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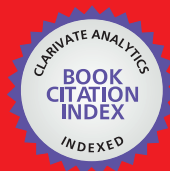
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Kinetics of Transesterification Processes for Biodiesel Production

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Additional information is available at the end of the chapter

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Abstract

Biodiesel is a renewable fuel mainly produced by transesterification of oils and fats that can be used as a transportation fuel, solvent and for energy generation with the potential to reduce the emissions of CO₂, SO₂, CO and HC, compared to fossil fuels. In this work, the kinetic behavior of triglycerides by different transesterification technologies is investigated through a critical review of the kinetic models reported in the study with the aim to establish a trend of the reaction mechanisms and the main variable effects and to further optimize the chemical process. The study of the transesterification reaction kinetics is performed for every type of transesterification, that is, homogeneous, heterogeneous, enzymatic and supercritical. The kinetic models are thus reviewed by describing the way they have evolved and how they can be used for process simulation and optimization. This chapter is divided in a study of the state of the art, an analysis and synthesis of research results, and an application for further optimization of the biodiesel production process.

Keywords: biodiesel, kinetics, transesterification, optimization, modeling

1. Introduction

Biodiesel is a renewable fuel of key importance to meet environmental and economic sustainability. It is produced by transesterification of vegetable oils or animal fats with an alcohol, such as methanol or ethanol, on an alkaline, acid or enzyme catalyst, and it is composed of a mixture with at least 96 wt% of fatty acid methyl or ethyl esters (FAME or FAEE).

A high percentage of the current investigations in the domain of biodiesel production is oriented toward the design of suitable solid catalysts, either with acid or with alkaline properties. Likewise, much emphasis is being placed on research on free or supported enzyme catalysts. Other transesterification methods that are under development include the application of supercritical conditions without the use of catalysts and the use of radiofrequency or ultrasonic assistance.

The development and optimization of biodiesel production processes involve much experimental work, as well as the application of kinetic models that try to describe the process in a more comprehensive and realistic way. Some of the variables that are commonly studied in the development of kinetic models are the reaction temperature, the feedstock composition, including different contents of free fatty acids (FFAs), the alcohol-to-oil molar ratio, the mixing speed and the reaction time. The internal and external mass transfer limitations when using solid catalysts have also been studied.

This chapter deals with the main challenges in the development and application of kinetic models for the transesterification reaction, as well as representative results of current developments in this area.

2. The importance of kinetic modeling for process optimization

The development of kinetic models of chemical transformation processes for the production of higher added-value products is a powerful tool for reactor design. The kinetic model is also necessary for the optimization of the complete process, including the separation and heating steps. Thus, the kinetic model must be incorporated into the reactor model and then applied in the process simulation.

Regarding chemical or biochemical transformations in reactors or bioreactors, the kinetic models are of great help in the selection of the most favorable reaction conditions (e.g. temperature, pressure, mixing rate) to maximize the formation of desired products with the least investment of material and the use of economic resources. This also applies to the different biodiesel production processes, including homogeneous, heterogeneous, enzyme catalysis, and so on, which will be addressed in the next sections.

A well-planned experimental study and the subsequent development of a kinetic model are considered one of the most crucial steps in the chemical process development for industrial applications.

Kinetic models may offer different levels of detail and predictive capabilities, as they can take into account mass and heat transfer phenomena, as well as thermodynamic equilibrium. The level of theory for modeling the reactions can go from the use of quantum chemistry to the individual elementary steps up to a series of encompassed reaction steps between pseudo-components (lumped model). The catalyst deactivation, the presence of undesired side reactions, the consideration of inhibition processes and a detailed feedstock composition are among other factors that can be considered to derive more realistic kinetic models and with a higher predictive capacity. A more comprehensive model can give a more significant

response and provide more detail on the composition and, therefore, on the quality of the products. Thus, a more robust model can be more useful; however, the number of kinetic parameters can increase significantly. The estimation of these parameters must be performed rigorously in order to generate reliable results.

On the other hand, modeling of chemical reactors is very useful for the simulation and control of the process involved. This requires a previous selection of the kinetic model to be applied. Reactor modeling is used to determine concentration, temperature and pressure profiles, generating valuable information for the scaling-up of the process. The reactor model may include more or less the detail of the variables of interest, being possible to determine temperature and concentration profiles at intraparticle conditions, as in the case of heterogeneous reactors.

The development of kinetic models of biodiesel production processes and their application to simulate and optimize these processes has been investigated and reported by a number of researchers. Portha et al. [1], for example, reduced the excess of ethanol used in the transesterification reaction of oils in a continuous process by using a two-stage continuous heterogeneous catalytic reactor. Their simulation results enabled them to determine that the overall performance of the system could be improved with the use of an inter-stage methanol addition as well as by changing the reaction temperature for the second reactor. In their experimentation with triolein as a model compound, the authors found converting the main part of triolein in the first reactor and converting diglyceride and monoglyceride in the second one to be useful. Their simulations also indicated that a higher temperature in the second reactor was advisable to enhance reaction rates at this stage. They also worked on the optimization of the inlet methanol-to-triolein molar ratio, finding that the use of a molar ratio larger than 25:1 mol/mol had no further significant impact on the biodiesel yield. Furthermore, by introducing the kinetic model into a reactor model, the authors calculated internal concentration profiles and found that the internal diffusion of triglycerides (TG), diglycerides (DG) and monoglycerides (MG) was the limiting phenomena in the overall transformation.

A kinetic model can also be applied as a strategic tool for obtaining a better understanding of the rates of product formation and the inhibition patterns present in the transformation scheme [2]. A reaction scheme for the biodiesel production, for example, through enzymatic processes, can consider much more reaction steps and thus a higher number of reaction parameters. This certainly introduces an additional complication in the development of a kinetic model, but when this model is solved, it can be used to design a reactor based on enzyme catalysis and ultimately to optimize the process.

In the field of research and process development, the application of kinetic models that are able to accurately simulate the process at different reaction conditions is useful to provide the guidelines for further experimental work, helping in this way to discard potentially unproductive experimental trials. Models can also help to predict the effect of composition on the quality of the product. For example, a model could predict how the FFA or the water content in the feedstock can affect the reaction conversion and therefore the yield and quality of biodiesel.

3. Kinetic modeling for biodiesel production

There is a consensus on the reaction steps involved in the transesterification process of triglycerides, which are indicated in **Figure 1**. These are the three consecutive and reversible reactions.

In the first reaction, triglyceride (TG) molecule reacts with an alcohol molecule, typically methanol (M) to produce diglyceride (DG) and a fatty acid methyl ester (ME). Then, in the second reaction, diglyceride reacts with alcohol to form monoglyceride (MG) and another molecule of fatty acid ester. In the third reaction, monoglyceride (MG) reacts with alcohol to produce glycerol (G) and a third molecule of fatty acid ester.

When the concentration of FFA present in the oil requires a previous (or simultaneous) stage of esterification, the following reaction that forms one molecule of methyl ester and one molecule of water (W) is considered in the model:



The development of kinetic equations is performed from the reactions taken into account for each particular case. The final form of the kinetic expressions is affected by the nature of the reacting mixture, homogeneous or heterogeneous, the selected alcohol, the alcohol-to-oil molar ratio and the influence of mass transfer effects, among other factors. In the following subsections, representative kinetic models for each type of reaction are discussed.

3.1. Homogeneous transesterification

Most of the work reported on the kinetics of transesterification of oils and fats has been derived from experiments with homogeneous catalysts and mainly with alkaline catalysts.

