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Heterogeneous Catalysts for Biodiesel Production: A Review

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Abstract Biodiesel is a biofuel and appears on the world energy scene as a strong substitute for petroleum diesel for its renewable and less environmentally polluting character. It can be obtained from transesterification reaction of triacylglycerol from vegetable oils or animal fats with short chainalcohol in the presence of homogeneous or heterogeneous catalysts. In recent years the production of alkyl ester by using heterogeneous catalysts it has excelled due to their capacity for regeneration, reuse and reduction of processing stages. Several parameters have been evaluated in the reaction steps, such as amount of catalyst, molar ratio of alcohol:oil, temperature, agitation speed and reaction duration. Intrinsic properties of catalysts are also studied, such as porosity, surface area, catalytic activity and others. Therefore, this review presents the transesterification reaction of several raw materials, as sources of triacylglycerols, using short chain alcohols and different heterogeneous catalysts. Optimal conditions for each catalyst, as well as its respective reaction mechanisms, were summarized.

Keywords Anion exchange resin, Alkaline earth oxides, Hydrotalcites

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1. Introduction

It is already quite evident that combating climate change needs urgent modifications in the way energy is generated and the replacement of fossil energy resources by renewable energies is very necessary [1].

Biodiesel appears in the bioenergy scenario as a good source in substitution of fossil fuels and has become a very relevant research topic due to its wide use in the energy and transport sector [2]. In the last 10 years more than 28,000 studies related to the production and consumption of biodiesel have been published on online research platforms, thus confirming what was said by Boloy et al. (2017) [2].

According to projections of the International Energy Agency, the production of biofuels will increase by 3.3 million barrels/day from 2012 to 2040 and its share will be 8% in demand for road transport fuels [3]. Therefore, due to renewable energy requirement, biodiesel will likely play an important function in increasing fuel demand in the coming decades. [4].

Different raw materials, sources of triacylglycerols, are used for biodiesel production. The most used are: soybean oil [5], rapeseed oil [6], canola oil [7], palm oil [8], cottonseed oil [9], *Jatropha curcas* oil [10], used cooking oil [11], and animal fats [12,13]. Vegetable oils used in transesterification reactions for the production of biodiesel depend mostly on crops adapted to the regional or local climate. An example, in the United States, the soybean oil is the most commonly used triacylglycerol source for alkyl ester production, while in Europe and in warmer climate countries, rapeseed oil and palm oil are more common, respectively. [14,15]. Whenever possible, the raw materials for biodiesel production must meet two conditions, one is the low cost of production and another one is the large scale of production [14], which makes its process economically viable and a competitive fuel to petroleum diesel. Conventionally, the biodiesel is obtained via transesterification of vegetable oils or animal fat. In the reaction, a triacylglycerol molecule, the main component of vegetable oils, reacts with three molecules of a short chain alcohol, normally, methanol or ethanol, in the presence of a catalyst. Producing three molecules of fatty acid methyl or ethyl esters (FAME or FAEE, respectively) and one molecule of glycerol [16].

Distinct catalysts are used to accelerate the transesterification reaction, and can be classified into homogeneous and heterogeneous catalysts.

The homogeneous catalysts used for the alcoholysis reactions may be acid or basic in nature. Industrially, basic catalysts are more commonly applied for biodiesel

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production. This is because the base catalyzed reaction is faster than the acid catalyzed reaction. In addition, the yield in fatty acid alkyl esters is higher and reaction conditions are relatively mild. However, the choice of this catalyst is dependent on the amount of free fatty acids (FFA) and the concentration of moisture present in the raw material [17].

The homogeneous catalysis systems have many disadvantages, such as the difficulty in separating the catalyst from the glycerin phase and the need to use a large amount of water in the purification of biodiesel, generating a large amount of wastewater.

Other considerable disadvantages of homogeneous catalysts are that they cannot be reused and their separation is difficult because the catalyst is dissolved in the reagents and requires specialized types of equipment for their recuperation that can result in increased process costs [18,19].

Thus, in order to overcome the disadvantages mentioned above, the heterogeneous catalysts have emerged as a viable substitute for homogeneous catalysts [20].

Heterogeneous catalysts are not dissolved in the reaction medium, thus, being separated easily from the reaction mixture. As advantage, the products contain less impurities and the purification costs from biodiesel are reduced [18]. These catalysts also have two beneficial advantages for industry and the environment because they can be easily regenerated and reused. Thus, they can be considered ecologically correct, since they do not require water treatment in the separation stage [21]. These advantages simplify washing, separation and purification processes after the reaction and there is no soap formation in the process [18].

With that, this article aimed to study the reaction mechanisms of the different types of solid heterogeneous catalysts, the optimum conditions and catalytic efficiency.

2. Homogeneous Catalysis

In the literature, significant amounts of studies involving the production of biodiesel by homogeneous catalysis have been reported.

The homogeneous catalysts can be acids or bases. Sulfuric acid and hydrochloric acid are the most employed as acid catalysts, especially when the oil has elevated percentages of FFA (> 1% by mass), these catalysts have the simultaneous ability to esterify and transesterify the triacylglycerols [20]. However, the process requires a high molar proportion of alcohol to oil and reaction time more larger to convert the oil into biodiesel [20,22]. Moreover, the acid environment can reduce the life of the equipment caused by corrosion [23].

