysis reactions activated via acoustic and hydrodynamic cavitation, respectively. Indeed, acoustic cavitation has been more widely studied than hydrodynamic cavitation and a detailed reviews of acoustic cavitation as a means for intensifying FAME production have been given in Gole and Gogate [94], Veljkovic et al. [96] and Badday et al. [97]. Ultrasonic cavitation using heterogeneous catalysts have also been reviewed by Ramachandran et al. [98] (see Tables 10 and 13).

In Table 8 it can be seen that the residence time of base-catalyzed transesterification reactions in the presence of ultrasounds is around 15–20 min for most of the cases and only a few minutes or seconds for others. This is significantly shorter than reactions times achieved in conventional reactors that are on the order of one hour. Another interesting point is that short reaction times and high yields can be achieved even at ambient temperature. On the other hand, the reaction time of acid-catalyzed esterification at overall ambient temperatures and pressures is not improved with acoustic cavitation. The heterogeneous superacid clay catalyst used gives

Table 6

Results obtained for acid-catalyzed esterification in microreactors. *y*: yield (%), *c*: conversion (%), *R*: molar ratio methanol:oil, *t*: residence time (min), *w*: weight fraction of catalyst (%), *T*: temperature (°C), ϕ : tube diameter (mm), *F*: flow-rate (mL/h) [87].

Reaction	Oil	Catalyst	Performance		Reaction conditions				Type of reactor	Material	ϕ	<i>F</i>	Reference
			<i>y</i>	<i>c</i>	<i>R</i>	<i>t</i>	<i>w</i>	<i>T</i>					
Esterification	Cottonseed (54% FFA)	H ₂ SO ₄	99.1	–	30	7	3	100	Micro-mixer + Tube	Stainless steel	1.2	12	[87]
Transesterification	Cottonseed (0.8% FFA)	H ₂ SO ₄	–	99.9	20	5	3	120	Micro-mixer + Tube	Stainlesssteel	1.2	12	

Table 7

Advantages and drawbacks of microreactors for transesterification, esterification with methanol and glycerol, as well as hydrolysis reactions.

Microreactors	Advantages	Drawbacks
Transesterification	– short reaction times – control of the flow pattern to increase mixing during the reaction and to facilitate the separation at the outlet of the reactor	– Low flow rates (10–200 mL/)
Esterification (with methanol)	– short reaction times – possibility to keep the same catalyst to transform the remaining glycerides after a pretreatment step	
Esterification (with glycerol)	<i>No studied</i>	
Hydrolysis	– Positive effect	– Yield still low with enzymatic catalysis

long reaction times of about 7 h for a conversion of 97%. Furthermore, the conversion was found to be only 41% when the catalyst is regenerated and reused a second time for a new reaction under the same conditions [110]. The feasibility of glycerol esterification of fatty acids with a homogenous acid catalyst in an ultrasonic reactor has also been demonstrated [111]. Although 98.5% conversion is obtained after a reaction time of 6 h and a temperature of 90 °C, these conditions are better than those required in conventional batch reactors (Gomes and Vergueiro [50] obtain a 90% conversion in 3 h with a molar ratio of fatty acid to glycerol of 3 at 220 °C, and Robles Medina et al. [55] obtain a 96.5% yield in 72 h with an enzymatic catalyst). Indeed, glycerol esterification typically requires high temperature conditions and good mass transfer, and cavitation (via the generation of localized hot spots) appears to be a promising way for enhancing the reaction. The generation of local-

ized hot spots at overall ambient operating temperatures is also the principal interest in performing hydrolysis reactions in cavitation reactors [112]. This reaction type typically requires high temperatures around 200 °C and the limit is set at 250 °C [115] in conventional processes. Cavitation reactors typically allow milder and safer operating conditions, do not require catalysts and enable the reaction time to be reduced (e.g. 10 h to obtain 80% of FFA compared with 12 h to obtain the same quantity of FFA with a solid catalyst in batch conditions [58]).

The most important issue concerning acoustic cavitation is related to reactor scale-up so that large fluid volumes can be processed. The ultrasound probe generates the cavitation phenomena in the vicinity of the probe tip and the major difficulty is then obtaining a homogeneous ultrasonic field throughout the entire reactor volume. Therefore, as the reactor volume increases, an increased amount of ultrasound power must be dissipated to the reaction mixture. A complex design with several powerful probes is required in order to obtain a homogenous acoustic field in larger reactors [96]. Continuous reactors may also be preferred to batch reactors as they enable processing with smaller volumes for the same production capacity. The results obtained by Thanh et al. [108] demonstrate the interest in employing acoustic cavitation in a continuous reactor. Their results show that high yield can be attained in less than a minute at room temperature conditions and a throughput capacity that is potentially of interest for industrial applications. Moreover, Thanh et al. [107] noticed that product separation is facilitated with the decrease of operating temperature and molar ratio of methanol to oil.

Hydrodynamic cavitation is more energy efficient than acoustic cavitation (1×10^{-4} – 1×10^{-3} g/J for hydrodynamic cavitation, 5×10^{-6} – 2×10^{-5} g/J for acoustic cavitation [110,114]) although academic examples of its use for FAME production are relatively rare. Industrial examples of hydrodynamic cavitation reactors are given by Arisdyne Syst. Inc. [116] and Hydro Dynamics Inc. [117], who commercialize the Controlled Flow Cavitation (CFC)

Table 8

Results obtained for transesterification, esterification (with methanol and glycerol) and hydrolysis in acoustic cavitation reactors. y: yield (%), c: conversion (%), R: molar ratio methanol:(acid or oil), t: residence time (min), w: weight fraction of catalyst (%), T: temperature (°C), P: power (W), f: frequency (kHz), V: volume (L), F: flow rate (L/h) [99–112].

Oil/acid	Catalyst	Performance		Reaction conditions								Reference
		y	c	R	t	w	T	P	f	V	F	
<i>Acoustic cavitation</i>												
<i>Transesterification (batch)</i>												
Neat vegetable oil	NaOH	98	–	6	20	0.5	25	400	40	–	–	[99]
Vegetable oil	NaOH	98	–	6	20	0.5	36	720 (60%)	40	0.1	–	[100]
Crude cottonseed oil	NaOH	98	–	6.2	8	1	25	–	40	–	–	[101]
Soybean	KOH	99.4	–	6	15	1	40	14.5	20	0.25	–	[102]
Soybean	KOH	99	–	6	5	1	89	400	24	0.125	–	[103]
Soybean	NaOH	95	–	5	1.5	1	40	2200	20	0.75	–	[104]
Soybean	NaOH	98	–	23.9	15	0.5	–	–	–	8	–	[95]
Triolein	KOH	99	–	6	30	1	ambient	1200	40	–	–	[105]
Beef tallow	KOH	–	92	6	1.17	0.5	60	400	24	2	–	[106]
<i>Continuous transesterification</i>												
Canola	KOH	>99	–	5	50	0.7	25	–	20	0.8	480	[107]
WCO	KOH	1st Reactor: 81	–	2.5	0.53	0.7	ambient	1000	20	0.8	90	[108]
		2nd Reactor: 97.5	–	1.5	0.4	0.3	ambient	–	–	–	120	
		Global: 93.8	–	–	0.93	–	–	–	–	–	–	
Commercial oil	KOH	–	95	6	20	–	40	600	45	2.62	7.8	[109]
		–	~85	6	20	–	40	–	–	6.35	19	
<i>Esterification (batch)</i>												
Caprylic (C8)	H ₂ SO ₄	–	99	10	75	2	40	120	20	3.5	–	[110]
Capric (C10)	H ₂ SO ₄	–	98	10	75	2	40	–	–	–	–	[110]
Fatty acid	Superacid clay	–	97	10	420	2	40	–	–	–	–	[110]
<i>Esterification with glycerol (batch)</i>												
FFA (C8–C10)	H ₂ SO ₄	–	98.5	3	360	5	90	–	–	–	–	[111]
<i>Hydrolysis</i>												
Kerdi oil	None	80	–	10	600	0	40	–	–	–	–	[112]

Table 9

Results obtained for transesterification in continuous hydrodynamic cavitational reactors. *c*: conversion (%), *R*: molar ratio methanol:oil, *t*: residence time (min), *m*: molar fraction of catalyst (%), *T*: temperature (°C), ΔP : pressure drop (bar), (1): first reactor, (2): second reactor [113,114].

Oil	Catalyst	Performance <i>c</i>	Reaction conditions				Configuration	ΔP		Reference
			<i>R</i>	<i>t</i>	<i>m</i>	<i>T</i>		(1)	(2)	
<i>Hydrodynamic cavitation</i>										
<i>Transesterification</i>										
Soybean	NaOH	98.7	6	0.12	3	100	1 Cavitational reactor	17.2	-	[113]
							2 Cavitational reactors in series	17.2	8.3	
Soybean	NaOH	99	6	0.71	3	60	4 Cavitational reactors in series	37.9 (total)		[114]
		99.9	6	0.71	3	100	4 Cavitational reactors in series	37.9 (total)		
Used Frying Oil	KOH	95	-	10	-	60	A plate with 1, 25, 16 or 20 holes	From 1 to 3		

Table 10

Results obtained for esterification with methanol in hydrodynamic cavitational reactors. *c*: conversion (%), *R*: molar ratio methanol:oil, glycerol: fatty acid and water: oil, *t*: residence time (min), *w*: weight fraction of catalyst (%), *T*: temperature (°C) [110].