Freedman et al. [3] carried out the homogeneous transesterification of soybean oil using butanol and methanol and both alkali and acid catalysts, finding that alkaline-catalyzed reactions proceed at considerably faster rates than acid-catalyzed transesterification. The kinetic coefficients reported at 60°C for the former were two to four orders of magnitude higher than the latter. For this reason and because alkaline catalysts are less corrosive to industrial equipment than acid catalysts, most commercial biodiesel processes are conducted with alkaline catalysts. Sodium alkoxides are among the alkaline catalysts that have been used extensively for this reaction [4]. Freedman et al. [3] also found that the reaction with butanol follows a second-order reaction. These authors performed alkaline- and acid-catalyzed experiments

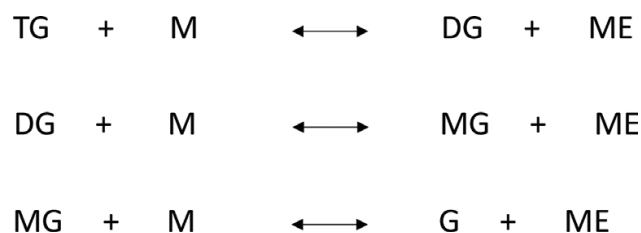


Figure 1. Consecutive reversible reaction steps considered in the formation of methyl esters from triglycerides.

using a larger excess of alcohol. From their results with a butanol-to-soybean oil molar ratio of 30:1 mol/mol, they found that the forward reaction followed pseudo-first-order kinetics for both alkaline and acid catalysts, as expected. The kinetic coefficients for the first reaction shown in **Figure 1** are higher than those for the second and third reactions. This is valid for the forward and reverse reactions and is a general result reported by different authors for alkaline-catalyzed transesterification [5]. In the case of acid-catalyzed tests, the rate coefficients for the first reaction were lower than those for the second and third reactions for both forward and reverse reactions. This has also been reported by other authors [6]. The activation energies for all the alkaline- and acid-catalyzed transesterifications using both butanol and ethanol ranged from 8000 to 20,000 cal/mol. These results are also in agreement with the activation energies reported by other researchers [5, 6].

Other kinetic models like the one proposed by Gonzalez-Brambila et al. [7] consider the effects of mass transfer phenomena on the transesterification of soybean oil with methanol and NaOH in a batch reactor, using the experimental data from the study [8] and by proposing a mass transfer-kinetic dynamic model. Two liquid phases were considered: a non-polar TG-rich phase and a polar methanol-rich phase, and the reaction was considered to take place only in the interphase of the drops. Besides the six kinetic coefficients derived from **Figure 1**, the mass transfer coefficient between drops and alcohol phase was evaluated. In this way, the model can not only describe the evolution on time of TG, DG, MG, glycerine, methanol and ester composition but also estimate the reduction of drops' radii during the reaction, which are relevant data considering that reaction takes place on the drops' surface.

3.2. Heterogeneous transesterification

The use of heterogeneous catalysts presents several advantages over the use of homogeneous catalysts, among which the ones that have been most emphasized include the elimination of the washing section and huge amounts of waste water, reusable catalyst and easier disposal of the spent one, high purity of glycerol and the end product [9]. Hence, several conventional solid bases and acids (with and without promoters/dopants) have been investigated with this purpose. These included different solid acid catalysts such as sulphated zirconia [10], zeolites [11], heteropolyacids [12], ion-exchange resins [13] and sulphonated carbons [14]. Moreover, it has been reported that working under optimal conditions, heterogeneous transesterification can approximate the activity obtained with homogeneous catalysts. For example, Kim et al. [15] used the heterogeneous catalyst Na/NaOH/ γ -Al₂O₃, reaching conversions of 95%, with a methanol-to-oil molar ratio of 9:1 mol/mol at an atmospheric pressure. These results are comparable to those obtained with the conventional homogeneous catalyst (NaOH).

Like homogeneous acid catalysis, when the oil to be fed has a concentration of FFA greater than 3 wt%, an acid solid catalyst that tolerates the presence of FFA and possess activity for both esterification and transesterification to convert FFA and oil to biodiesel should be used.

Normally, the first option to carry out the scaling-up of a continuous heterogeneous transesterification process is the use of a fixed bed reactor (FBR), due to the simplicity of its design and the ease of its operation. However, the effect of the diffusive resistances must be considered in order to obtain a reactor design that meets the expected conversion levels.

The transesterification reactions of oils in a fixed bed reactor (FBR) present different mass transport processes that affect the rate of production of biodiesel. The reaction system has two liquid (L) phases and one solid (S) phase represented by the catalyst. One of the liquid phases is rich in oil, while the other is rich in methanol, or any other alcohol. In this way, the external diffusive resistances associated with the transport of methanol and triglyceride toward the surface of the catalyst must be considered and the intraparticle diffusive resistances as well. The modeling of these complex processes involves the calculation of mass transfer coefficients of the components involved in the chemical reactions. Moreover, as reaction proceeds, the solubility of methanol in the oil-rich phase is increased due to a higher presence of esters, which act as co-solvents for methanol. The formation of monoglycerides and diglycerides increases the solubility of methanol in the oil-rich phase. As this solubility increases, the diffusive resistances at the L-L interface decrease [8], accelerating the transport of the reactants and therefore increasing the reaction rates. A similar effect is observed in the case of feedstock with a high FFA content, giving rise to a greater solubility and ease of transportation of the reactants in the L-L interface and thus allowing higher rates of biodiesel formation. This was confirmed by the results of Bhoi et al. [16], who reported that the rates observed for pure TG were significantly lower than those for a mixture of TG and FFA. They also estimated that for a mixture containing 20 wt% FFA, the rise in solubility was of the order of 1.35–1.5 times the solubility in pure TG. Similar results have also been reported by Singh et al. [17].

The application of a model that considers the mentioned effects in the three consecutive reversible reaction steps shown in **Figure 1** is not an easy task, since it requires data on liquid-liquid distribution for reactants and products and the relative proportion of each phase at different reaction conversions.

Bhoi et al. [16] developed a model that incorporates the effect of mass transfer resistances at both L-L and L-S interfaces for the transesterification reaction and simulated an FBR. Experimental data were obtained from two reactors, a spinning basket reactor (SBR) and an FBR and using a catalyst in pellets of a 6-mm diameter and an 8–10-mm length. Higher reaction rates in the reactor free of external diffusive resistances, that is, the SBR, were observed, concluding that the FBR is strongly hampered by external mass transfer resistances. The estimated kinetic parameters with the SBR were observed to be affected by internal diffusive resistances, which were corroborated by an estimated value of the activation energy of 25 kJ/mol, corresponding to the first reaction (forward) shown in **Figure 1**. Although this reaction was only considered in their kinetics for lower conversions, they were able to estimate the L-L and the L-S mass transfer coefficients. The latter was found to be four to eight times higher. Thus, they concluded that resistance in the L-L interface determined the overall rate of the process.

Bhoi et al. [1] developed a model for an FBR with axial dispersion considering mass transfer limitations in the catalyst as well as dynamic aspects. The reactor was considered to operate isothermally considering that transesterification reactions are almost athermic. The reaction stage consisted of two FBR connected in series and at 50 bar and 175°C. The simulations yielded a conversion of triolein (model feedstock) of 87% with a methanol:triolein ratio of 36:1 mol/mol, over a solid alkaline catalyst. It was found that the kinetic system behaves according to a second-order rate law. Adsorption terms were not included in the developed kinetic expressions. Similar to what has been reported for homogeneous-catalyzed transesterification of triglycerides, the calculation of the kinetic coefficients for the three reactions shown in

Figure 1 indicated that the first reaction was the fastest, while the second and third reactions were about one order of magnitude lower.

In an experimental study that considered the adsorption process, Dossin et al. [18] evaluated the intrinsic kinetics of the transesterification of ethyl acetate with methanol over an MgO catalyst. Among the evaluated models, the one that best fitted the experimental data corresponded to an Eley-Rideal (ER) type model, with the adsorption of methanol as the rate-limiting step.

3.3. Other transesterification methods

Other promising transesterification methods for producing biodiesel that are gaining more relevance as research progresses are enzyme catalysis and supercritical methanol.