The transesterification using alkaline catalysts as sodium and potassium hydroxide (NaOH and KOH, respectively), although have a high conversion percentages, faster reaction rate and moderate reaction conditions [24], they still have challenges that include separation and purification of products and non-reuse of catalysts [25]. For processes involving alkali catalysis, special steps are required to make the raw material suitable for reaction. Oils with high percentages of FFA and water produce large amounts of soap and more water. The soap that is produced is removed with glycerol or washed with water. When the FFA amount is higher than 5%, the soap makes it difficult the separation of the esters and glycerol and contributes and assists in emulsion formation during washing [26], thus providing, a greater water consumption and higher costs for the treatment of this water. In addition, the water promotes the hydrolysis of triacylglycerols, producing new free fatty acids and diacylglycerols [25]. Therefore, the transesterification reactions using alkaline catalysts require refined raw materials, with concentrations of free fatty acids and water lower than 0.5% and 0.06% by mass, respectively [24,27].

These conditions restrict the number of raw materials used for homogeneous processes since cheap raw materials such as cooking oil and acid oils require a pretreatment. This, coupled with the treatment of wastewater generated from the biodiesel purification stages and the loss of the homogeneous catalysts can cause financial losses and make the product less competitive with the petroleum diesel [28].

Thus, as a way of overcoming the difficulties encountered with the use of homogeneous catalysts, the use of heterogeneous catalysts appears to be more beneficial to the environment and industry because they have the facility of being regenerated and reused and do not require a water treatment at purification steps [18,21].

3. Heterogeneous Catalysis

The main focus of the recent studies on biodiesel production is the development of heterogeneous catalysts that can be reused. These catalysts were proposed with an advantageous form of replacing the use of acidic and alkaline homogeneous catalysts [25].

The main reasons by which heterogeneous catalysts have received great attention is the fact that they are non-corrosive [29], can be regenerated, reused, applied in continuous processes [30], and have easy separation of the obtained product. In addition, they lack sensitivity to free fatty acids, the washing step is eliminated, since they do not produce side products such as soap [25].

Thus, several heterogeneous solid catalysts have been studied. Calcium and magnesium oxides [31,29,32-40], hydrotalcites [41-44] and ion exchange resins [45-53] were studied in the yield of the transesterification reaction, as shown in Table 1.

Table 1. Reaction conditions using different heterogeneous catalysts and their respective yields on methyl and ethyl esters

Catalyst	Oil	Alcohol	MR A:O[A]	Ratio catalyst/ Oil (w/w)	Temperature (℃)	stirring speed (rpm)	Time (h)	Conversion (%)	Reference
CH_3CO_2K/ CaO	Bitter almond oil	Methanol	9:1	2.0 %	60 ℃	600	2.0 h	91.22 %	[29]
CaO/SiO_2	Cooking oil	Methanol	14:1	8.0 %	60 ℃	-	1.5 h	91 %	[32]
Mayenite impregnated with 10% lithium	Refined rapeseed oil	Methanol	6:1	5.0 %	60 ℃	180	2.0 h	100 %	[33]
Na_2ZrO_3	*Ricinus communis* oil	Methanol	15:1	5.0 %	65 ℃	-	3.0 h	99.9 %	[54]
MgAl hydrotalcites containing K (HTCRk)	Sunflower oil	Methanol	3:10[B]	3.0 %	65 ℃	200	3.0 h	>80 %	[41]
MgO supported on γ-Al_2O_3	Soybean oil	Methanol	6:1	5.0 %	60 ℃	-	6.0 h	60 %	[37]
$MnCO_3$	Soybean oil	Subcritical methanol	21:1	2.0 %	180 ℃	200	1.0 h	98.1 %	[55]
Potassium methoxide	Soybean oil	Methanol	6:1	2.0 %	80 ℃	-	0.25 h	91 %	[56]
Mixed oxide of Ca and Li ($CaLiZrO_{3)}$	Soybean oil	Ethanol	12:1	10 %	50 ℃	1100	0.5 h	92 %	[57]
Mixed oxide of Ca and Al derivative of (Ca_2Al-c)	Macaúba oil	Ethanol	14:1	3.0 %	65 ℃	600	12 h	91 %	[58]
Hydrotalcite – hydroxyapatite doped with nano carbon tubes	Soybean oil	Methanol	12:1	2.5 %	240 ℃	700	4.0 h	40.5 %	[44]
Hydrotalcite – hydroxyapatite	Soybean oil	Methanol	12:1	5.0 %	240 ℃	700	4.0 h	80.4 %	[43]
Hydrotalcite - Ga^{3+}	Soybean oil	Ethanol	20:1	20 %	120 ℃	-	12 h	75.5 %	[59]
Hydrotalcite of Mg/Al	Cooking oil	Methanol: ethanol (4:2)	6:1	1.5 %	80 ℃	300	2.5 h	95.2 %	[42]
Zn/Ca/Al2O3	Cooking oil	Methanol	24:1	6.0 %	65 ℃	-	3.0 h	97.8 %	[11]
Molecular sieve AL-SBA-15	*Jatropha curcas* oil	Methanol	12:1	6.5 %	180 ℃ (4MPa)	400	24 h	>99.0 %	[60]
Amberlyst- A26 OH	Canola oil	Methanol	6:1	3.0 %	45 ℃	1000	1.5 h	67 %	[61]
Amberlyst- A26 OH	Canola oil	Ethanol	6:1	3.0 %	45 ℃	1000	1.5 h	63 %	[61]
D261 anion exchange resin	Soybean oil	Methanol and n-hexane[C]	9:1	80 g[E]	50 ℃	-	0.92 h	95,2 %	[62]
D261 anion exchange resin	Soybean oil	Methanol and n-hexane[D]	9:1	80 g[E]	50 ℃	-	0.92 h	96,7 %	[62]
Diaion PA306S resin	Triolein	Ethanol	10:1	40 %	50 ℃	-	3.0 h	80 %	[63]
Diaion PA306S resin	Cooking oil	Methanol	3,5:1	50 %	50 ℃	-	10 h	>90 %	[30]
Amberlyst-A26 OH	Tallow fat	Methanol	6:1	2,2 mol/ L	65 ℃	-	8.33 h	>95 %	[64]
Amberlyst-A26 OH	Soybean oil	Ethanol	16:1	20 %	50 ℃	500	6.0 h	>99 %	[65]
Amberlyst-A26 OH	Soybean oil	Methanol	10:1	20 %	50 ℃	550	18 h	not reported	[48]
Diaion PA306S resin	Acid rice bran oil	Methanol	-	33 %	50 ℃	-	40 h	97.1 %	[53]