Reactant	Catalyst	Performance <i>c</i>	Reaction conditions				Reference
			<i>R</i>	<i>t</i>	<i>w</i>	<i>T</i>	
<i>Hydrodynamic cavitation</i>							
<i>Esterification with methanol</i>							
FFA	H ₂ SO ₄	92	10	90	1	30	[110]

and the Shockwave Power Reactor (SPR), respectively. These reactors allow flexible industrial scale flow conditions with capacities ranging from hundreds to tens of hundreds of liters per hour. An example of results obtained for the transesterification of soybean oil using one cavitational reactor or several in series are given in Table 9. Clearly, the main advantage of these reactors is the possibility to obtain almost 100% conversion in only few microseconds. Moreover, an important consequence of such short reaction times is also the reduction of soap formation and emulsification [118], which in turn facilitates the decantation and separation of the products.

The advantages and drawbacks of acoustic and hydrodynamic cavitation for FAME production are summarized in Table 11. From the literature data it can be concluded that transesterification is clearly intensified by cavitation phenomena, which provides short reaction times especially in industrial hydrodynamic cavitational reactors. For the esterification of methanol, however, cavitation does not allow a reduction in reaction times, although it does enable the reaction to be carried out at ambient conditions. Esterification of glycerol is conventionally performed at high temperatures and the use of cavitation allows the operating temperature to be decreased and, at the same time, provides shorter reaction times. Finally, the use of cavitation in hydrolysis of oils has proved to enable milder operating conditions than the usual high temperature and pressure requirements, however, the reaction times still remain long. In terms of flow rate or processing volumes, hydrodynamic cavitation appears to be more adapted to high capacity demands compared with acoustic cavitation devices since obtaining a uniform acoustic field in large volumes is difficult. Indeed, hydrodynamic cavitation has proved to be industrially interesting for the intensification of transesterification reactions; however too few data for the other types of reactions in such reactors are available making it difficult to definitely conclude on the potential of this technique for the intensification of FAME production. Esterification with methanol has been performed in an hydrodynamic cavitational reactor, see Table 10. The performance is similar to esterification in acoustic cavitational reactor.

2.3. Microwave reactor

The development of microwave technology for the process industries is rather recent and relatively slow because of the lack

of control and reproducibility of results, the poor understanding of the dielectric phenomenon occurring, several safety issues and the difficulty to scale-up microwave processes for industrial production. The two major mechanisms involved in microwave technology are dipolar polarization and ionic conduction. Dipolar polarization occurs when dipoles are forced to align with the direction imposed by the electric field, which is caused by the microwave irradiation. The electric field, however, rapidly oscillates and the dipole therefore tries to realign itself with this electric field as fast as possible by rotation. The frequency of microwaves is sufficiently high to cause a phase difference between the field and the dipole orientation and the resulting frictional and collision forces between the molecules thus generate heat. Ionic conduction occurs as the charged dissolved particles oscillate under the influence of the microwave field. When the direction of the electric field is changing, the ions slow down and change direction thereby dissipating kinetic energy as heat. This dissipation is caused by friction [119,120]. A more detailed description of microwaves applied in chemistry can be found in [121,122]. In addition, two recent reviews focus on biodiesel production assisted by microwaves [123,124].

Microwaves are a technology of interest for transesterification, esterification or hydrolysis reactions since they allow increased heating of the reaction medium, which leads to an increase in reaction rate. In early studies on the effects of microwaves in organic synthesis, Lidström et al. [120] observed that for a reaction rate $K = A \cdot \exp(-\Delta G/RT)$, the constant *A*, which describes the molecular mobility, is increased under microwave irradiation due to the increased vibration frequency of the molecules. Terigar et al. [125] also observed that transesterification reaction rates are significantly increased under microwave irradiation and that transesterification with methanol is more sensitive to microwaves than that with ethanol due to the lower gyration radius and molecular inertia of methanol. The efficiency of the transesterification reactions is explained by the dielectric properties of the ionic mixtures and the polar compounds present in the vegetal oil, alcohol and catalyst. Asamuka et al. [126] further attributed the positive effect of microwaves on transesterification to factors other than heating efficiency. Firstly, the conformational isomer of the triglyceride has a lower dipolar moment under microwave irradiation and consequently a lower activation energy. Secondly, the vibration around the C=O bond is stronger under microwave irradiation, thereby

Table 11

Advantages and drawbacks of acoustic and hydrodynamic cavitation for transesterification, esterification with methanol and glycerol, and hydrolysis reactions.

Cavitation	Advantages		Drawbacks	
	Acoustic	Hydrodynamic	Acoustic	Hydrodynamic
Transesterification	<ul style="list-style-type: none"> – Shorter reaction times than conventional reactors – Ambient temperatures and pressures conditions 	<ul style="list-style-type: none"> – Reaction times of only a few microseconds – Ambient temperature and pressure conditions – Less saponification and emulsion – Less energy consumption than acoustic cavitation 	<ul style="list-style-type: none"> – Processing of high volumes is difficult due to non-uniform acoustic fields 	<ul style="list-style-type: none"> – A minimum flow rate is required in order to generate the cavitation phenomenon
Esterification (with methanol)	<ul style="list-style-type: none"> – Ambient temperature conditions 		<ul style="list-style-type: none"> – No particular improvement on reaction rates 	
Esterification (with glycerol)	<ul style="list-style-type: none"> – Milder temperatures than in conventional processes – Shorter reaction times than conventional reactors 	<i>No data available</i>	<ul style="list-style-type: none"> – Reaction times remain long 	<i>No data available</i>
Hydrolysis	<ul style="list-style-type: none"> – Milder operating conditions than in conventional processes 	<ul style="list-style-type: none"> – Milder operating conditions than in conventional processes 	<ul style="list-style-type: none"> – Long reaction times 	

facilitating the reaction. Finally, the conformational isomer has a planar structure, which is more easily accessible for the nucleophile attack.

A comparison of the literature data for homogeneous and heterogeneous base-catalyzed transesterification and for heterogeneous acid-catalyzed esterification is given in Tables 12 and 14, respectively. From this information, it can be clearly seen that the effect of microwaves on both the transesterification and esterification reactions is a drastic reduction in reaction time (down to several minutes, and even less than a minute in some cases) when compared with conventional processes and without excessive operating temperatures. Indeed, in conventional processes, heterogeneous catalysts for transesterification and esterification are usually associated with low reaction rates and high working temperatures, even though heterogeneous catalysts can facilitate product separation downstream since the solid catalyst is more easily recovered without a neutralization step thereby allowing high purity glycerol as a side product [59]. The literature data also show that under microwave irradiation the performance of heterogeneous catalyzed transesterification reactions – in terms of yield and conversion – are comparable to or better than that when a homogeneous catalyst is used. Indeed, strontium oxide as a solid catalyst gives excellent performance – high conversions for very short residence times – compared with the conventional homogeneous potassium hydroxide catalyst [138], see Table 13. In the case of heterogeneous catalyzed esterification, however, the conversions are typically lower than those obtained with a homogeneous catalyst. Indeed, it does appear that the catalyst type has a strong effect since a 100% yield was obtained with scandium triflate, which continues to provide high conversion even after 5 cycles [136], even though process volumes are very low. Further work in the area of catalyst choice is therefore necessary before solid conclusions on the performance of esterification under microwaves can be made. It may also be interesting to test the scandium triflate catalyst in a larger reactor and then develop a continuous process similar to the experimental setup presented by Barnard et al. [135] in order to investigate the industrial potential of this catalyst.

Although glycerol esterification and hydrolysis reactions under microwaves have been rarely studied, the available data suggests that reaction times are typically reduced and less harsh operating conditions are required under microwave irradiation. For example, Luque et al. [144] obtained 99% conversion in 30 min at 130 °C for

glycerol esterification of acetic acid using a heterogeneous catalyst (Starbon®-400-SO₃H) under microwave irradiation, but only 85% conversion with a sulfuric acid catalyst under the same conditions. Marcel et al. [145] showed that it takes only 5 min to obtain a 100% yield of free fatty acid via the hydrolysis of castor oil triglycerides (in the presence of KOH and ethanol) using microwave irradiation. Another example is given by Saxena et al. [146]: they demonstrated that the complete hydrolysis of triolein with an enzymatic catalyst can be performed in just 75 s at a high power level (800 W, 90 °C), whereas the reaction time needed without at 37 °C and atmospheric conditions is 24 h.