Among the main advantages of using enzymes (free or immobilized) is that they can process variable and low-quality feedstocks, as they are less sensitive to high FFA and water content. Then, enzymes can process FFA and TG in a single reaction step. Moreover, when using enzymes, there is no need for a subsequent washing step. On the other hand, lipases have the disadvantage of being sensitive to high concentrations of methanol, and their implementation is currently more expensive compared with other methods. The mechanism widely accepted for describing enzymatic transesterification corresponds to a double-displacement type or a ping-pong mechanism [19]. This reaction scheme presents a great complexity to be modeled, since the number of kinetic coefficients involved is high, and their experimental determination is a great challenge. Due to this complexity, simplified models are used, which generally do not describe the formation and transformation of di- and monoglycerides, as well as the influence of temperature on the enzyme deactivation and the conversion limits derived from equilibrium. The complexity of the process can further increase if the presence of multiple phases is taken into account when immobilized enzymes are employed. Moreover, steric effects may have an important impact due to the large size of the glyceride molecules. To promote the fitting of experimental data to kinetic models of the process, simplified models such as the Michaelis-Menten type are used [20], although their predictive capacity is limited generally. Kinetic studies on the enzymatic production of biodiesel have been performed mainly with immobilized lipases, and most of these simplified models consider only irreversible reactions. Firdaus et al. [2] applied a simplification of the ping-pong model that resulted in the evaluation of about 30 rates coefficients, including those corresponding to the reversible steps. This model was later applied to describe the transformation of oil with a liquid lipase from *Thermomyces lanuginosus* in a 24-h reaction at 35°C. The authors analysed, among other aspects, the effect of water and FFA content and reported that the biodiesel obtained nearly complies with the quality standards.

Catalytic and non-catalytic transesterification using an alcohol at supercritical conditions is another method under intensive investigation. This process has a high potential for both the transesterification of TG and for the esterification of FFA. Conversions reported are commonly greater than 90%, and reaction times are as short as 10 min or less [21]. The high temperatures and pressures required for the application of this technique represent, however, a limitation for its development and application, mainly due to the high energy costs of the process. In recent years, there have been an increasing number of reports in which this process is applied, either with the use of a catalyst or without it. In a recent work [22], the application

of simplified kinetic models that describe only the formation of esters and disappearance of triglycerides as a function of conversion has been performed.

4. Analysis of general aspects affecting the kinetics of transesterification

4.1. Homogeneous catalysis

Homogeneous catalysis is commonly used during transesterification reaction, and alkaline and acid catalysts are used. The most active catalysts have been reported to be alkaline ones [23].

4.1.1. Reaction mechanisms

Two mechanisms are involved in transesterification reaction depending on whether acid or basic catalysts are used.

4.1.1.1. Basic catalysis

In the case of alkaline catalysts, the reaction proceeds very fast, hydroxides, alkoxides, and sodium and potassium carbonate being the most commonly used catalysts (**Figure 2**). When an alkali is used, the first step is the formation of an alkoxide, which is a strong nucleophile that attacks the electrophilic carbon in a carbonyl group of the triglyceride. This attack turns the carbonyl into a tetrahedral intermediate as shown in the second step. Then, the tetrahedral carbon is separated from the intermediate to form an alkyl ester (third step). Deprotonation of catalyst regenerates the alkali, whereas the proton is attached to a diglyceride anion as shown (fourth step). Catalyst can react with another alcohol molecule and the mechanism is repeated until the catalyst reacts once again with an alcohol molecule to produce glycerol and alkyl esters [24].

4.1.1.2. Acid catalysis

When sulphuric or sulphonic acid is used, a very high yield of alkyl esters is obtained. In this case, the reaction mechanism is acid catalyzed. Early research [3] has reported that transesterification of soybean oil with methanol reached almost 100% after 50 h of reaction at 65°C using 1 mol% of sulphuric acid with an alcohol-to-oil molar ratio of 30:1 mol/mol, whereas using ethanol and 1-butanol as alcohols took 18 and 3 h, respectively; however, reaction temperature was higher (78 and 117°C, respectively). Inconvenience such as glycerol recovery due to alcohol in excess is to be expected by which the oil-to-alcohol molar ratio needs to be optimized [24].

Figure 3 shows a schematic reaction mechanism when an acid is used as catalyst, which is valid not only for a monoglyceride but also for di- and triglycerides. Protonation of the carbonyl group is the first stage (I). A carbocation (II) is then formed and undergoes a nucleophilic attack. Alcohol is attached to the tetrahedral intermediate (III), and a new ester (IV) is obtained by glycerol elimination and catalyst regeneration. The carbocation formed in step II is highly reactive by which water must be avoided during reaction because this molecule can act as a nucleophile and form carboxylic acids, which is a competitive reaction [24].

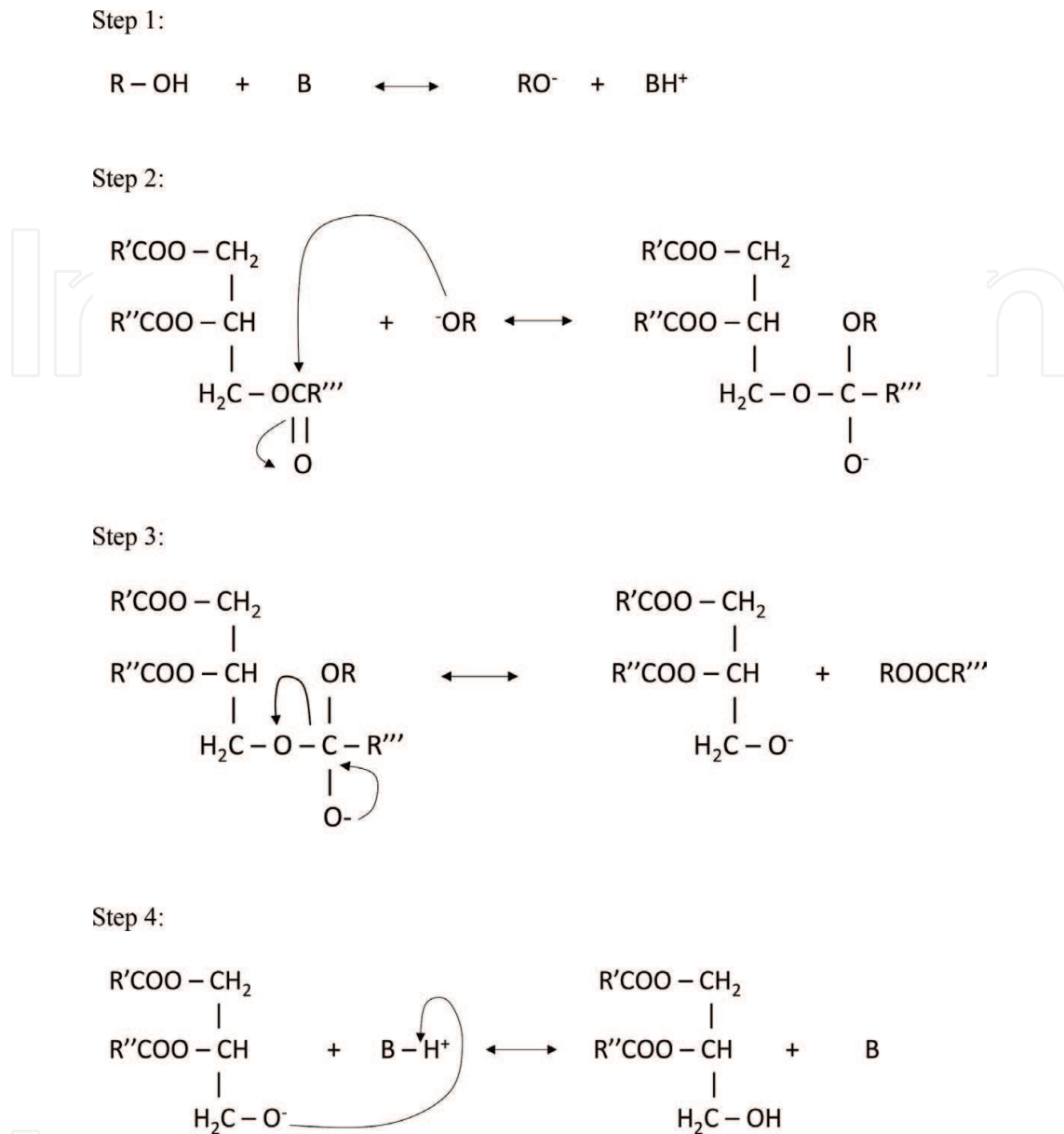


Figure 2. Alkali-catalyzed reaction mechanism.