[A] Molar ratio of alcohol:oil (A:O); [B] The author used a methanol/oil mass ratio of 3:10; [C] n-hexane/soybean oil weight ratio of 0.5; [D] n-hexane/soybean oil weight ratio of 0.9 [E] Fixed bed reactor loading with 80 g of resin and feedstock flow rate of 1.2 ml/min for 0,92 hours

3.1. Ion Exchange Resin

An ion exchange resin is an insoluble solid material that has the ability to retain and release ions simultaneously. The resin has a functional group responsible for permutation of ions. The insoluble structure allows the diffusion of the ions, this is, the solid must contain a fixed ionic charge, called counterion. The electrical neutrality of the structure is achieved when there is a mobile ion of ionic charge opposite to the fixed ion. If the resin has a fixed anionic insoluble complement it will be a cation exchanger, if the fixed charge is cationic the resin will be an anion exchanger [66].

Recently, the cationic resins attracted a great deal of attention due to the soft reaction conditions, non corrosion in the equipment, a high concentration of active sites and lower residual waters production. These catalysts have numerous active acid sites that are used for esterification and transesterification reactions [67,51]. Therefore, in this review, only the use of anion exchange resins will be addressed, since, for biodiesel production, they have applications only in transesterification reactions.

3.1.1. Anion Exchange Resin

The anion exchange resins have been studied by several researchers in the conversion of triacylglycerols (T) to fatty acid alkyl esters (E). According to Shibasaki-Kitakawa et al. (2007) [63] in the transesterification reaction, the first step of the reaction is the adsorption of the alcohol at the active site of the ion-exchange resin ($S(OH^-)$) with formation of an alkoxide (A^-) and an H^+ ion. The formed alkoxide attacks the triacylglycerol (T) molecule, thereby producing a fatty acid alkyl ester (E) molecule and an ionized diacylglycerol (D-) molecule. The negatively charged diacylglycerol undergoes an electrophilic addition with the H^+ ion to form the neutral diacylglycerol (D). In the second step, occurs the formation of the second alkyl ester molecule from the nucleophilic attack of A^- to the diacylglycerol, forming, in addition to the alkyl ester, a monoacylglycerol (M) molecule. In the third step, the formation of the third alkyl ester molecule and the production of a glycerol (G) molecule take place.

According to the authors, in the proposed mechanism, during the reaction, the resin has the regeneration capacity, maintaining its active catalytic sites.

Shibasaki-Kitakawa et al. (2007) [63] also reported that the adsorption force on the resin was much higher for the alcohol than for the triacylglycerols, exhibiting the opposite behavior of the cation exchange resins that showed a greater force to adsorb first the fatty acids in esterification reaction. For this reason, the authors state that anion exchange resins showed greater activity than cation exchange resins to convert triacylglycerols to biodiesel. Evaluating the different types of resin, the authors observed that the porous type Diaion PA308, PA306 and PA306S (Mitsubishi Chemical Corporation, Japan) presented higher conversion rates than the highly porous type resin Diaion HPA25 (Mitsubishi Chemical Corporation, Japan). Diaion PA306S resin with lower *cross-linking* density and particle size provided a higher reaction rate, with 80% conversion to ethyl esters using an expanded bed column with recirculation system packaged with 40% resin in relation to the mass of oil and a molar ratio of ethanol and triolein of 10: 1, during 3 hours of reaction at a temperature of 50℃. Thus, it was observed that these two characteristics had greater influence on the reaction rate when compared to resin porosity. According to Rios et al. (2005) [68] a higher *cross-linking* density (higher divinylbenzene content) decreases the resin swelling property, thus, the catalytic sites stay less accessible to the substrate [68].

1° step

$$A + S(OH^-) \rightleftarrows A^- + S(OH)^- - H^+$$

$$A^- + T \rightleftarrows AT^-$$

$$AT^- \rightleftarrows E + D^-$$

2° step

$$D^- + S(OH^-) - H^+ \rightleftarrows D + S(OH)^-$$

$$A^- + D \rightleftarrows AD^-$$

$$AD^- \rightleftarrows E + M^-$$

3° step

$$M^- + S(OH^-) - H^+ \rightleftarrows M + S(OH)^-$$

$$A^- + M \rightleftarrows AM^-$$

$$AM^- \rightleftarrows E + G^-$$

$$G^- + S(OH^-) - H^+ \rightleftarrows G + S(OH)^-$$

Figure 1. Mechanisms of anion exchange resin reaction. Source: Adapted from Shibasaki-Kitakawa et al. (2007) [63]

In the literature, the resistance of the resin to water has also been studied. Using the Nankai D261 anionic resin (Chemical Nankai, Japan) commercialized in Cl^- form with quaternary ammonium functional group, Ren et al. (2012) [62] found that conversion to methyl esters reduced from 95.2% to 87.7% with water content heightened from 0.0% to 1.0% by mass of oil. According to the authors, water can deactivate the active sites OH^-, it happens because water molecules bind more effectively to catalytic sites than methanol. Peterson et al. (2013) [50], evaluating the Amberlyst 15 resin (Alfa Aesar Co., USA) by adding water up to 1.0% by mass, observed no significant effects on the reaction products measured by HPLC (0.1%, 0.5% and 1.0% of water, the conversions were of 95.8%, 95.2% and 96.3%, respectively). At 2.0% by mass, a reduction in the conversion to products (92.6%) was verified.