In summary, as presented in Table 15, the current literature shows that microwave irradiation enables a noteworthy reduction of reaction times for transesterification, esterification and hydrolysis and it offers the possibility to operate under milder conditions compared with conventional processes. In addition, the use of microwaves provides a means to obtain good reaction performance with heterogeneous catalysts, which facilitate product separation and higher purity products. Moreover, microwave irradiation is known to break emulsions between a polar and an oil phase [147] thereby facilitating separation further. However, the use of microwave batch reactors for industrial production (i.e. high volumes) is limited for a number of reasons. Firstly, specific security measures have to be taken if microwaves are used at high intensities (power up to 5000 W) that typically require sophisticated cooling systems, thereby increasing the complexity, cost and size of the reactor. Secondly, the penetration depth of microwaves is only few centimeters, which means that a homogeneous field of microwave intensity is extremely difficult to achieve in large volume reactors. For these reasons, most batch experiments in the literature are limited to low volume processing. Indeed, if industrial scale FAME production processes are to be intensified using microwaves then continuous processing will be required and the feasibility of such processes (432 L/h and 98.9% conversion) has already been demonstrated [135]. Furthermore, the combination of microwave-assisted heterogeneous catalysis and continuous processing may have strong industrial potential for FAME production.

2.4. Oscillatory baffled reactors

An oscillatory baffled reactor (OBR) is composed of a tube containing equally spaced orifice plate baffles, as shown in Fig. 7a. It

Table 12

Results obtained for homogeneous and heterogeneous base-catalyzed transesterification in microwave reactors. *y*: yield(%), *c*: conversion (%), *c/n*: conversion after *n* cycles, *R*: molar ratio methanol:oil, *t*: residence time (min), *w*: weight fraction of catalyst (%), *T*: temperature (°C), *P*: Power (W), *V*: Volume (mL), *F*: flow rate (L/h) [127–139].

Oil	Catalyst	Performance			Reaction conditions							Reference
		<i>y</i>	<i>c</i>	<i>c/n</i>	<i>R</i>	<i>t</i>	<i>w</i>	<i>T</i>	<i>P</i>	<i>V</i>	<i>F</i>	
<i>Homogenous base-catalyzed transesterification</i>												
Vegetal	NaOH	>97	–	–	–	<2	–	–	750	250	–	[127]
Triolein	KOH or NaOH	–	98	–	6	1	5	50	25	–	–	[128]
WCO	KOH	100	–	–	6	2	1	65	500	500	–	[129]
Rapeseed	KOH	–	93.7	–	6	1	1	40	1200 (67%)	–	–	[130]
Yellow horn	KOH	>96	–	–	6	6	1	60	500	50	–	[131]
Soybean	NaOH	–	98.64	–	5	20	0.15–0.18	80	1600	270	–	[132]
Rice	NaOH	–	98.82	–	5	20	0.15–0.18	80	1600	270	–	
Safflower	NaOH	98.4	–	–	10	6	1	60	300	500	–	[133]
Frying palm oil (waste)	NaOH	–	>97	–	12	0.5	3	–	800	16	4.5	[134]
Vegetal	KOH	–	98.9	–	6	0.56	1	50	1600	4000	432	[135]
<i>Heterogeneous base-catalyzed transesterification</i>												
Palmitate	Sc(Otf) ₃	99	–	97/5	48	2.5	10	20	–	0.2–2	–	[136]
Yellow horn	CS _{2.5} H _{0.5} PW ₁₂ O ₄₀	96.2	–	96/9	12	0.17	1	60	1000	50	–	[137]
Cooking oil (without FFA)	SrO	–	99	–	6	0.66	1.84	60	900	50	–	[138]
Soybean	SrO	–	–	96/4	6	2	1.84	–	–	–	–	[138]
Cooking oil (without FFA)	SrO	–	99.8	–	–	0.17	1.84	–	1100	–	–	[138]
Palm	Eggshell waste (CaO 99.2 wt%)	96.7	–	–	18	4	15	122	900	43	–	[139]

Table 13

Results obtained for transesterification in microwave reactors. *R*: molar ratio methanol:oil, *t*: residence time (s), *P*: Power (W), *V*: Volume (mL) [138].

Oil	Conversion (%)		Reaction conditions				Reference
	With SrO	With KOH	<i>R</i>	<i>t</i> (s)	<i>P</i> (W)	<i>V</i> (mL)	
Cooking oil (without FFA)	99	83	6	40	900 (70%)	50	[138]
Soybean	96	87	6	120	–	–	

Table 14

Results obtained for heterogeneous acid-catalyzed esterification in microwave reactors. *y*: yield(%), *c*: conversion (%), *c/n*: conversion after *n* cycles, *R*: molar ratio methanol:oil, *t*: residence time (min), *w*: weight fraction of catalyst (%), *T*: temperature (°C), *P*: power (W), *V*: volume (mL) [136,140–144].

Acid	Catalyst	Performance			Reaction conditions						Reference	
		<i>y</i>	<i>c</i>	<i>c/n</i>	<i>R</i>	<i>t</i>	<i>w</i>	<i>T</i>	<i>P</i>	<i>V</i>		
<i>Heterogeneous acid-catalyzed esterification with methanol</i>												
Oleic	Sc(Otf) ₃	100	–	97/5	48	1	1	150	–	0.2–2	–	[136]
Oleic	NbO ₂ and ZrO ₂	–	68	68/3 and 58/3	5	20	10.5	200	1400	80	–	[140]
Oleic	None	–	60	–	5	60	0	200	1400	80	–	[141]
Oleic	Dry Amberlyst15	–	39.9	–	20	15	10	60	1600 (100%)	1000	–	[142]
		–	66.1	–	20	15	10	60	1600 (pulsed 10%)	1000	–	[142]
Oleic	S–ZrO ₂	–	>90	–	20	20	5	60	1600	2000	–	[143]
<i>Heterogeneous acid-catalyzed esterification with glycerol</i>												
Acetic	Starbon-400-SO ₃ H	–	>99	–	1	30	1.8	130	300	<100	–	[144]

operates with an oscillatory or pulsed flow rate, which creates recirculation flow patterns in the vicinity of the baffles as illustrated in Fig. 7b, thereby enhancing mixing and mass and heat transfer. Due to this recirculating flow, OBRs can thereby provide flexible and long residence times, which are comparable to those achieved in batch reactors [148], without having a high length-to-diameter ratio tube. Smaller reactors called mesoscale oscillatory baffled reactor (MOBR) designs with sharp periodic baffles and sharp-edged helical baffles also exist, as presented in Fig. 8.

The OBR technology is particularly adapted to liquid–liquid reactions, such as transesterification, because it allows good inter-phase contacting, enhanced mixing and sufficiently long residence times for reaction. Table 16 compares FAME production data obtained in OBRs; note that the literature studies have been limited to transesterification only. The results show that in an OBR, 99% conversion can be reached in only 10 min at 60 °C, which is half the time required to carry out the reaction in conventional reactors [148]. Furthermore, the same study shows that the meth-

anol stream can be recycled in the continuous OBR technology, thereby allowing a very low methanol to oil ratio to be used. Mesoscale OBRs, which are particularly adapted to feasibility studies and screening tests due to their lower capacity, have also been shown to provide high conversions and yields in short times compared with what can be achieved in conventional batch tanks [149,150].

In addition to the advantages of OBRs for reaction performance, which are summarized in Table 17, this type of equipment is particularly suited to industrial scale production where a certain flow capacity may be required. Indeed, commercial equipment exists – such as that developed by NiTech Solutions®, which has demonstrated successful biodiesel production [151]. OBRs have also been shown to provide good solids handling, whether it be solids suspension or crystallization applications [148,151], which is interesting if heterogeneous catalysis is to be used. Although only transesterification reactions in OBRs have been demonstrated in the literature, the results of these studies and the characteristics

Table 15

Advantages and drawbacks of microwave reactors for transesterification, esterification with methanol and glycerol and hydrolysis reactions.

Microwaves	Advantages	Drawbacks
Transesterification	<ul style="list-style-type: none"> - Reaction times reduced - High flow rates for continuous processes - Excellent results with heterogeneous catalysis - Separation of emulsions 	<ul style="list-style-type: none"> - Scale-up difficult in batch conditions
Esterification (with methanol)	<ul style="list-style-type: none"> - Reaction times reduced - Good results with heterogeneous catalysis (scandium triflate) 	<ul style="list-style-type: none"> - Studies done with low volumes
Esterification (with glycerol)	<ul style="list-style-type: none"> - Milder temperatures - Good results with heterogeneous catalysis (Starbon-400-SO₃H) 	<ul style="list-style-type: none"> - Study done with low volumes
Hydrolysis	<ul style="list-style-type: none"> - Short reaction times - Effective enzymatic catalysis 	<ul style="list-style-type: none"> - Literature data found with enzymatic catalysis only

of this continuous process equipment suggest that they could also provide significant advantages for esterification and hydrolysis reactions.