To select the most suitable transesterification reaction pathway, either alkaline or acid, it is necessary to determine firstly the FFA content. This value must be lower than 3 wt% to proceed by the alkaline-catalyzed route without the significant formation of soap. This can lead to an emulsion that makes difficult the biodiesel and glycerol phases separation. Thus, oils with a high FFA content require a two-step process to be converted into biodiesel: (1) the FFAs are converted to fatty acid methyl esters as a pre-treatment with acid and (2) transesterification with basic catalyst is carried out [4, 25]. In this way, both the acid- and alkaline-catalyzed processes are efficiently used.

4.1.2. Mass transfer limitations and reactors for transesterification

Since alcohol and triglycerides are immiscible at room temperature, stirring needs to be carried out to enhance the contact between phases so that a perfect mixing is achieved, avoiding

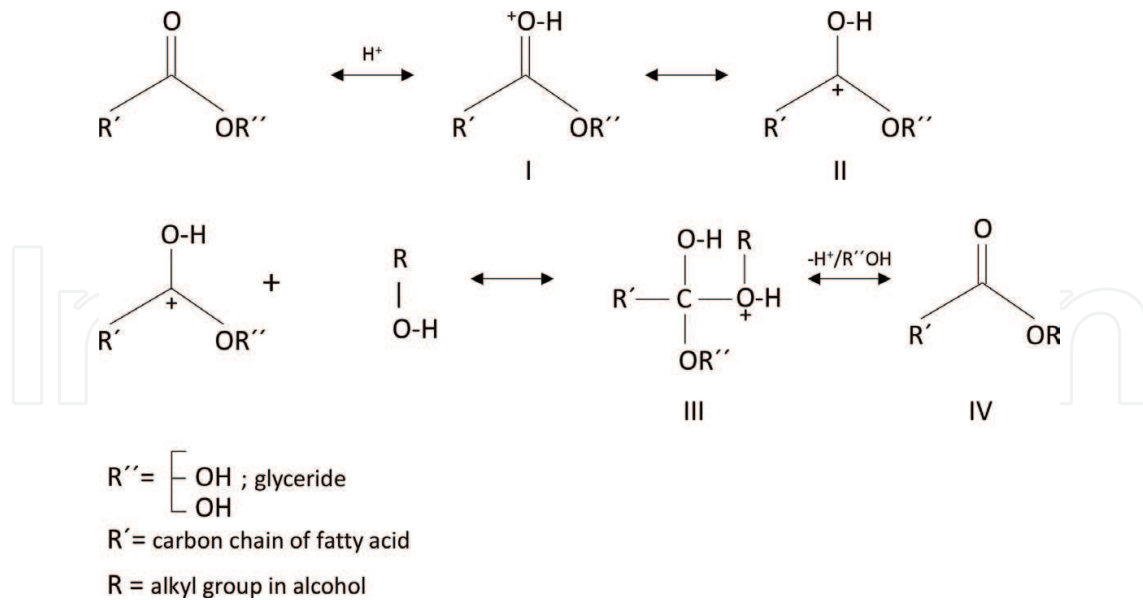


Figure 3. Acid-catalyzed reaction mechanism.

mass transfer limitations and performing the reaction under an intrinsic kinetics. This is not so easy to achieve.

Mass transfer limitation studies have been reported and modeled in detail in a continuous tubular reactor at different reaction conditions [26, 27]. According to the authors, there are two steps that need to be addressed: (1) the reaction mixture passes through the mass transfer-determining region (heterogeneous system where methanol is the dispersed phase and the oil is the continuous phase) to (2) the kinetic-determining region (pseudo-homogeneous system in a single phase).

When using methanol, an emulsion is very quickly formed which is then broken down into two phases, that is, an upper phase constituted by methyl esters and a lower one formed by glycerol. When NaOH is used as catalyst, for example, it dissolves into the alcohol and then triglycerides diffuse through this mixture, and so the reaction is initially mass transfer controlled [4].

Transesterification by supercritical conditions is another reported process to reduce the mass transfer limitations. Several reports have discussed different supercritical conditions to carry out transesterification [28–45] ranging in the case of temperature from 270 to 350°C and pressure from 10 to 45 MPa to ensure only one reacting phase, which eliminate the mass transfer limitations; however, an increase in operation cost is to be expected, while high temperature and pressure could enhance the degradation of fatty acids or FAME, which is known to occur above 250°C. Reaction time has also been reported to vary from 4 to 110 min. The alcohol-to-oil molar ratio is also quite high at these conditions, that is, from 20 to 40. At supercritical conditions, alcohol acts as an acid catalyst [29] and FFA and water present in the feed do not affect the transesterification conversion [46].

To further minimize the mass transfer limitations, reactors that enhance the contact between phases can be used. One of these reactors is the so-called oscillatory baffled reactor (OBR) composed of a tube containing equally spaced orifice plate baffles in which the oscillatory flow forms

vortices, improving radial mixing and plug flow behavior [47]. Optimal baffle spacing has been previously calculated, and it was found that mass transfer rate depends on this spacing along with oscillation frequency and amplitude [48]. A better contact between phases is obtained with the use of static mixers consisting of motionless elements inside a pipe or a column to create radial mixing between immiscible liquids [49, 50]. A micro-channel reactor also improves the mass and heat transfer because of its high surface area/volume ratio which enhances the yield of methyl esters (above 90% in short reaction time) as reported elsewhere [51]. Cavitation-based reactors use acoustic energy to collapse cavities that increase local temperature and pressure. Cavitation intensifies the mass transfer rate creating local turbulence and reaching a high yield of FAME at room conditions [52]. Other studies have reported a FAME yield higher than 95% at 35°C, with an ultrasound frequency of 40 kHz at 1200 W of power using 1 wt% of KOH as catalyst, a methanol-to-oil molar ratio of 6:1 mol/mol, for 25 min [53].

4.1.3. *Effect of catalyst concentration*

As mentioned earlier, if FFA or water content is high, then acid-catalyzed transesterification is preferred. In this case, sulphuric, phosphoric, hydrochloric, or sulphonc acids are the most used catalysts. A comparison among HCl and H₂SO₄ as catalyst was made elsewhere and the latter behaved better at 2.25 M [54]. Sulphuric acid at 0.87 M was used during transesterification of *Hevea brasiliensis* at ca. 56°C and 240 min of reaction time [55].

Alkaline catalysts such as sodium alkoxide are very active in short reaction times at low catalyst amount but anhydrous conditions are required. Instead, KOH and NaOH can be used in typical concentrations from 0.4 to 2% w/w of oil [4]. Earlier studies have reported that potassium carbonate (2–3%) as catalyst yielded a high content of methyl esters with minimal soap formation [56]. Encinar et al. [23] used KOH at 0.7% w/w of oil and obtained around 98% of methyl esters. The higher the catalyst concentration, the higher the reaction rate. However, catalyst in excess will turn the separation of products very difficult by which the amount of catalyst must be optimized.

4.1.4. *Effect of mixing speed*

When the methanol and sodium hydroxide solution are immiscible, mixing is necessary to promote the reaction [57]. The initial agitation improves the contact among phases and reduces the mass transfer limitations. Once reaction advances, methyl esters formed act as solvent for reactants and mixing needs to be continued for promoting the reaction rate. Mixing speed was studied by Encinar et al. [23] varying from 500 to 1100 rpm. The optimal mixing speed was stated at 700 rpm, and only a slight increase on the yield of methyl esters was observed above 95%.