Deboni et al. (2018) [65], using soybean oil with ethanol and Amberlyst A26 OH resin (Dow Chemical Company, USA) in preliminary experiments, observed that the presence of water inside the resin decreased the reaction rate. As a way of overcoming this problem, a pretreatment by conditioning the resin with ethanol was added to the process with the aim of eliminate the water present in the resin.

Evaluating simultaneously the removal of FFA and the production of biodiesel Deboni et al. (2018) [65] observed that it is possible to deacidify the raw material and produce biodiesel simultaneously, since large amounts of resin are used, because the adsorption of the free fatty acids deactivated the sites. Quantities of resin above the saturation concentration of the active sites should be used in order to provide catalytic sites for the transesterification. In addition, the authors state that the unnecessary addition of solvent can be avoided by taking into account the alcohol content present in the resin from its conditioning.

3.2. Alkaline Earth Oxide Catalysts

Several studies have been reported in the literature using alkaline earth oxides as heterogeneous catalysts of the transesterification reaction. Recently, studies involving the use of CaO, MgO and CaO impregnated with silica or potassium acetate have been reported in the literature [39,21,38,29,32].

Sousa et al. (2018) [39] studied the commercial CaO and CaO obtained from the calcination of eggshells as catalysts and obtained a 96% conversion to fatty acid methyl esters (FAME) for both of them using a soybean oil: methanol molar ratio of 1:12, 3% (w/w) catalyst and a temperature of 65℃ for 4 hours of reaction under stirring at 600 rpm. In addition, a study was realized to verify if the catalyst was leached to the liquid phase, causing a homogeneous catalytic reaction. In this case, the authors observed that after the removal of the solid phase the conversion to methyl esters ceased, confirming that reaction is a heterogeneous catalytic one, since, the FAME contents did not increase after the removal of the solid catalyst [39].

A study of Putra et al. (2018) [32] involving the use of CaO doped with SiO_2 provided a greater conversion due to an increase in the surface area of the catalyst caused by SiO_2 impregnation. Using only CaO, 71% of conversion to methyl esters was obtained. After impregnation, the percentage increased to 91%. This fact was also caused by the possible process of esterification of the FFA caused by the presence of silica, a material with a high acidity that facilitates the esterification reaction, as shown in Figure 2, where in the first step the SiO_2 is responsible for attracting the FFA to its active site. In the second step, the hydroxyl (-OH) of methanol binds to O of the catalyst, and thereby, releases H_2O by the catalyst. In the third step, according to the author, CH_3 is incorporated into the O atom to form the fatty acid methyl ester.

After two cycles of use of the catalyst, a reduction of only 2% in biodiesel conversion was observed [32]. In addition, Putra et al. (2018) [32] propose that the reaction mechanism for transesterification has as its first step the adsorption of triacylglycerol and soon after the methanol, both react on the surface of the catalyst producing the biodiesel, as shown in Figure 3.

In this mechanism, CaO first interacted with triacylglycerol, as shown in the first step of the reaction. According to the author, triacylglycerol bounds to CaO forming a Ca and O-CH_2 bond. The presence of the -CH_2 aliphatic group was determined by FTIR of the catalyst. For the authors this revealed the existence of triacylglycerols on the surface of the catalyst, confirming the theory that before reacting with the methanol, the catalyst reacted with triacylglycerols. In step 2, the excess methanol disrupted the interaction of the triacylglycerol with the catalyst. Thus, CH_3O^- of methanol would replace the O^- position in the catalyst to form the biodiesel, so the methyl ester was released of the surface as shown the step 2. In the third step glycerol formation occurs and its desorption from catalyst surface.

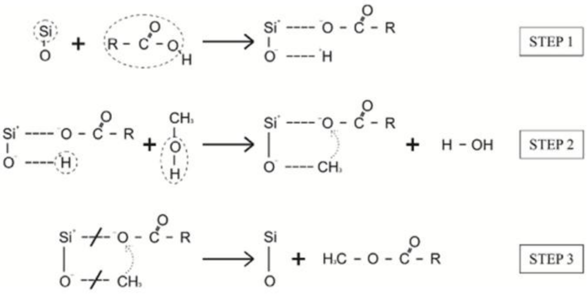

Figure 2. Mechanisms proposed by Putra et al. (2018) [32] for esterification reaction