2.5. Static mixers and other motionless inline device

Static mixers are motionless elements that are inserted in a tube or pipe and enable fluid mixing by creating transverse flows. They are typically used in continuous processes but can also be employed in a closed loop system or for premixing before feeding to a batch tank. Static mixers are well adapted to variety of applications, including simple blending and multiphase mixing problems, in both the laminar and turbulent flow regimes [152]. The advantages of static mixers over conventional batch stirred tanks are their smaller size, a lower energy consumption, a very good control of the residence time with a plug flow reactor behavior, and finally very good mixing with low shear rates [153]. A large number of more or less intricate static mixer designs exist – about 2000 US patents have been granted and more than 30 models are commercially available, e.g. Kenics, HEV, KMS and KMX mixers by Chemineer Inc., Dayton, OH (see Fig. 9) and the SMX and SMX plus mixers by Sulzer Chemtech, Switzerland. However, other inline devices, such as randomly packed beds of spherical particles

and metallic foams, can also be used to ensure mixing in tubes and pipes with relatively low pressure drop [154,155].

Amongst the different applications, static mixers are well adapted to liquid–liquid dispersion processes, including extraction, reaction and emulsification, providing a means to disperse immiscible phases with typically less energy requirements than other technologies. This has been demonstrated by Frascari et al. [157] who have shown that in the case of a transesterification reaction, the energy consumption for a static mixer is less than that required by mechanical stirring. In particular, they show that if the reactants are premixed using a static mixer and fed to a batch reactor with two 4-bladed disk turbines rotating at 100 rpm, the conversion is the same as that achieved in the batch reactor alone with an impeller speed of 700 rpm. Further, they show that the droplet size created by the static mixer is comparable to that generated with mechanical agitation at 700 rpm, which explains the similar reaction performance.

The studies reported in the literature concerning the transesterification of vegetable oil mostly employ static or inline mixing devices in a continuous mode. The transesterification reaction performance obtained in different static mixer and inline mixing configurations are summarized in Table 18. Thompson and He [158] developed a static mixer closed-loop system, which allows the residence time to be easily varied. With this system, the production of total free glycerol (ASTM D6584 specification, 0.24%w max.) was achieved in a residence time of 15 min. Boucher et al. [159] designed a system with a static mixer and an integrated decanter as shown in Fig. 10. The immiscible reactants are contacted in the static mixer and the products are released into a glass column. Where the glycerol settles to the bottom and is continuously removed, whilst the esters are continuously removed from the top of the column. The same group then improved the transesterification process performance by inclining the reactor as presented in Fig. 11 [160]. By inclining the reactor, larger glycerol droplets are formed, thereby facilitating the separation of the esters and glycerol, although the conversion is slightly affected with a decrease from 99% to 95% probably due to the increased drop size. In both reactor designs, the phase contacting via the static mixer and the continual removal of glycerol enhance the reaction and high conversion is obtained in less than 30 min, which is significantly faster than in conventional equipment. Metallic foams and other inserts, such as steel spheres and various types of fibers, have also shown to enhance transesterification reactions [155,161–163]. These devices create tortuous interstices with micron-sized dimensions that promote fluid contacting and mixing, and consequently the chemical reaction. The data show that these mixing devices allow high conversion rates in short residence times, which are of the order of several minutes. Furthermore, some authors also observed

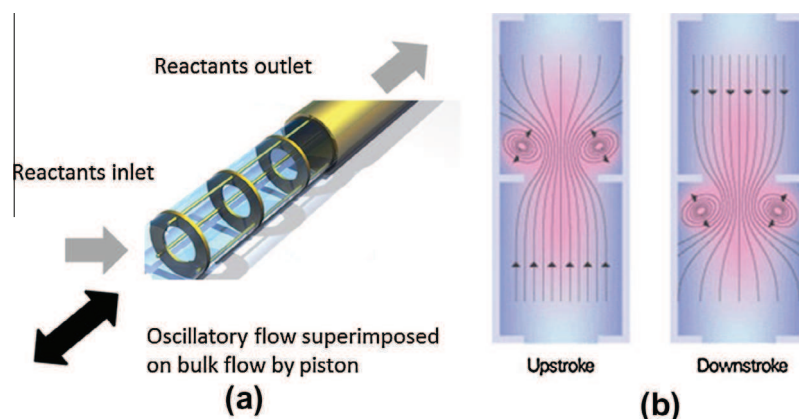


Fig. 7. The oscillatory baffled reactor (a) and the flow-pattern corresponding to a upstroke or downstroke current (b) [150].

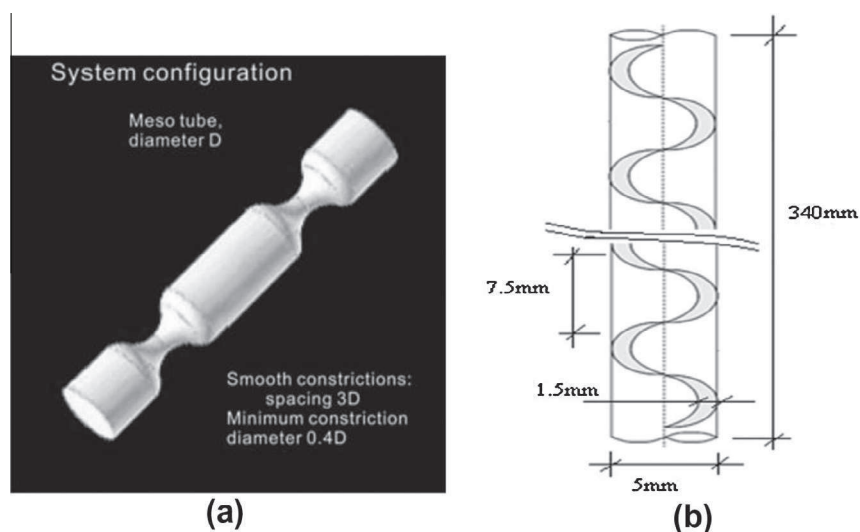


Fig. 8. Mesoscale oscillatory baffled reactors with (a) sharp periodic baffles (SPB) [150] or (b) sharp-edged helical baffles (SEHB) [149].

Table 16

Results obtained for transesterification in oscillatory baffled reactors. y : yield(%), c : conversion (%), R : molar ratio methanol:oil, t : residence time (min), T : temperature ($^{\circ}\text{C}$), V : volume (mL), F : flow rate (L/h) [148–150].

Oil	Catalyst	Performance		Reaction conditions					Type of reactor	Reference
		y	c	R	t	T	V	F		
Rapeseed	NaOH	–	99	1.5	30	50	1.56	3.12	OBR	[148]
Refined vegetable oil	NaOMe	–	99	6	40	60	0.005	0.126	SPB-MOBR	[150]
Rapeseed	KOH	90	–	9	20–25	50	0.04	0.12	SEHB-MOBR	[149]

Table 17

Advantages and drawbacks of OBRs for transesterification reaction.

OBR	Advantages	Drawbacks
Transesterification	<ul style="list-style-type: none"> – Reaction times significantly reduced compared with batch processing – Compatible with heterogeneous catalysis – Molar ratio methanol to oil reduced – Large flexibility in residence times 	<ul style="list-style-type: none"> – No integrated separation unit for end products

good product separation at the reactor outlet, despite the formation of liquid–liquid emulsions [163].

A summary of the advantages and drawbacks of static mixers and inline devices is given in Table 19. In general, this type of

equipment allows high reaction conversions to be reached in relatively short times and requires less energy input compared with conventional batch processing. A novel attribute of these devices is the possibility to couple the mixing/reaction and separation steps that are required for the transesterification process. Continual separation and removal of products during the reaction shifts the equilibrium and means that the sequential product separation steps that are required in conventional processes can be avoided. Indeed, the other reactions related to FAME production, i.e. esterification with various alcohols and hydrolysis, could potentially benefit from the integration of the reaction and separation steps in one device, although no studies have yet been dedicated to this. Also, heterogeneous catalysis has not yet been tested with static mixing and inline technologies; indeed solids handling in some of these devices may be difficult (e.g. due to clogging), however catalytic coatings on foams or fibers may be a means to resolve such problems.



Fig. 9. Geometries of commercially available mixers [156].

Table 18

Results obtained for transesterification in static mixer reactors. *y*: yield(%), *c*: conversion (%), *g*: glycerol treatment, *R*: molar ratio methanol:oil, *t*: residence time (min), *w*: weight fraction of catalyst (%), *T*: temperature (°C), *F*: flow rate (L/h) [158–163].