4.1.5. *Effect of solvent/co-solvent*

Oil concentration in alcohol is low, particularly when methanol is used once transesterification reaction begins. As oil concentration increases in alcohol, the reaction rate is also increased and triglycerides are converted into diglycerides, which subsequently can react in the alcohol phase rather than being dispersed into the oil phase. As reaction progresses, a glycerol layer is separated. To reduce the mass transfer limitations, the use of nonreactive co-solvents to form a single phase is recommended [58]. Co-solvents such as tetrahydrofuran (THF), dimethyl

ether and methyl tert-butyl ether (MTBE) have been reported to improve miscibility among alcohol and oil. Previous reports [58] have stated that THF and MTBE behave as good co-solvents, THF being better than MTBE. Using a ratio of 1.25 vol/vol of methanol and keeping the methanol-to-oil molar ratio in 6:1 mol/mol at 23°C, the yield of methyl esters was 95% at 20 min. Other authors have studied the influence of methanol/co-solvent molar ratio in the range of 1:0.5–1:2 mol/mol and different co-solvents such as acetone, diethyl ether, dibutyl ether, methyl tert-butyl ether, diisopropyl ether and tetrahydrofuran [23]. Diethyl ether was the preferred co-solvent in a methanol/co-solvent molar ratio of 1:1 mol/mol.

Acetone was used as co-solvent at 25 wt% using KOH as catalyst at 1 wt% and 4.5:1 mol/mol as methanol-to-oil molar ratio, and a yield of 98% of methyl esters was obtained at room temperature after 30 min [59]. Acetone at 20 wt% as co-solvent has also been reported elsewhere [60]. Other authors used dichlorobenzene and acetone at 10% (vol/vol) in methanol as co-solvents and reducing the reaction time by 60% [61]. THF was used as co-solvent in a methanol/co-solvent molar ratio of 1:1 mol/mol and 0.5 wt% of catalyst along with a methanol-to-oil molar ratio of 4:1 mol/mol, and a yield of 98% of methyl esters was obtained after 10 min at 40°C and 200 rpm [62].

When selecting a suitable co-solvent, one has to take into account that at the end of reaction, it will be removed and if possible it will be reused. Thus, its boiling point needs to be maintained low.

4.1.6. *Effect of temperature*

Temperature influences on kinetics and equilibrium of reaction. It diminishes the viscosity of products and improves the mass transfer. At high temperature values, saponification is enhanced, lowering the yield of methyl esters. If methanol is used, the reaction temperature is commonly set at a value lower than its boiling point [63]. The effect of temperature on FAME yield has been studied from 20 to 40°C. If co-solvent is used, then temperature will be lower than its boiling point to avoid vaporization. The authors found that the yield of methyl esters at 30°C was optimal [23]. Some authors have reported temperature values ranging from 50 to 60°C [64]. The use of novel reactors as mentioned earlier is intended to reduce the reaction temperature at near room temperature.

4.1.7. *Effect of methanol-to-oil molar ratio*

Stoichiometrically, three moles of methanol are required by one mole of triglycerides. Since transesterification is a reversible reaction, the addition of methanol in excess displaces the equilibrium toward products in such a way that triglycerides will be converted into methyl esters, by which commonly methanol-to-triglycerides molar ratio is set to 6:1 mol/mol or higher. Nevertheless, methanol in excess increases the cost of biodiesel production, and therefore its recovery is one of the options used to improve the economy of the process. Some reports have studied the effect of methanol-to-oil molar ratio on FAME yield and have found an increase in the yield of methyl esters from 86 to 95% when increasing the molar ratio from 6:1 to 10:1 mol/mol [65]. When using waste cooking oil as feedstock, a higher methanol-to-oil molar ratio of 16:1 mol/mol decreased the yield of FAME, probably because of a reduced catalyst concentration in the reacting mixture. Thus, the optimal molar ratio was 10:1 mol/mol

[65]. In other cases, the optimal alcohol-to-oil molar ratio has been reported to be 9:1 mol/mol that yielded ~94% of methyl esters [23]. This molar ratio is also reported in previous reports [66]; however, depending on the type and quality of the oil, the methanol-to-oil molar ratio must be optimized in each case as in catalyst concentration.

4.1.8. Effect of reaction time

The conversion of triglycerides increases as the reaction time gets longer. In the case of alkaline catalysts, the reaction time is lower than 90 min to reach a maximum yield of methyl esters. As the alcohol and oil mixing starts, their immiscibility slows down the reaction within the first minutes; however, when reactants are well mixed, the reaction proceeds fast [63]. When acid catalysts are used, the reaction time is commonly increased up to several hours as reported before where sulphuric acid in the presence of soybean oil and methanol took 50 h to reach almost 100% of yield of methyl esters [3]. As in the case of methanol-to-oil molar ratio and temperature, the optimal values need to be found for each case depending on the catalyst type and the oil to be used.

4.2. Heterogeneous catalysis

The transesterification of triglycerides by heterogeneous catalysis is an alternative way to produce a biofuel that could help to reduce CO₂ emissions at reduced production costs, becoming thus competitive with petroleum-based diesel fuel [67–69]. There are still many areas of opportunity to improve the economy of the process. Heterogeneous transesterification has been shown to reduce the separation operations, the generation of waste and the use of large quantities of water [70]. One of the most difficult challenges is to find a catalyst with comparable activity to that of homogeneous catalysis, that is, at the same pressure and temperature and in which leaching is not present [71].

4.2.1. Kinetics

The kinetics of the transesterification reaction of oils and fats by heterogeneous catalysis is not so well understood as it is for homogeneous catalysis [72]. Most research works on heterogeneous catalysis have been focused on the synthesis and application of catalysts, and only a few deal with kinetic modeling. Among these, the efforts have been put on the use of small solid particles to obtain reaction conditions under an intrinsic kinetics and in which the phenomena of both intraparticle and external mass transfer are negligible.

Thus, most heterogeneous vegetable oil transesterifications have found to follow a pseudo-first-order rate law. For example, Kaur and Ali [73], in their study with 15-Zr/CaO-700 catalyzed methanolysis and ethanolysis of *Jatropha curcas* L. oil, found that both reactions followed a pseudo-first-order rate law. The negligibility of the transport influences was demonstrated by the Koros-Nowak test. Lukić et al. [74] also found at optimal conditions for the transesterification of sunflower oil a first-order reversible rate law using a ZnO-alumina/silica-supported catalyst and by evaluating both the effects of the calcination temperature and the effects of various supports. A number of kinetic modeling works of heterogeneous transesterification are presented in **Table 1**.