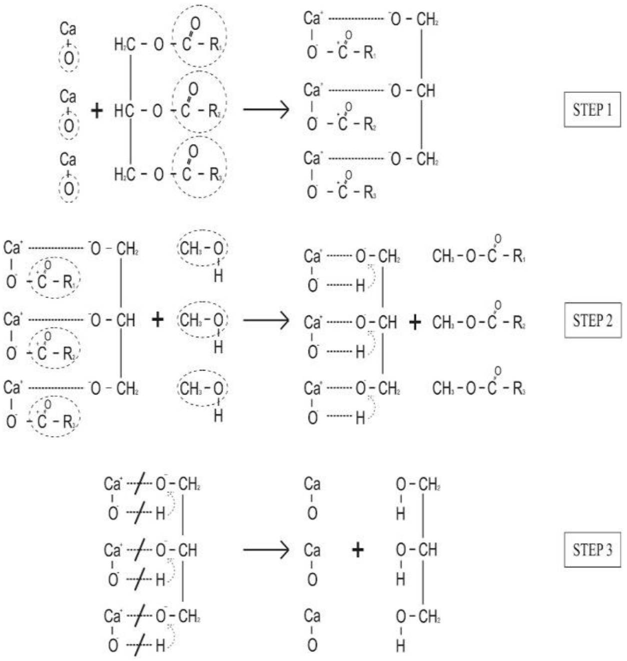

Figure 3. Mechanisms proposed by Putra et al. (2018) [32] for transesterification reaction

Unlike CaO, for MgO, Dossin et al. (2006) [21] proposed by Eley-Rideal kinetic model that the limiting step of the process is the adsorption of methanol at the active sites of the catalyst, ie, the reaction does not start without the adsorption of methanol in the catalyst. The mechanism was similar to that proposed for anion exchange resins and different from that mentioned for CaO by Putra et al. (2018) [32].

Navas et al. (2018) [37] studied the transesterification of soybean oil using methanol as solvent and MgO and CaO in bulk and doped with γ-Al_2O_3 as heterogeneous catalysts [37]. For the catalysts formed only by Ca or Mg, the conversions observed were of 38% and 13%, respectively. For the supported catalysts the conversions were 55% and 60%, respectively. According to these authors, the presence of the alumina improved the dissociation of the methanol in CH_3O^- and H^+, which occurs in the basic surface of the catalyst. In a first step, the methanol is adsorbed on the surface of the solid and the H^+ ion is abstracted from the methanol molecule to form a methoxide anion, the second step consists of the anion attack to the carbonyl carbon to generate an alkoxycarbonyl intermediate, which dissociates to form a fatty acid methyl ester and anionic diacylglycerol. This anion is attracted by a cation of the methoxide to form a diacylglycerol. The reaction is repeated twice to form monoacylglycerol and glycerol [37]. In his study, Navas et al. (2018) [37] show schematically the mechanism of reaction mentioned.

Fadhil et al. (2008) [29] also observed a loss in the catalytic activity of CaO doped with potassium acetate, a gradual decrease with the use was observed reaching 75% conversion in the 4th cycle. They attributed this decrease to the leaching of the active metals from the catalyst surface, as well as a change in the surface of the solid caused by washing and recalcination for the regeneration of the catalyst. In addition, the deactivation of the active sites may have been caused by the adsorption of oil, glycerol and free fatty acids on the surface of the catalyst, thus reducing the active sites.

3.3. Catalysts based on Hydrotalcite

Hydrotalcite (HT) is a double hydroxide, which can be found in its natural or synthetic form, contains in its structure interlayers of anionic species. The hydrotalcites are within the category of basic anionic clays and their general formula is given by $[M^{2+}{}_{(1-x)}M^{3+}{}_{x}(OH)_2]^{x+}A^{m-}{}_{x/m}nH_2O$, where M^{2+} is the divalent metal cation, M^{3+} is the trivalent metal cation, A^{m-} is the compensation anion, x is the molar ratio $M^{3+}/(M^{2+} + M^{3+})$ and *n* is the degree of hydration [43] [69]. Several studies involving catalysts based of hydrotalcites to produce biodiesel via transesterification are available in the literature [69-76].

Three kinetic mechanisms, Eley-Ridal (ER), Langmuir-Hinshelwood-Hougen-Watson (LHHW) and Hattori were studies by Kapil et al. (2011) [77] based on pseudo-stationary states for surface reaction and methanol adsorption as limiting steps in the conversion rate for biodiesel production using triacylglycerols and methanol in the presence of different heterogeneous catalysts based on hydrotalcites ($Mg_{0,81}Al$; $Mg_{1,38}Al$; $Mg_{1,62}Al$ and $Mg_{2,93}Al$).

Table 2. Steps considered for the ER and LHHW models

Reaction step	ER model	LHHW model
Methanol adsorption	$MeOH + * \underset{K-1}{\overset{K\,1}{\rightleftarrows}} MeOH*$	$MeOH + * \underset{K-1}{\overset{K\,1}{\rightleftarrows}} MeOH*$
Triacyglycerol adsorption	Not exist	$T + * \underset{K-2}{\overset{K\,2}{\rightleftarrows}} T*$
Surface reactions	$T + MeOH* \underset{K-2}{\overset{K\,2}{\rightleftarrows}} E + D*$ $D + MeOH* \underset{K-3}{\overset{K\,3}{\rightleftarrows}} E + M*$ $M + MeOH* \underset{K-4}{\overset{K\,4}{\rightleftarrows}} E + G*$	$T* + MeOH* \underset{K-3}{\overset{K\,3}{\rightleftarrows}} E* + D*$ $D* + MeOH* \underset{K-4}{\overset{K\,4}{\rightleftarrows}} E* + M*$ $M* + MeOH* \underset{K-5}{\overset{K\,5}{\rightleftarrows}} E* + G*$
Desorption	$D + * \underset{K-5}{\overset{K\,5}{\rightleftarrows}} D*$ $M + * \underset{K-6}{\overset{K\,6}{\rightleftarrows}} M*$ $G + * \underset{K-7}{\overset{K\,7}{\rightleftarrows}} G*$	$E + * \underset{K-6}{\overset{K\,6}{\rightleftarrows}} E*$ $D + * \underset{K-7}{\overset{K\,7}{\rightleftarrows}} D*$ $M + * \underset{K-8}{\overset{K\,8}{\rightleftarrows}} M*$ $G + * \underset{K-9}{\overset{K\,9}{\rightleftarrows}} G*$

k or $K_i = k_i/k_{-i}$ are rate constants; * = surface site; [MeOH] = methanol concentration; [G] = glycerol concentration; [FFA] = free fatty acid concentration; [T] = triacylglycerol concentration; [E] = ester concentration; term for free fatty acid adsorption = $FFA + * \underset{K-9}{\overset{K\,9}{\rightleftarrows}} FFA*$ where, k_8 and k_{-8} are rate constants for ER model and k_{10} and k_{-10} are rate constants for LHHW model.