Oil	Catalyst	Performance			Reaction conditions					Type of reactor	Reference
		<i>y</i>	<i>c</i>	<i>g</i>	<i>R</i>	<i>t</i>	<i>w</i>	<i>T</i>	<i>F</i>		
Canola	NaOH	–	–	–	6	30	1.5	60	0.104	Closed-loop system	[158]
Waste canola (pretreated)	KOH	99	70–99% removal	–	6	19	1.3	40–50	72	Reactor-separator	[159]
Waste oil	KOH	96	36–95% separation	–	6	17.5	1–1.3	40–50	72	Reactor-separator	[160]
Soybean	NaOH	95.2	–	–	10	2.16	1	55	0.918	Metal foam	[155]
Soybean	KOH	98.2	–	–	6	0.99	2	60	0.366	Tube filled with stainless steel spheres (2.5 and 1.0 mm)	[161]
	KOH	97.05	–	–	6	3	1	60	0.279	Packed bed reactor with 2.5 mm spheres	[162]
Soybean	NaOMe	–	99	–	–	5.8	2	60	1.44	216,000 Fibers 8 μm	[163]

2.6. Membrane reactors

Microporous inorganic membranes enable product separation by a molecular sieving effect. They can be made of ceramic, zeolites, silica, carbon or polymers. Carbon membranes are most commonly used due to their easy production and low cost [164]. Membrane reactors are also employed for pervaporation processes that enable the separation of a liquid retentate from a vapor permeate [165]. A detailed review of membrane technology as an alternative means for biodiesel production has been given by Shuit et al. [166].

In the case of transesterification, the principal objective of the membrane reactor is to retain the triglycerides [167–172]; this then facilitates the downstream purification steps [167]. The retention of mono- di-, and triglycerides is also possible [168], thus allowing the separation of FAME and glycerol at room temperature and avoiding onerous downstream processing. Furthermore, the separation of glycerol reduces waste water generated by washing steps [171]. The retention of soaps and glycerol is also possible by adding a little amount of water as depicted in Fig. 12 [172]. Membrane separation also allows product specifications to be met (i.e. glycerol < 0.2%w in FAME), as well as the treatment of waste cooking oils with high FFA content (5%) [173]. As it is summarized by Sdrula [170], others advantages of membrane reactors for transesterification are the high purification of glycerol, the absence of chemical additives and the low process cost.

Numerous studies have shown that membranes reactors can improve conversion and facilitate the product purification step of transesterification reactions, compared with conventional processes [172]. A summary of the performance of transesterification reactions carried out in membrane reactors is given in Table 20. It can be seen that in most cases good conversion and acceptable flow rates can be achieved, however the time required for the reaction is on the order of 1–2 h, which is similar to conventional batch processing.

Esterification has been demonstrated in membrane reactors via a pervaporation process where water is removed in a vapor stream allowing a shift in the reaction equilibrium, thereby leading to higher conversion rates. The results obtain by Sarkar et al. [174], which are given in Table 21, show that almost 100% conversion of the fatty acid is achieved in 6 h.

The advantages and drawbacks of membrane reactors for FAME production processes are summarized Table 22. The major advantage of this technology is that separation is integrated in the reaction step. This in turn allows high reaction conversion to be achieved, however there is no reduction in reaction time compared with conventional processing. Although no studies have yet focused on the hydrolysis of triglycerides or esterification using glycerol, membrane reactors could potentially provide benefits by shifting the reaction equilibrium, thereby promoting product formation and facilitating the product separation. Heterogeneous catalysts can be incorporated in and mobilized on the membranes,

leading to conversions superior to 90% without washing steps [175–177]. The use of membrane reactors with an immobilized enzymatic catalyst for hydrolysis has also been demonstrated [178].

2.7. Reactive distillation

Reactive distillation combines reaction and distillation in a multifunctional reactor and is suited to heterogeneous, homogeneous and non-catalyzed reactions [179]. The principle is based on the removal of one reaction product in order to shift the reaction equilibrium, thereby leading to high and even total conversions. A more complex configuration is the reactive divided-wall column, which enables three high-purity streams to be obtained at the outlet of a single distillation tower as depicted in Fig. 13 [180]. In conventional distillation, two distillation columns are required to separate three products.

Reactive distillation has shown to be particularly adapted to transesterification and esterification reactions since these are equilibrium reactions that benefit from equilibrium shifts. The literature data on the performance of transesterification and esterification reactions are presented in Tables 23 and 24, respectively.

In the case of reactive distillation for transesterification reactions, the reaction of methanol and triglycerides and the separation of any excess or unreacted methanol are achieved simultaneously [181,184]. Unreacted methanol is recovered at the top of the column and is recycled to the feedstock, whilst the glycerol and esters are recovered at the bottom of the column and sent to a decanter. This processing method enables the use of a lower methanol to oil molar ratio and provides short residence times.

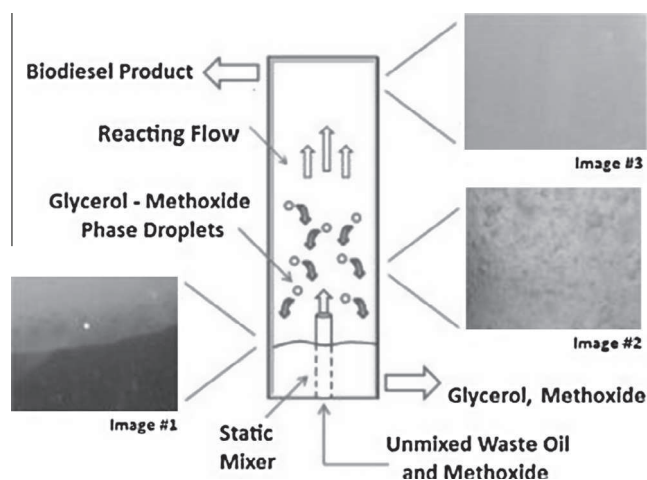


Fig. 10. Schematic diagram of the static mixer reactor/separator and corresponding images of the flow at different positions within the reactor [159].

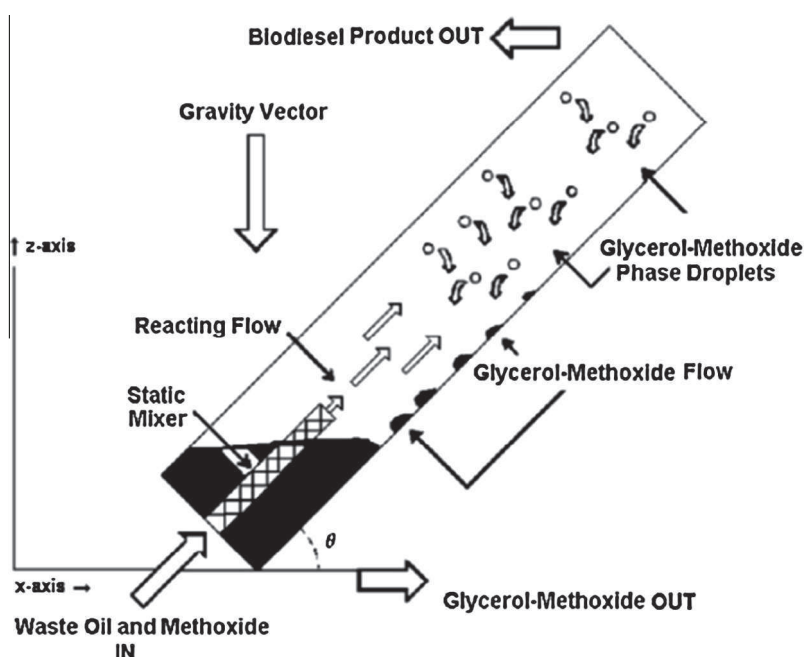


Fig. 11. Schematic diagram of the inclined static mixer reactor/separator and operating concept [160].

Table 19

Advantages and drawbacks of static mixers for the reaction of transesterification.

Static mixers	Advantages	Drawbacks
Transesterification	<ul style="list-style-type: none"> - Reaction times reduced ($\times 2-10$) - Low energy-consumption - Relatively simple devices - Separation step implemented in the reactive part for the reactor-decanter 	<ul style="list-style-type: none"> - May not be adapted to heterogeneous catalysis

Esterification has also been successfully carried out by reactive distillation. It provides the opportunity to use a heterogeneous catalyst, thereby avoiding the neutralization, washing, separation and waste recovery steps [185]. It also enables the removal of water throughout the reaction at the top of the column, which shifts the reaction equilibrium and promotes product formation. Steini-geweg and Gmehling [182] used Amberlyst 15, an ion exchange resin that is fixed on the packing, to esterify decanoic acid and obtained 100% conversion at a pilot scale with a flow rate of 34 mol/h. Kiss et al. [185] investigated the choice of the heterogeneous catalyst. They found that zeolites have too small pores, which limit the diffusion of large molecules like fatty acids or esters. Ion exchange resins, such as Nafion or Amberlyst, have strong acid activity but a low thermal stability. Tungstophosphoric acid is very active but is also soluble in water and therefore cannot be reused. The authors concluded that sulfated zirconia is a good candidate as catalyst for esterification because it is active, stable and selective. Dimian et al. [186] investigated the possibility of using a co-solvent - 2-ethylhexanol - to increase the immiscibility between water and fatty acids so that the water can be more easily separated.