Oil source and catalyst	Reaction conditions	Kinetic model: rate constant (k) and activation energy (E_a)	Ref.
Soybean oil Catalyst: Amberlyst A26-OH basic ion-exchange resin	Molar ratio 10:1, methanol:oil with 5% oleic acid and without acid Agitation speed: 550 rpm Temperature: 50°C	Kinetic model: Eley-Rideal $k = 7.48 \times 10^{-4} \text{ h}^{-1}$ without FFA $k = 1.94 \text{ h}^{-1}$ with FFA	[72]
<i>Jatropha Curcas L.</i> oil Catalyst: Zr/CaO	Agitation speed: 500 rpm Methanolysis Molar ratio 15:1 methanol:oil Temperature: 65°C Ethanolysis Molar ratio 21:1 ethanol:oil Temperature: 75°C	Kinetic model: Pseudo-first order $E_a = 29.8 \text{ KJ mol}^{-1}$; $k = 0.062 \text{ min}^{-1}$ $E_a = 42.5 \text{ KJ mol}^{-1}$; $k = 0.0123 \text{ min}^{-1}$	[73]
Sunflower oil Catalyst: ZnO/alumina-silica, 2 wt %	Molar ratio 30:1 methanol:oil Temperature: 200°C Pressure: 37 bar Reaction time: 4 h Catalyst ZnO Al/Si ratio 3/1 Calcination 600 °C, 12 h Catalyst ZnO Al/Si ratio 3/1 Calcination 300 °C, 12 h Catalyst ZnO Al/Si ratio 1/0 Calcination 600°C, 12 h Catalyst ZnO Al/Si ratio 1/0 Calcination 300 °C, 12 h	Kinetic model: First-order, k model irreversible (for catalyst with lower activity) k_f, k_{-1} model reversible $k = 0.0138 \text{ min}^{-1}$; $k_1 = 0.0190 \text{ min}^{-1}$ $k_{-1} = 0.00140 \text{ min}^{-1}$ $k = 0.0027 \text{ min}^{-1}$; $k_1 = 0.0054 \text{ min}^{-1}$ $k_{-1} = 0.00170 \text{ min}^{-1}$ $k = 0.0036 \text{ min}^{-1}$; $k_1 = 0.0059 \text{ min}^{-1}$ $k_{-1} = 0.00082 \text{ min}^{-1}$ $k = 0.0064 \text{ min}^{-1}$; $k_1 = 0.0068 \text{ min}^{-1}$ $k_{-1} = 0.00014 \text{ min}^{-1}$	[74]
Sunflower oil CaO, 1 wt % Ca(OH) ₂ , 1 wt % CaO-ZnO, 2wt %	Temperature: 60 °C Agitation speed: 900 rpm Molar ratio 6:1, methanol:oil Agitation speed: 900 rpm Molar ratio 6:1, methanol:oil Agitation speed: 300 rpm Molar ratio 10:1, methanol:oil	Kinetic model: Miladinovic model, k is an apparent reaction rate constant and K is a model parameter defining the TG affinity for the catalyst active sites. $k = 0.063 \text{ dm}^6 \text{ mol}^{-2} \text{ min}^{-1}$; $K = 1.63 \text{ mol dm}^{-3}$ $k = 0.025 \text{ dm}^6 \text{ mol}^{-2} \text{ min}^{-1}$; $K = 0.539 \text{ mol dm}^{-3}$ $k = 0.043 \text{ dm}^6 \text{ mol}^{-2} \text{ min}^{-1}$; $K = 3.414 \text{ mol dm}^{-3}$	[75]
Sunflower oil Catalyst: Ca(OH) ₂ , 1-10 wt % based on oil weight	Molar ratio 6:1 methanol:oil Reaction time: 5 h Temperature: 60 °C Agitation speed: 900 rpm	Kinetic model: Pseudo-first order. $k = 0.07(1 - \exp(-C_{\text{cat}}/2.86)) \text{ min}^{-1}$ Where C_{cat} is the catalyst amount (in wt% based on the oil weight)	[77]

Oil source and catalyst	Reaction conditions	Kinetic model: rate constant (k) and activation energy (E_a)	Ref.
Sunflower oil	Molar ratio 6:1 methanol:oil	Kinetic model: Pseudo-first order reaction	[78]
Catalyst: CaO, 1, 2.5 and 10 wt %	Temperature: 60 °C	$k = 0.07 \text{ min}^{-1}$	
Canola oil	Molar ratio 16:1 ethanol: oil	Kinetic model: First order	[79]
Catalyst: Mg-Co-Al-La HDL, 2 wt%	Reaction time: 5 h	E_a : 60.5 KJ/mol	
Sunflower and waste cooking oil	Temperature: 413-473 K	Kinetic model: Pseudo-first order	[80]
Catalyst: CaO·ZnO 2 wt %	Molar ratio 10:1 methanol:oil	Constant k and triglycerides (TG) mass transfer coefficient k_{mtTG}	
	Agitation speed: 300 rpm		
	Temperatures range: 60-96 °C		
	With sunflower oil		
	Temperatures:		
	60 °C	$k = 0.043 \text{ min}^{-1}$; $(k_{mt,TG})_0 = 0.00021 \text{ min}^{-1}$ $(k_{mt,TG})_{AVE} = 0.012 \text{ min}^{-1}$	
	70 °C	$k = 0.051 \text{ min}^{-1}$; $(k_{mt,TG})_0 = 0.00244 \text{ min}^{-1}$ $(k_{mt,TG})_{AVE} = 0.151 \text{ min}^{-1}$	
	84 °C	$k = 0.083 \text{ min}^{-1}$; $(k_{mt,TG})_0 = 0.00285 \text{ min}^{-1}$ $(k_{mt,TG})_{AVE} = 0.244 \text{ min}^{-1}$	
	96 °C	$k = 0.120 \text{ min}^{-1}$; $(k_{mt,TG})_0 = 0.140 \text{ min}^{-1}$ $(k_{mt,TG})_{AVE} = 0.170 \text{ min}^{-1}$	
	With waste cooking oil		
	60 °C	$k = 0.120 \text{ min}^{-1}$; $(k_{mt,TG})_0 = 0.0038 \text{ min}^{-1}$ $(k_{mt,TG})_{AVE} = 0.311 \text{ min}^{-1}$	
	84 °C	$k = 0.140 \text{ min}^{-1}$; $(k_{mt,TG})_0 = 0.0033 \text{ min}^{-1}$ $(k_{mt,TG})_{AVE} = 0.493 \text{ min}^{-1}$	
	96 °C	$k = 0.170 \text{ min}^{-1}$; $(k_{mt,TG})_0 = 0.0038 \text{ min}^{-1}$ $(k_{mt,TG})_{AVE} = 1.664 \text{ min}^{-1}$	
Waste cooking oil	Molar ratio 70:1 methanol:oil	Kinetic model: First order	[81]
Catalysts: Heteropoly acid, 10 wt %	Agitation speed: 300 rpm	$E_a = 53.99 \text{ KJ/mol}$	
	Reaction time: 14 h		
	Temperatures:		
	50 °C	$k = 0.059 \text{ min}^{-1}$	
	55 °C	$k = 0.067 \text{ min}^{-1}$	
	60 °C	$k = 0.091 \text{ min}^{-1}$	
	65 °C	$k = 0.144 \text{ min}^{-1}$	
	70 °C	$k = 0.1062 \text{ min}^{-1}$	

Oil source and catalyst	Reaction conditions	Kinetic model: rate constant (k) and activation energy (E_a)	Ref.
Sunflower oil Catalyst: CaO, 1 wt %	Molar ratio 6:1 methanol:oil Agitation speed: 200 rpm Pressure: 1-15 bars Temperature: 60-120 °C Reaction time: 1.5 h Reaction time: 2.5 h Reaction time: 3.5 h Reaction time: 4.5 h Reaction time: 5.5 h	Kinetic model: Pseudo-first order with significant diffusion restrictions at 80 °C k [=] (10^{-3} min^{-1}) $k(60^\circ\text{C}) = 2.67, k(80^\circ\text{C}) = 73.71, k(100^\circ\text{C}) = 175.4, k(120^\circ\text{C}) = 220.86$ $k(60^\circ\text{C}) = 3.08, k(80^\circ\text{C}) = 88.09, k(100^\circ\text{C}) = 140.77, k(120^\circ\text{C}) = 131.96$ $k(60^\circ\text{C}) = 3.26, k(80^\circ\text{C}) = 81.81, k(100^\circ\text{C}) = 100.41, k(120^\circ\text{C}) = 94.25$ $k(60^\circ\text{C}) = 5.32, k(80^\circ\text{C}) = 77.68, k(100^\circ\text{C}) = 76.94, k(120^\circ\text{C}) = 72.79$ $k(60^\circ\text{C}) = 8.3, k(80^\circ\text{C}) = 65.63, k(100^\circ\text{C}) = 61, k(120^\circ\text{C}) = 59.22$	[9]

Table 1. A review of kinetic models and reaction conditions of heterogeneous transesterification of vegetable oils.

4.2.2. Reaction mechanisms

The heterogeneous catalysis of vegetable oils takes place in a number of steps and in a three-phase system consisting of a solid (heterogeneous catalyst) and two immiscible liquid phases (oil and alcohol, usually methanol or ethanol). To determine the rate-limiting step, a comparison of rates of the different elementary steps should be performed. This has been tried by several researchers by using either the Eley-Rideal (ER) or the Langmuir-Hinshelwood-Hougen-Watson (LHHW) methods.