In the ER mechanism, for modeling the adsorption of methanol in the active sites was considered, forming the methoxide and reacting with triacylglycerols, diacylglycerols and monoacylglycerols, thus producing methyl esters and glycerol.

In the LHHW kinetic mechanism the first step is the adsorption of methanol with the subsequent adsorption of triacylglycerol. The main difference between the ER and LHHW model is the adsorption of triacylglycerols on the surface of the catalyst. Both adsorbed compounds react with each other on the surface of the solid to form diacylglycerol and methyl ester. Subsequently, the adsorbed methanol reacts with diacylglycerol and monoacylglycerol to form biodiesel and glycerol. Jamal et al. (2015), in their study on determining reaction constants, described the reaction steps considered in ER and LHHW kinetic reaction models, as shown in Table 2. In addition, the authors considered the effect of FFA adsorption on reaction kinetics, more details can be observed in the item kinetic models.

The Hattori mechanism is similar to the LHHW mechanism, in this mechanism also if considers the adsorption of triacylglycerols on the surface of the catalyst as a limiting step of the process. the difference of these mechanisms is that in Hattori mechanism occur the formation of intermediate species from the reactions between the adsorbed methanol and the adsorbed tri, di and monoacylglycerols. Where, first, methanol is adsorbed, followed by triacylglycerol. At the respective catalytic sites, the triacylglycerol moves to the methanol containing site, leaving its site empty, thus forming an intermediate (methanol-triacylglycerol-active site). Soon after, this intermediate decomposes into diacylglycerol and methyl ester. The di, monoacylglycerol and glycerol adsorbed soon thereafter emerge from the surface of the catalyst to the volume.

The LHHW kinetic mechanism, where was considered adsorption of methanol as a limiting step of the conversion presents a best adjustment to the experimental data, in addition, presented less parameters. Thus, the adsorption of methanol as a first step is crucial for the reaction to occur and to obtain larger conversions. The parameters: the rate coefficient for adsorption of methanol (k_{MeOH}); the adsorption equilibrium coefficient of the total transesterification reaction (K_{eq}); and the adsorption equilibrium constant of methanol (K_M). The reaction constant values and other results and tables with the model equations can be found in the study by Kapil et al. (2011).

A hybrid material formed by the association of hydrotalcite and hydroxyapatite (HT-HAp) was studied by Brasil et al. [43] in the methylation reaction of soybean oil using the temperatures of 100, 180 and 240℃ in three different times (2, 4 and 6 hours) and methanol:oil molar proportions of 9:1, 12:1 and 15:1 in the presence of 5% by weight of HT-HAp. At the lower temperature, the authors did not observe conversions to methyl esters independently of the other variables and concluded that higher temperatures are required for higher conversions. The maximum yield obtained by the author was 80% at the temperature of 240℃ and the methanol:oil molar ratio of 12:1 for 4 hours of reaction.

The temperature, in this case, may be a limiting factor for transesterification reaction, requiring high temperatures to activate the catalyst, which may render the process unfeasible.

The hydrotalcites have basic properties, but their primitive form is not often used in catalysis because their catalytic sites do not have easy access (Cavani et al. 1991) [78]. Therefore, Benedicto et al. (2018) [41] studied the deposition of potassium salts on the surface of the catalyst as a way of improving the catalytic capacity of the MgAl hydrotalcite The original synthesized material was called HTk and the rebuilt catalyst was called HTCRk, both catalysts were used for biodiesel synthesis under temperatures not exceeding 65℃. With the simple hydrotalcite, after 20 hours of reaction no conversion was observed, but with the catalyst modified with K^+ (potassium) cation a conversion of more than 80% was observed after 3 hours of reaction. The reaction conditions are shown in Table 1. The increased catalytic activity is associated with increased distortion of the catalyst layers, improving accessibility to active sites.

3.4. Kinetic Models

In this item, kinetic models used to describe the transesterification reactions using different heterogeneous catalysts will be discussed. In this review, only studies with conversion above 96.5% in ethyl or methyl esters were referenced, since in computational process simulation, reactions with high alkyl ester conversions normally meet the biodiesel specifications of regulatory agencies with lower costs.

Several kinetic models have been used to describe the reaction of transesterification catalyzed by heterogeneous catalysts, the pseudo-first-order and the pseudo-second-order models being more common and the more complex models based on the reaction mechanisms of ER and LHHW.

Prado et al. (2016) [58] studied soybean oil and macauba oil as the source of triacylglycerols, methanol and ethanol as solvents and Ca and Al mixed oxide as heterogeneous catalyst, obtained from the synthetic hydrocalumite (Ca-Al). Using soybean oil, they obtained a conversion to fatty acid methyl esters of 97% after 1.5 h of reaction, and 91% of conversion to fatty acid ethyl esters (FAEE) after 12 h of reaction. For macauba oil, 95% FAME conversions were observed after 1.5h of reaction and 69% FAEE conversion ester after 12 hours of reaction. The transesterifications were performed using a catalyst percentage of 3% in relation to the mass of oil, a molar ratio of alcohol:oil of 14:1, subjected to a temperature of 65℃ and stirring at 600 rpm.