Fig. 14 shows the concept of reactive absorption using a heterogeneous catalyst as proposed by Kiss and Bildea [187]. Fatty acids

and methanol are fed at the top and bottom of the column, respectively, and water with some acid exits at the top of the column, whilst the bottom outlet stream contains FAME with some methanol.

The reactive distillation process can be further improved by using a divided wall column (DWC), which is particularly useful for reactive systems that have more than two products or that operate with an excess of reagent. This technology, which is analogous to the assembly of two distillation columns in one unit, allows the separation of multicomponents [188] and solves the problem encountered in reactive absorption, which is the necessity to use methanol in an exact stoichiometric ratio since it has to be completely converted. Indeed, this ratio is difficult to obtain especially because the amount of fatty acids in the feed is often unknown. Reactive distillation using a DWC allows the use of an excess of methanol, which is then recovered as the top distillate; water is then recovered as a side stream and FAME as the bottom product, as depicted in Fig. 15 [183].

Although there have been no demonstrative studies on the use of reactive distillation for the esterification with glycerol presented in the literature, this technology may be of interest for the reaction due to the high boiling points of glycerol and fatty acids, thereby allowing the removal of methanol and water. The use of reactive distillation for hydroesterification (i.e. combination of hydrolysis and esterification) is also of potential interest. Indeed, hydrolysis can be firstly performed with reactive distillation to concentrate the FFA content of oils that already have a high level of FFA before carrying out the esterification. This has been demonstrated numerically in a two-section reactive distillation process using WCO and Jatropha oil [189].

The advantages and drawbacks of reactive distillation for FAME production are summarized in Table 25. The main advantage of reactive distillation for FAME reactions is the fact that reaction and separation can be combined in the same device, thereby enabling the reaction equilibrium to be shifted and enhancing product formation. The principal disadvantage of this type of process is the high energy requirement, which is also an issue in conventional distillation processes.

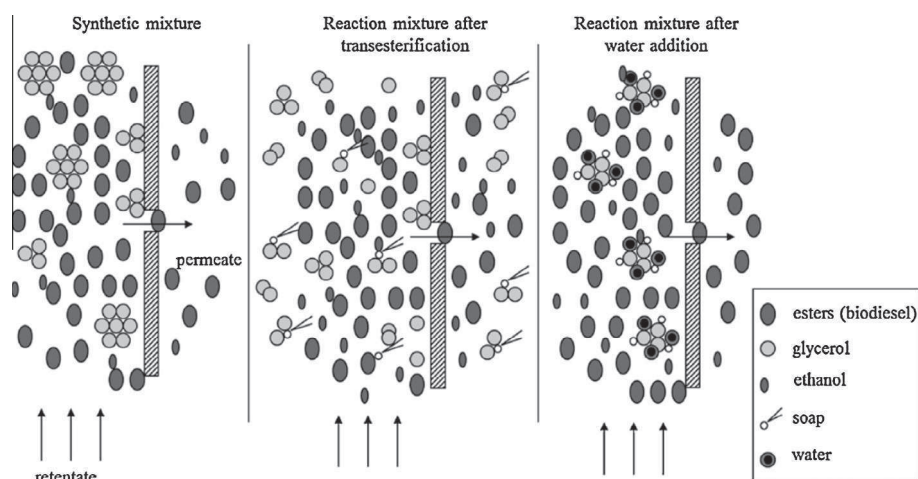


Fig. 12. Mechanism of separation of glycerol by microfiltration with a ceramic membrane [172].

Table 20

Results obtained for transesterification in membrane reactors. *y*: yield(%), *c*: conversion (%), *g*: glycerol content in permeate (%), *R*: molar ratio methanol:oil, *t*: residence time (min), *w*: weight fraction of catalyst (%), *T*: temperature (°C), *F*: flow rate. ϕ : pore size (μm), *V*: volume of the reactor (L) [167–169,171–173].

Oil	Catalyst	Performance			Reaction conditions					Reactor			Reference
		<i>y</i>	<i>c</i>	<i>g</i>	<i>R</i>	<i>t</i>	<i>w</i>	<i>T</i>	<i>F</i>	Membrane	ϕ	<i>V</i>	
Canola	H ₂ SO ₄	64	–	–	–	49	6	70	16.6 L/m ² /h	Carbon	0.05	0.3	[167]
	NaOH	96	–	–	–	49	1	70	16.6 L/m ² /h	Carbon	0.05	0.3	
Canola	NaOH	98.7	–	0	16	210	0.5	–	9 L/m ² /h	Carbon	0.2	0.32	[168]
Canola	NaOH	98	–	–	24	5	0.5	65	120 kg/h	Filtanium ceramic	–	6	[169]
Canola	NaOH	–	–	<0.02	6	180	1	25	40–180 L/m ² /h	Polyacrylonitrile membrane	–	–	[171]
Soybean (Ethanol)	NaOH	–	98.7	<0.02	9	80	1	30	10.3 kg/m ² /h	Ceramic	0.2	0.25	[172]
WCO (FFA = 5%)	Base	>99	–	<0.02	23.9	35–105	0.5–1.4	65	30–40 L/m ² /h	Titanium oxide	0.03	0.48–0.63–0.74	[173]

Table 21

Results obtained for esterification in membrane reactors. *y*: yield(%), *c*: conversion (%), *g*: glycerol content in permeate (%), *R*: molar ratio methanol:oil, *t*: residence time (min), *w*: weight fraction of catalyst (%), *T*: temperature (°C), *t*: residence time (h) [174].

Acid	Catalyst	Performance		Reaction conditions				Reactor			Reference
		<i>y</i>	<i>c</i>	<i>R</i>	<i>w</i>	<i>T</i>	<i>t</i>	Membrane	ϕ (μm)	<i>V</i> (L)	
Oleic	H ₂ SO ₄	–	99.9	27	0.3	65	6	Polyvinylalcohol on polyether sulfone	–	0.073	[174]

Table 22

Advantages and drawbacks of membrane reactors for the reaction of transesterification.

Membrane reactors	Advantages	Drawbacks
Transesterification	<ul style="list-style-type: none"> Retains Triglycerides (unreacted glycerides stay in the reactor), economy of downstream process costs Retains Di and Monoglycerides, allowing phase separation at room temperature Better separation of glycerol means less washing and less waste water Retains Glycerol, separation step during the reaction Low cost 	<ul style="list-style-type: none"> No increase of reaction rates
Esterification	<ul style="list-style-type: none"> Separation of water during the reaction: shift of the equilibrium 	<ul style="list-style-type: none"> No heterogeneous catalysts used

3. Recommendations for the choice of process technologies for FAME production

Mass-transfer is the main limitation of the WCO transformation reactions, however, two additional parameters are also important when considering the choice of process technology. Firstly, the choice of the catalyst directly impacts the process performance. Secondly, the possibility to combine the reaction and separation steps to shift reaction equilibriums and easily separate products is important for process efficiency. The objective of this section is to give recommendations, following the review of literature data, on the choice of equipment taking into account the catalyst type and the separation aspects for the intensification of the different transesterification, esterification and hydrolysis reactions.

3.1. Catalyst type

Table 26 summarizes the different types of catalysts that have been used for FAME production in various types of innovative process equipment. It can be seen that majority of studies have employed homogenous catalysts for transesterification and

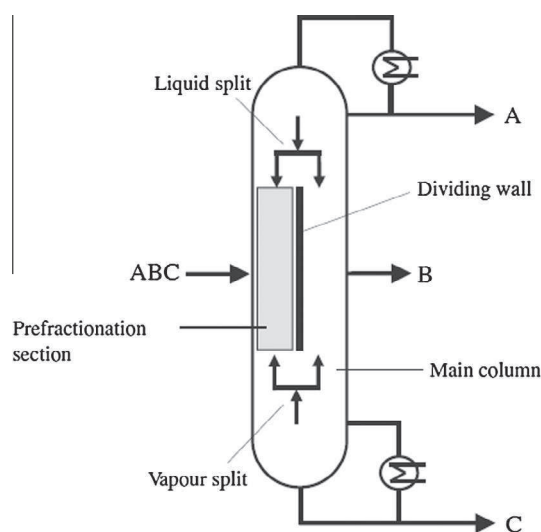


Fig. 13. Dividing wall column [180].

Table 23

Results obtained for transesterification in a reactive distillation column. y : yield(%), c : conversion (%), R : molar ratio methanol:oil, t : residence time (min), w : weight fraction of catalyst (%), T : temperature ($^{\circ}\text{C}$), F : flow rate (L/h) [181].