Jamal et al. [72] have used both ER and LHHW in the transesterification of soybean oil on an Amberlyst A26-OH basic ion-exchange resin and in the presence and absence of free fatty acids. They proposed a four-step mechanism: (1) methanol adsorption by ion exchange on basic resin surface; (2) fatty acid (oleic acid) adsorption by ion exchange on basic resin surface; (3) hydrolysis of tri-, di- and monoglycerides from soybean oil; and (4) transesterification of glycerides (tri-, di- and mono-) with basic resin surface-bound methoxide. By considering the first step as the rate-limiting step, they showed that the ER model describes better the surface interactions occurring on the resin.

Some other authors have developed kinetic models based on first-order rate law. The following three cases show how sunflower methanolysis kinetics has been modeled within two stages, the first one being the initial TG mass transfer limitations and the second one the chemically controlled region.

Tasić et al. [75] have developed a reaction model for the methanolysis of sunflower oil on three calcium-based catalysts: CaO, Ca(OH)₂ and CaO·ZnO, by using the chemical kinetics reported by Miladinović et al. [76], in which it is assumed that the methoxide ions are first adsorbed on the active centers and then they react with the liquid phase TG that are close to the active centers. The mass transfer limitations of the methanol adsorption were found to be negligible.

Miladinović et al. [76] also used a first-order reaction rate with respect to TG and FAMES, respectively. Tasić et al. [75] also showed that the TG mass transfer limitation depends on the methanol-to-oil dispersion. When it is not fine enough, the available active surface is small. To reduce that effect, that is, to increase the TG-methanol miscibility, a co-solvent can be added. However, these authors found that FAME can act as a co-solvent, and therefore as it is formed, the interfacial area gets larger, and hence the transfer limitations become smaller.

Stamenković et al. [77], studied the kinetics of the methanolysis of sunflower seed oil at 60°C, using a methanol-to-oil molar ratio of 6:1 mol/mol and different amounts of Ca(OH)₂ catalyst. They proposed a pseudo-first-order reaction kinetic model and related the TG mass transfer limitations to the limited available surface area that resulted from the high adsorbed methanol concentration in the first stage of the reaction. Mass transfer limitations were also important when small amounts of catalyst were used (1–2.5 wt%, oil based). When the catalyst was used in amounts greater than 10 wt%, the significant agglomeration of catalyst particles occasioned the limitation of TG mass transfer.

4.2.3. *Effect of particle size*

Practically, the entire active surface of the porous granules is internal, and the reaction that takes place inside the pellet consumes reactants and induces internal gradients of concentration and temperature which may be of sufficient magnitude to cause a significant variation of the reaction rate. Thus, the size of the particles of the catalyst affects the mass transfer at both intraparticle and at the interface. A suitable size of particle can be found experimentally so that a reaction rate and the final conversion degree do not depend on it, which is fundamental in kinetic studies to obtain the intrinsic kinetics.

There are few studies on particle size in the production of biodiesel by heterogeneous catalysis. Veljković et al. [78] in their study on sunflower methanolysis with CaO showed that the intraparticle diffusion of reactants from the surface to the active sites was the rate-controlling step; however, when they used catalyst particles in between 3 and 15 μm, they found no influence of the average particle size on the reaction rate and the final conversion, which indicated that the resistance due to intraparticle mass transfer was negligible in this size range.

Li et al. [79] in their study on ethanolysis of canola oil using a lactate dehydrogenase (LDH) oxide catalyst (Mg₂CoAl) compared the reaction rates for two different particle sizes, one being greater than 1 mm and another being less than 100 μm, both at the same conditions. In both cases, a reduction in the conversion was found, indicating that there is a resistance to internal mass transfer and therefore an intraparticle diffusion control. However, for both cases, the rates were very similar in between 30 and 90 min, but with a delay of about 15 min for the larger particles. They concluded that the conversion rate was kinetically controlled rather than intraparticle diffusion.

4.2.4. *Effect of stirring speed*

The stirring speed plays an important role in the evaluation of the limitations of external mass transfer, so to corroborate if there are external mass transfer limitations from the reactants to the particle surface, a study of the reaction rate is usually carried out at different agitation

speeds. Veljković et al. [78] carried out studies at agitation speeds of 700 and 900 rpm for a methanolysis reaction with 1 wt% catalyst and speeds of 900–1250 rpm with a 10 wt% catalyst, and by using the correlation of Dossin et al. [18], they found that the minimum stirring speed to carry out a perfect mixture and a complete suspension of catalyst particles was 430 rpm for the former and 740 rpm for the latter. They found that agitation speeds of 1250 rpm introduced air inside the reactant mixture. The experimental conditions and values of the kinetic constants are summarized in **Table 1** [78].

4.2.5. Effect of temperature

The effect of temperature on the reaction rate plays also a very important role since the rate constants are temperature-dependent. The temperature can influence transport phenomena in heterogeneous catalysis; Lukić et al. [80], for example, conducted the transesterification of sunflower and waste cooking oil using methanol at temperatures in a range between 60 and 96°C. As catalyst, they used CaOZnO with a methanol-to-oil molar ratio of 10:1 mol/mol. They showed that at relatively low temperatures of 60–70°C and at the start of the reaction for the production of esters, there is a resistance to the mass transfer, but with an increase in the production of methyl esters, the resistance to mass transfer reduced, so that the initial TG mass transfer limits the rate process, and eventually as biodiesel concentration increases, the chemical reaction is the rate-limiting step. For temperatures higher than 84 and 96°C, the resistance to mass transfer is almost negligible, and thus the conversion rate is controlled by the chemical reaction. The reaction rate was expressed by a pseudo-first-order model and corresponding values of the mass transfer coefficients.

In another study [81], a heteropoly acid catalyst was used to carry out the transesterification reaction of waste cooking oil with methanol temperatures in the range of 50–70°C to determine how temperature influences the conversion of TG. The conversion degree had a considerable increase when the temperature increased from 50 to 65°C, in the range of 40% (from 20 to 60%) at 50°C and 57.6% (from 31 to 88.6%) at 65°C. However, above 65°C, the conversion rate decreased, which was claimed to be due to the chemical reactions that occur during the cooking process, as these reactions can generate undesirable components such as free fatty acids that cause a decrease in the conversion of TG and therefore the production of biodiesel.

4.2.6. Effect of alcohol-to-oil molar ratio

Methanol is mostly used for transesterification of vegetable oils, mainly to avoid the formation of a stable emulsion between biodiesel and glycerol. In practice, it is better to perform a study at different molar ratios for each specific case of conditions and catalysts. Vujicic et al. [9], for example, used CaO as catalyst to transesterify sunflower oil. An excess of alcohol was observed to influence the reaction kinetics, and the overall reaction rate was found to follow strictly a fourth-order kinetics, since each TG molecule should be converted into glycerol by consecutive reactions, first becoming diglyceride, then monoglyceride and finally glycerol, but when carrying out the reaction with a large alcohol excess, the kinetics was observed to follow a pseudo-first order (**Table 1**).

4.2.7. Effect of reaction time

Reaction time is very significant in the production of biodiesel by heterogeneous catalysis, since to obtain the same yields as those in homogeneous catalysis sometimes need up to more than five times the time that is carried by homogeneous catalysis. In the abovementioned work carried out by Vujicic et al. [9], the achieved activities at reaction temperatures of 80 and 100°C were significantly affected by the reaction run, and high steady-state conversions were reached after 5.5 and 2.5 h, respectively.

5. Simulation and optimization of biodiesel production

5.1. Simulation of transesterification process

The economic evaluation of biodiesel production is based on general mass and energy balances that can be obtained from process simulation [82]. Among the most common process simulators used for the simulation of biodiesel production are Aspen Plus®, Aspen HYSIS, PRO/II, SuperPro Designer, and VMGsim. These programs can be used to design and optimize a large-scale biodiesel production. **Table 2** shows relevant data for different simulation studies. Complimentary numbers can be found elsewhere [83–85].