Using these conditions, the authors modeled the reaction kinetics considering a pseudo-first-order model due to the great excess of ethanol or methanol in the reaction, according to the equation below

$$-\frac{d[TG]}{dt} = k[TG][ALCOHOL] \quad (1)$$

where, -d[TG]/dt is the consumption of triacylglycerols (TG) per unit of time (t), *k* is the reaction rate constant, *[TG]* is the concentration in TG, [ALCOHOL] is the concentration of ethanol or methanol.

In the reaction, the author considers that in the catalytic surface only the alcohol adsorbs, because it is considered to follow the Eley-Rideal mechanism, according to Dang et al. (2013) [79]; an insignificant change in catalyst concentration was also considered; very low values in the concentrations of monoacylglycerols and diacylglycerols were assumed, considered, therefore, constant; and it was also adopted that the reaction occurs in a set of three steps and no reverse reaction was evaluated. After all the considerations, the author reduced the equation as described below.

$$-\frac{d[TG]}{dt} = k[TG]\theta_{alcohol} = k^{'}[TG] \quad (2)$$

where $\theta_{alcohol}$ is adopted as being the degree of recovery of alcohol after being adsorbed at the catalytic sites and $k' = k\theta_{alcohol} \approx$ *constant*, because, according to the authors, this value can be considered constant when alcohol is used in excess.

Rearranging and integrating, the following equation was obtained:

$$\ln[TG] = \ln[TG]_0 - k't \text{ Eq.} \quad (3)$$

The graphs of ln[TG] versus time was plotted and k' is the slope of the regression line.

Prado et al. (2016) [58] determined kinetic data using soybean oil and macauba oil and ethanol and methanol as solvents. In their study, they observed much slower reaction rate when ethanol was used, with an apparent velocity constant (*k'*) equal to 0.22 h^{-1} ($R^2 = 0.98$). For methanol, the constant found was 2.88 h^{-1} ($R^2 = 0.98$). The authors concluded that the reaction rate was higher for methanol due to its higher acidity (pKa = 15.5) in relation to ethanol (pKa = 15.9), which is lightly fewer acidic. Thus, they noted that methanol favors the transesterification reaction. In addition, the authors observed a slower reaction rate for macauba oil with a constants k' = 2.57 h^{-1} using methanol and k' = 0.13 h^{-1} when using ethanol. They attributed this behavior to a higher external diffusion resistance due to a higher viscosity of macauba oil caused by the higher amount of saturated compounds present.

Jamal et al. (2015) [48] in their research evaluated the reaction of transesterification of soybean oil with methanol and Amberlyst A26OH resin as heterogeneous catalyst with and without the presence of FFA. Two kinetic models of surface reaction (ER and LHHW) were used to explain the rate of methanolysis with and without the presence of FFA and help elucidate the reaction process that occurs on the surface of the catalyst. These reaction conditions are described in Table 1. These authors considered that the conversion rates of di and monoacylglycerols (the intermediates formed during the reaction) were much higher than the adsorption rate of methanol (the adsorption of methanol is the limiting step of reaction, because without the formation of methoxide the reaction will not begin) and therefore could be disregarded. These authors also observed by means of the reaction kinetics that the presence of the FFA favors the transesterification reaction promoting higher methanolysis rates. According to them, when the FFA approaches the basic surface of the catalyst, triacylglycerol, diacylglycerol and monoacylglycerols interact with the FFA by means of hydrophobic interactions and the hydrophilicity of the anion exchange resin is reduced. This interaction allows the acylglycerols to approach with greater ease of the basic surface, resulting in higher reaction rates. the simplified models can be seen in Table 3 and all the kinetic parameters can be found in the article of Jamal et al. (2015) [48] and the full version of the calculations can be found in the supplemental material of this study.

Table 3. Kinetic models used to adjust the experimental data

Model	Rate equation, ($\frac{d[MeOH]}{dt} =$)
ER kinetic model without FFA	$\frac{-k[MeOH]}{(1 + K_7[G])}$
ER kinetic model with FFA	$\frac{-k[MeOH)}{(1 + K_7[G] + K_8[FFA])}$
LHHW kinetic model without FFA	$\frac{-k[MeOH]}{(1 + K_2[T] + K_6[E] + K_9[G])}$
LHHW kinetic model with FFA	$\frac{-k[MeOH]}{(1 + K_2[T] + K_6[E] + K_9[G] + K_{10}[FFA])}$

Source: Adapted from Jamal et al. (2015) [48].

Where [MeOH] = methanol consumed; k = constant of rate methanol consumption;

K_7 e $K_9 = \frac{k_{forward}}{k_{reverse}}$ =constant of the reaction rate for glycerol;

K_8 and K_{10} = rate constant for FFA adsorption; $K_{2=}$ rate constant for triacylglycerol adsorption; K_6= constant of the reaction rate for methyl ester; [G] = concentration of glycerol; [FFA] = concentration of FFA; [T] = concentration of triacylglycerol; and [E] = concentration of methyl ester.