Oil	Catalyst	Reaction conditions						Reference
		y	c	R	t	w	F	
Canola	KOH	94.4	95	4	3	1	4.9 L/h	[181]

esterification reactions because they are inexpensive and easy to use. On the other hand, heterogeneous catalysts have been less widely used due to traditionally higher operating temperatures and long reaction times. However, new catalysts, such as strontium oxide, scandium triflate or sulfated zirconia, have been developed and give similar performance to homogenous catalysts. For sustainable FAME production processes, the ensemble of the literature studies suggest that heterogeneous catalysts may be preferred over the conventional homogeneous catalysts because they can be easily reused and regenerated, and also allow easy product separation and elimination of the neutralization step. Moreover, heterogeneous catalysts coupled with intensified processes, such as micro-waves and reactive distillation, have been shown to significantly enhance FAME production [136,183]. It is expected that heterogeneous catalysts may also provide improved reaction performance in other types of innovative continuous flow equipment, e.g. microstructured reactors, cavitation reactors, OBRs and static mixers, which have been proven successful for other applications in solids handling (suspensions or catalytic reactions) [110,190–192]. Indeed, further exploratory work on the use of heterogeneous catalysts in innovative process equipment for transesterification or other FAME production reactions is still required.

Table 24

Results obtained for esterification in a reactive distillation column. y : yield(%), c : conversion (%), R : molar ratio methanol:oil, t : residence time (min), T : temperature ($^{\circ}\text{C}$), P : pressure (bar), F : flow rate [182,183].

Acid	Catalyst	Reaction conditions								Reference
		y	c	R	t	T	P	F (mol/h)		
Decanoic	Amberlyst 15		100	2	–	50	3	34 mol/h	[182]	
Dodecanoic			>99.99	1				1250 kg/h	[183]	

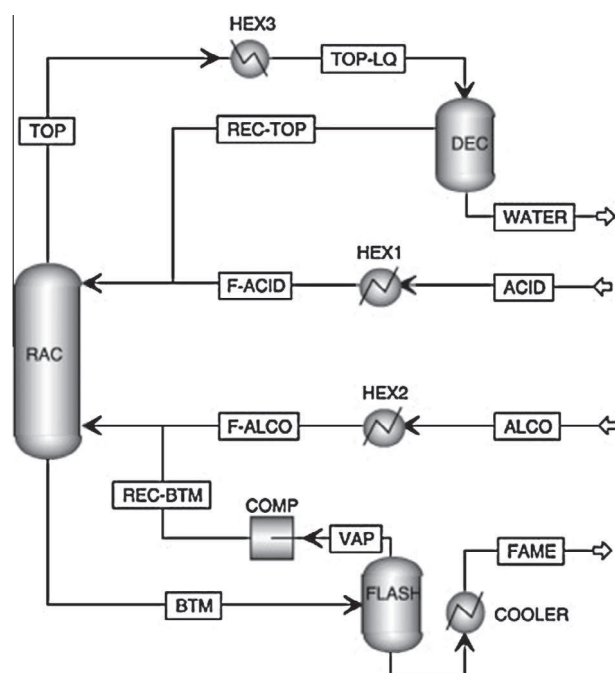


Fig. 14. Diagram of the reactive absorption. Water is recovered at the top of the column, FAME is recovered at the bottom of the column [187].

3.2. Product separation

Product separation is an important point to be considered in the design of sustainable processes since separation steps can be highly costly in terms of energy and time [38]. Separation steps can be combined with mixing and reaction operations in innovative equipment thereby shifting reaction equilibrium and enhancing process performance. Product separation and purification can also be facilitated by the use of heterogeneous catalysis and by inducing specific physical or chemical phenomena in the different process equipment.

Table 26 indicates how easy it is to separate products for the four reactions with different types of catalysts in various process equipment. Results from the literature show that microstructured reactors accelerate decantation due to the formation of parallel flow patterns or of bigger droplets with slug-flow. In cavitation reactors, the reaction is very fast, thereby hindering the formation of di and monoglycerides, which have surfactant properties. As a result, the emulsion is unstable and the phases are easy to separate. Microwave irradiation has also shown to accelerate the decantation process by enhancing drop coalescence. Membrane reactors have been shown to retain glycerides and soaps in transesterification, leading to highly pure products. Pervaporation membrane is also used to remove continuously water during esterification. It is expected that this type of technology may also be of interest for the other reactions. Reactive distillation has of course proven to be adapted to product separation for transesterification and esterification. However, it may not be of interest for

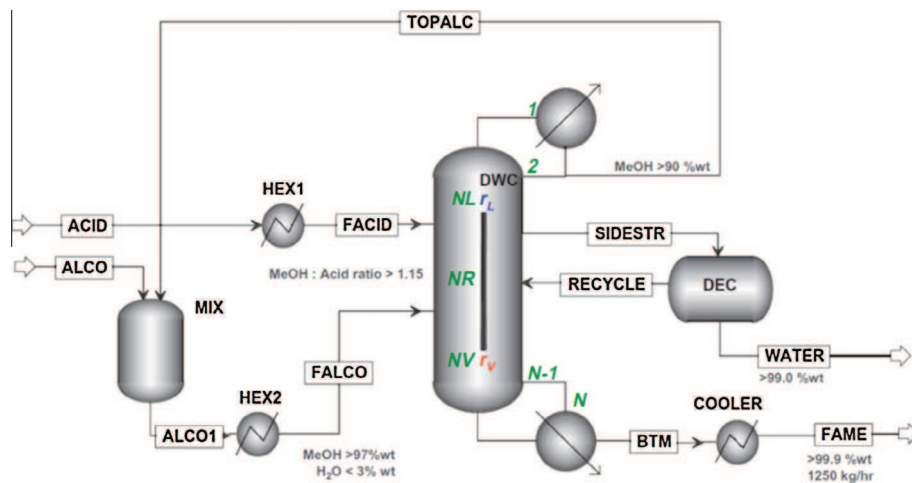


Fig. 15. Reactive dividing-wall column configuration [183]. Excess of methanol is recycled at the top, water is removed at the side and FAME is recovered at the bottom.

Table 25
Advantages and drawbacks of reactive distillation columns for the reaction of transesterification, esterification and hydrolysis.

Reactive Distillation	Advantages	Drawbacks
Transesterification	- Reaction and separation of the methanol in one single step	- Energy requirements
Esterification (with methanol)	- Reaction and separation in one single step - Possibility to have 3 streams, methanol (top), water (middle) and FAME (bottom) with R-DWC - Compatible with a heterogeneous catalyst	- Energy requirements ($10^{-3} \text{ g}_{\text{FAME}}/\text{J}_{\text{reboiler}}$) (136 kW at the reboiler for a production of 1250 kg/h, data of Table 3 from Ref. [187])
Esterification (with glycerol)	- Remove of water (with methanol)	- No results found
Hydrolysis		- Products with high boiling points

Table 26
Summary of the type of catalyst used and the ease of separation in different process technologies for the four reactions. + indicates a positive effect of the technology; - indicates a negative effect; 0 indicates no effect. The data without brackets has been proven in literature studies whereas data between brackets is deduced from the results in the literature.

Reactor	Catalysis			Hydrolysis	Separation facilitation			
	Trans-esterification	Esterification			Trans-esterification	Esterification		Hydrolysis
		Methanol	Glycerol			Methanol	Glycerol	
Microreactor	Homogenous base Homogenous acid	Homogenous acid	Enzymes	Enzymes	++	(++)	(++)	(++)
Cavitation	Homogenous base	Homogenous acid Heterogeneous acid	Homogenous acid	None	+	(0)	(0)	(0)
Microwave	Homogenous base	Homogenous acid	Enzymes	Homogenous base	++	++	++	++
	Heterogeneous base	Heterogeneous acid	Heterogeneous acid	Enzymes				
Oscillatory Baffled	Homogenous base	Homogenous acid	/	/	0	(0)	(0)	(0)
Static mixers	Homogenous base	Homogenous acid	/	/	0	(0)	(0)	(0)
Membrane reactor	Homogenous base	Homogenous acid	/	/	+++	+++	(+++)	(+++)
Reactive distillation	Homogenous base	Homogenous acid	Homogenous acid	None	+++	+++	(+++)	(- - -)
		Heterogeneous acid						

the hydrolysis of triglycerides because it would remove water, which is in this case a reactant, and would shift equilibrium in the wrong direction. Oscillatory baffled reactors and static mixers do not integrate any specific separation operation. As a result, they

most often followed by a decanter for phase separation. However, novel devices such as static mixer with integrated decanter have shown to shift the transesterification reaction equilibrium by withdrawing the glycerol product [159,160].

Table 27

Summary of heterogeneous catalyzed reactions with forces of the different technologies. Technologies highlighted in bold are technologies of interest on an energy consumption criterion. *c*: conversion (%), *t*: residence time (min).