The typical process simulation procedure involves definition of the components, selection of the thermodynamic model, property estimation, drawing of the flowsheet, definition of chemistry and kinetic models, and the input of units and operation conditions.

Most simulators do not contain all the components present in the transesterification reaction, so that their properties cannot be estimated. Thus, triolein ($C_{57}H_{104}O_6$) is regularly used as a model compound of TG, mainly because it accounts for 40–75 wt% in most used oils for biodiesel production, such as olive, canola, palm and jatropha oils [83, 86], and hence biodiesel is represented by methyl oleate ($C_{19}H_{36}O_2$). When the oil contains FFA that requires an esterification pre-treatment process, oleic acid ($C_{18}H_{34}O_2$) is used as a model compound.

The most recent version of Aspen Plus® (ver. 10) includes most of the TG and methyl esters present in the transesterification reaction, including (tri)ricinoleine, which is the main component in castor oil. The properties of these components are estimated in the simulators. However, some important properties estimated for these components, for example, normal boiling points and vapor pressures, are somehow inconsistent with experimental data and databases, and therefore some researchers choose to update their values from either experimental data [87, 88], contribution methods [89] or from properties databanks such as NIST [83].

The Non-Random Two Liquid (NRTL) or the Universal Quasi Chemical (UNIQUAC) models are the preferred thermodynamic models, mainly because of the presence of highly polar compounds, such as methanol and glycerol. In Aspen Plus, however, the binary NRTL coefficients usually need to be estimated, which is commonly carried out by the UNIFAC LLE model for liquid-liquid equilibrium and Peng-Robinson or SRK equations of state for vapor. The performance of NRTL has been shown to be better than UNIQUAC [90]. These mod-

Materials		Reactor models		Operation mode	Thermodynamic model	Program	Production size Tonnes/year	Reference
Feedstock (Model compound)	Catalyst	Transesterification	Esterification					
Rapeseed (triolein)	MgO	Eley-Rideal Pseudo second-order reversible	none	Bach and continuous (slurry)	UNIFAC	Aspen Plus	100000	[94]
Rapeseed (triolein)	KOH/Enzyme	Yield model (96 %)	None	Continuous (CSTR)	Dortmund UNIFAC	Aspen Plus	8000	[84]
Seven kinds of vegetable oils	NaOH	Second order reversible	None	Batch	Dortmund UNIFAC	Aspen Plus	9125	[83]
Cottonseed (pseudo-components)	NaOH	Second order irreversible	None	Continuous/Batch	Dortmund UNIFAC	Aspen HYSYS	562 (feed)	[95]
Soybean (triolein)	Nb ₂ O ₅	Pseudo homogeneous (hydrolysis) reversible	Pseudo homogeneous	Continuous (Pack bed reactor/RDC)	Dortmund UNIFAC	Non-commercial computational code	2134	[96]
Soybean (triolein)	Mg(OCH ₃) ₂ (heterogeneous)	Second order reversible	None	Continuous (CSTR/RD)	Dortmund UNIFAC	Aspen Plus	7542	[97]
Palm (triolein)	KOH or NaOH	Second-order reversible	Second-order reversible	Continuous (CSTR)	UNIFAC and NRTL	Aspen Plus	100000	[98]
Soybean (trilinolein)	NaOCH ₃	Conversion reactor (99%)	None	Continuous	NRTL UNIQAC	Aspen Plus	150000	[99]
Jatropha (triolein)	NaOH	Conversion reactor (98.86%)	None	Continuous (CSTR)	NRTL UNIFAC	Aspen HYSYS	8000	[100]
Waste cooking oil	Tungsten on alumina supported (WAI)	Conversion reactor (96.54%)	Conversion reactor (92.34%)	Membrane reactor	NRTL	Aspen HYSYS	N/A	[101]

Table 2. Key features of some simulation studies for biodiesel production.

els present different characteristics that make them complimentary [91], and the use of both (UNIQUAC as referenced model) can achieve more reliable simulations.

The Dortmund UNIFAC excess free energy model has also been used for the estimation of activity coefficients [84], as it has been found to provide good fit between estimated and measured methanol-biodiesel and methanol-glycerol vapor-liquid equilibrium data [92]. In this study performed by Kuramochi et al. [92], the Dortmund-UNIFAC was found to represent the best way to model the liquid-vapor equilibrium in the biodiesel process, while UNIFAC-LLE was found to be the best method to model the liquid-liquid equilibrium with methanol, methyl oleate and glycerin mixture and methanol water system. The COSMO-SAC model, included in Aspen Plus, has also been used for VLE calculations in the esterification reactor [93]. The advantages of this method compared to NRTL are that its predictions are based on quantum chemistry, and the parameters required for its use are of molecular and electronic nature, and therefore they will not be affected by temperature changes along the process [93].

The selection of a kinetic model for both the transesterification and esterification reactions is very important for determining the product yield and performance of the equipment. Despite the multiple kinetic models found in the study, as shown in Section 3, a number of simulation studies do not include a detailed kinetic model to simulate the reactors. Instead, the simulation is performed by using a stoichiometric or an equilibrium reactor and using a specific value for the conversion or yield. Different studies for base-catalyzed reaction use a conversion value in between 95 and 99%. Some authors [100] argue that the various kinetics and mechanisms are not clear enough to design methods to follow and hence they prefer to simulate the reactors as conversion reactors.

Similarly, since many kinetic models for transesterification reaction have been obtained for the entire mixture of TG and FFA, the use of triolein in the simulation does not entirely represent the observed kinetic behavior in the reactor. In addition, most kinetic models found in the study have only been derived for one TG as a pseudocomponent. A detailed kinetic, and hence a more realistic simulation, should include triolein, tripalmitin, trilinolein and tristearin, as they account for more than 90 wt% of jatropha, palm, soybean, rapeseed and sunflower oils [84, 102].

Lee et al. [103] have developed a kinetic model based on three TGs, that is, for each component, kinetics parameters have been estimated. This model was used by Garcia et al. [90], who simulated the biodiesel production by considering a feedstock containing four TGs.

Most simulation studies found in literature have been performed at a large-scale process; however, there seems to be a lack of data about industrial performances that are not totally realistic. A more comprehensive and close comparison between real plant operation and process simulation could help to reduce this gap.

5.2. Process optimization for biodiesel production

Optimization is one of the most quantitative tools in the industrial decision-making process [91]. The purpose of biodiesel production optimization is to find the value of the variables

involved in the process that maximizes the profit, minimizes the cost of the process or maximizes the yield of biodiesel, so that the process becomes competitive in the fuel market. The optimization of biodiesel process should start from the optimization of the reaction conditions at a laboratory scale. This is usually performed by running a design of experiments and optimizing the conditions by the use of the surface response methodology (SRM). The model can later be validated at bench or pilot plant scale. Thus, the model can be used in the simulation process as a yield model.

The use of a simulator can also be useful to add different factors that are not present at a laboratory scale, as well as to optimize the operation of the different equipment in the industrial plants by performing a sensitivity analysis. Several optimization studies have been reported in literature, mainly to perform an economic analysis [84, 88], to determine the optimal conditions to maximize the conversion of vegetable oils [104], to perform sensitivity analysis of design parameters and operating conditions to optimize the operation of each step [96], to study the excess methanol recovery in continuous production [105] and to evaluate new process intensification technologies [106], among others.

6. Conclusions

The goal in the development of heterogeneous catalysis seems to be the development of catalysts with high activity at low temperatures and pressures, being selective, being stable and should not be deactivated by water or leached. The kinetic modeling of the transesterification reaction should include more TG components; this, however, requires a more detailed characterization of both the feedstock and reaction products. These detailed kinetic models should also allow the simulation of TG mixtures or feedstocks such as waste cooking oil. By doing so, a more realistic simulation and optimization of the process could be obtained. As chemical process simulators have been incorporating most of the components in the biodiesel process, it is expected that the estimation of the properties becomes more reliable in these programs and provide more realistic simulated results. There is, however, a need for information on industrial data for the different biodiesel technologies, so that the biodiesel simulation studies can be compared and be validated with industrial data.

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