Catalysis		Process Equipment					
		Reactor performance		Recommended equipment for mass transfer	Selection criteria	Recommended equipment for product separation	Energy requirements (g/J)
<i>c</i> (%)	<i>t</i> (min)						
Transesterification	Heterogeneous (SrO/SiO ₂) FFA and water tolerance increase to 3%	96–99	2–30	Static mixers	Less energy consuming Reaction time reduced	Decanter: glycerol removal	10 ¹
		97–100	1–6	Millireactors		Flow-pattern: accelerated decantation	10 ⁻²
		95–99	<1 μs	Cavitation reactors	No DG/MG formation	10 ⁻⁴	
		96–99.8	1–6	Microwave	Break emulsion between a polar and an oil phase	10 ¹	
		96–99	5–210	Membrane	Integrated separation unit Membrane: Keep unreacted glycerides (higher purity)	/	
Esterification (Methanol)	Heterogeneous (Sulfated zirconia, Scandium trisulfate)	100	/	Reactive distillation	Shifted equilibrium due to product removal	Separation of water, methanol and esters	10 ⁻⁶
		/	/	Static mixers		Decanter (water removal)	10 ¹
		99.9	/	Membrane		Membrane: Removal of water	/
Esterification (Glycerol)	Heterogeneous (Sulfated zirconia, Scandium trisulfate)	/	/	Cavitation Millireactors	Mixing intensification (reduce T, P) Reaction time reduced	Compatibility with an integrated decanter	10 ⁻⁴ 10 ⁻²
		/	/	OBR		Recovery of unreacted glycerol	-
		99	30	Microwave	Break emulsion between a polar and an oil phase	10 ¹	
		/	/	Reactive distillation	Removal of water	>10 ⁻⁶	
		/	/		Shifted equilibrium due to product removal		
Hydrolysis	Heterogeneous (SrO/SiO ₂) (FFA and water tolerance increase to 3%)	/	/	Cavitation Millireactors	Mixing intensification (reduce T, P)	Compatibility with an integrated decanter	10 ⁻⁴ >10 ⁻⁶
		/	/			Recovery of unreacted glycerol	
		100	5	Microwave	Distillation (under vacuum)	10 ⁻²	
		/	/	Membrane	Integrated separation unit	Membrane: Keep unreacted glycerides (higher purity)retains soaps	/

3.3. Equipment choice

Table 27 presents recommended choices of catalyst type and process equipment, for both reaction and separation, for the four different reactions related to FAME production and provides characteristic information on reaction conversion, time and the process energy requirements.

3.3.1. Transesterification

Transesterification is the most common reaction used for obtaining FAME. In terms of catalysts, strontium oxide with silica is a very good candidate for transesterification reactions because its tolerance to FFA and water is high compared with other catalysts. Indeed, conversion of more than 90% can be achieved with FFA and water contents greater than 3 wt.%. Under these conditions, this means that WCO pretreatment steps may be not always be essential.

In transesterification reactions, the mixing process is important at the beginning of the operation where the objective is to increase the interfacial area between the triglycerides and the alcohol so that the reaction can take place. However, once the reaction starts, the generation of interfacial area by mixing is less difficult due to the formation of di- and monoglycerides, which facilitate liquid-liquid contacting and dispersion, leading to a pseudo-homogenous phase. Therefore, sophisticated mixing technology is not particularly required, which is why a low energy consumption reactor with static mixers may often be preferred. However, if the process objective is to reduce processing times, other intensified reactors

such cavitation, microstructured, microwave or oscillatory baffled reactors are recommended. In such equipment, the separation step of the transesterification process is facilitated naturally by inherent characteristics of the process and flow conditions or by combining it with a specific device for separation. For example: micro/microstructured reactors enable the generation of liquid-liquid flow patterns that ease product separation at the outlet; the formation of di- and monoglycerides and consequent pseudo-homogenous phase is avoided in cavitation reactors, thereby leading to a less stable emulsion and facilitating phase separation; microwaves promote the drop coalescence process, thereby speeding up the separation process. These different equipment types can also be used in combination with a decanter for product separation or with a membrane, which retains any unreacted glycerides and allows high purity esters to be obtained at 90% conversion.

3.3.2. Esterification with methanol

In FAME production processes, esterification with methanol is often performed to reduce FFA levels in feedstock before performing base-catalyzed transesterification. Heterogeneous catalysts are preferred for the same reasons than previously. Good catalyst candidates are sulfated zirconia or scandium trisulfate, which have demonstrated high performance in reactive distillation and microwave reactors, respectively.

In esterification reactions, the mixing process has a more or less important role depending on the miscibility of the reactants, which is related to the length of the carbon chains. For immiscible reactants, mixing must be able to generate sufficient interfacial area

between the phases and flow circulation to promote the reaction. In the case of partially miscible reactants, drop break-up is less important but the mixing of reactants is still vital for reaction performance. Amongst the different innovative process equipment, both reactive distillation and static mixer systems with an integrated decanter appear to give best results for esterification. Indeed, in these systems the products are continuously separated from the reactive media, thereby shifting the reaction equilibrium and enhancing product formation. The use of membranes could also be considered in order to retain unreacted glycerides and produce high purity esters.

3.3.3. Esterification with glycerol

Esterification using glycerol, which is a side-product of transesterification, is an interesting way to decrease the FFA levels in high FFA content WCO. Heterogeneous acid catalysis using sulfated zirconia or scandium triflate appears to be the most appropriate means to catalyse the reaction.

In esterification reactions using glycerol, mixing is an important step of the process due to the very low solubility of reactants (i.e. fatty acids and glycerol). Indeed, the mixing operation determines interfacial area available for mass transfer and the fluid circulation, both of which are important for the progress of the reaction. Conventionally, high temperatures are used to increase reactant solubility and to facilitate fluid contacting with the disadvantage of high operating costs. Cavitational, microwave, oscillatory baffled and microstructured reactors provide a means to intensify mixing and fluid contacting at ambient operating conditions, thereby being more energy efficient. Reactive distillation under vacuum conditions can also be used to shift the reaction equilibrium and separate products, but with the disadvantage of requiring higher energy input. A static mixer reactor-decanter that shifts the reaction equilibrium may also be a recommended choice if reaction yield is the principal process objective.

3.3.4. Hydrolysis

The primary interest of the hydrolysis of triglycerides is to concentrate fatty acids in the feedstock. Strontium oxide is possibly a good candidate for heterogeneous catalysis. Like for the esterification reaction with glycerol, the mixing process is very important due to low solubility of reactants. As a result, conventional processing often requires high temperatures and pressures to ensure sufficient yield and acceptable reaction times. Intensified process technologies such as cavitational, microwave, oscillatory baffled or microstructure reactors can be used to intensify mixing and allow good reaction performance with milder operating conditions. Reactive distillation is not recommended since it would result in the removal of water and would not promote the formation of products. The separation of products – fatty acids and glycerol – can be carried out with a distillation column under vacuum conditions or in microstructured reactors by generating slug-flow or parallel flow, which accelerate the decanting process. Since glycerol and fatty acids are miscible if the reactive medium is basic [193], the combined reactor-decanter is a means to facilitate product separation and limit the formation of soap. Contactors combined with membranes, which retain unreacted glycerides, are also a recommended means for obtaining high purity products.

4. Conclusion

A review of the different process equipment that can be used to intensify FAME production has been presented. Continuous process technologies that intensify mixing and fluid contacted are recommended because the four reactions related to FAME production involved immiscible liquid–liquid reactants. The product separation

step has been taken into account in the discussion and equipment that combine the reaction and separation steps are particularly recommended. The implementation of heterogeneous catalysis in these innovative process intensification technologies has also been discussed. Finally, specific process equipment has been recommended for the intensification of FAME based on different selection criteria.

It can be seen from this review that various types of innovative process equipment, such as cavitational reactors, oscillatory baffled reactors, microwave reactors, reactive distillation, static mixers and microstructured reactors enable significant mass transfer enhancement and improved performance of FAME production compared with conventional batch tank processes. Furthermore, the integration of continuous reaction and separation units appears to provide the best means for intensifying FAME production, leaving thus a vast number of configurations to be explored or invented. Amongst the different reactor types mentioned in this review, several are poorly understood in terms of physical phenomena and operating characteristics in liquid–liquid reaction applications. In particular, much fundamental knowledge on the operation of cavitational reactors, oscillatory baffled reactors and microwave reactors is still required. Further to this, the development of microwave reactors that are adapted to industrial FAME demands still requires significant work and considering this, continuous microwave reactors may be particularly interesting to explore. It should also be pointed out that heterogeneous catalysts have shown provide attractive results in terms of reaction performance in certain equipment (e.g. microwave reactors, reactive distillation) and therefore deserve to be explored further in other innovative process equipment, such as oscillatory baffled reactors and cavitational reactors.

Indeed, the choice of one process technology over another for FAME production is not that straightforward and it clearly depends on the global process objectives. Of course, some equipment (e.g. static mixers and microwave reactors) may be attractive due to their low energy consumption; others, such as reactive distillation, may be preferred due to effective product separation despite high energy requirements. However, although the number of studies on the feasibility of different process technologies for FAME production is significant, detailed economical and energy efficiency analyses of the various technologies and processes are still needed. These, in addition to studies on reaction performance, will of course be vital for the development of sustainable and green FAME production processes and therefore should be considered in the future studies.

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