Jamal et al. (2015) [48] evaluated the methanol consumption over the course of time for each model obtained. Using ER model, the methanol consumption rate constant was 7.48 x 10-4 h-1 without the presence of FFA and 1.94 h-1 with FFA present. For the LHHW model, the constant found for alcohol consumption was 6.20 x 10^{-2} h^{-1} without FFA and 1.71 h^{-1} with FFA. Therefore, the author concluded that the FFA when present increases the rate for the consumption of methanol. The authors also concluded that the mechanism of reaction tends towards a hypothetical ER mechanism due to the methanol in excess used in the reaction. They further stated that the triacylglycerol concentration of the LHHW model provides a small influence in the denominator of the equation at excess level of methanol. But, as the molar ratio of methanol to triacylglycerol reduce, the importance of sorption of triacylglycerol in the resin increases, favoring the model. Thus, informed the reaction parameters, the models used point that methanol adsorption in the catalytic it's the crucial step in reactions where methanol is present in amounts above reaction stoichiometry.

Solis et al. (2017) [33] also performed kinetic studies using a catalyst that promoted the highest yield in biodiesel. Mayenite impregnated with 10% lithium (M2) was used to transesterify rapeseed oil. The molar ratio of methanol:oil was 6:1, with a percentage of catalyst of 5% with respect to the mass of oil, subjected to 60℃ and stirring of 180 rpm for 2 hours. These parameters were sufficient to reach the maximum yield in FAME conversion (100%).

Initially, to model the kinetics of reaction, Solis et al. (2017) [33] made a mass balance on a discontinuous reactor with agitation, according to the equation that follows.

$$V_{cat}\, r_A = \frac{dC_A}{dt} V_{tot} \rightarrow r_A = \frac{dC_A}{dt}\frac{V_{tot}}{V_{cat}} \qquad (4)$$

where, r_A is the reaction rate for triacylglycerol; C_A is the triacylglycerol concentration, t is the reaction time; V_{tot} is the total volume of the mixture inside the reactor; V_{cat} is the volume of catalyst and C_A is the triacylglycerol concentration at time t, and can be defined according to equation 5.

$$C_A = C_{A0}(1 - X_A) \qquad (5)$$

Where C_{A0} is the triacylglycerol concentration in the time t=0 and X_A is the degree of conversion of triacylglycerol to alkyl esters.

Based on previous study, Solis et al. (2017) mentioned that the reaction of transesterification catalyzed by heterogeneous catalysts has three steps:

1) Initially, considering a three-phase system (methanol, catalyst and oil), the conversion into fatty acid methyl esters may be low due to the mass transfer resistance which may increase the time for formation of the reactive phase of methoxide on the surface of the catalyst. These circumstances suggest a pseudo-second-order reaction rate;
2) In the second stage of the reaction, the production of biodiesel increases because the liquid mixture phase becomes more homogeneous and the methoxide formation occurs more quickly, now in a 2-phase reaction system (liquid-solid), causing an increase in the reaction rate. Thus, the reaction rate, according to the author, has been reported as being of pseudo-first-order;
3) And the third stage is represented by a decrease in the conversion rate due to the lower concentration of triacylglycerol.

Solis et al. [33] also cited that the overall equation of the transesterification reaction follows a fourth-order reaction rate. For displace the transesterification reaction to the formation of the product, methanol in excess was used. In this case, considering that the second step was predominant in the reaction (two-phase system), a kinetic model approximation of pseudo-first order was made. According to the equation below..

$$r_A = -k C_A C_B^3 \cong -k^* C_A \qquad (6)$$

where C_B is the concentration of excess methanol; k * is the pseudo-first order reaction constant.

Replacing, integrating and rearranging the equations for r_A and relating the variables of concentration, density and mass, we have to

$$\frac{d_{C_A}}{dt} = -k^* C_A \rightarrow \ln\left(\frac{C_A}{C_{A_0}}\right) = -k^*\left(\frac{V_{cat}}{V_{tot}}\right) t + C \rightarrow$$

$$\ln\left(\frac{C_A}{C_{A_0}}\right) = -k^*\left(\frac{\rho_{tot}}{\rho_{cat}}\right)\left(\frac{m_{cat}}{m_{tot}}\right) t + C \qquad (7)$$

The author has suggested a constant density ratio between total volume density and catalyst density which can be included in the apparent reaction rate constant as k^{**}, resulting in

$$-\ln(1 - X_A) = k^{**}\left(\frac{m_{cat}}{m_{tot}}\right) t + C \qquad (8)$$

where, X_A is the mole fraction of triacylglycerol, m_{cat} is the mass of the catalyst and m_{tot} is the total mass.

To obtain the value of the apparent reaction constant, the author plotted a graph of -ln (1-XA) versus t, where k^{**} corresponds to the slope of the line. The value obtained for the apparent rate constant (k^{**}) was 0.0447 min^{-1} with an R^2 = 0.97, indicating an acceptable curve fit.

4. Discussion

As can be seen, optimum conditions for temperature, alcohol:oil molar ratio, catalyst concentration and stirring rate change for each type of catalyst to convert triacylglycerols into ethyl or methyl esters.

For the ion exchange resins, it was observed that the crosslinking density, porosity and degree of swelling of the catalyst have influence on the catalyst activity. Evaluating the results, the anion exchange resins showed to be more efficient for biodiesel production using low temperatures, which is a limitation for these materials because of their low thermal stability. However, in terms of the process, high conversion at mild temperatures is an important advantage that reduces costs and energy requirements and makes their use viable.

In the studies cited using anion exchange resins, no author took into account in the calculations of the molar ratio alcohol: oil the alcohol adsorbed in the resin during their conditioning. In addition to avoiding the unnecessary addition of alcohol, conditioning is beneficial because, according to Deboni et al. (2015) [80], alcohol causes a resin swelling effect. This effect promotes a reduction of the internal resistance to diffusion caused by the increase of the free path inside the resin, facilitating the diffusion of the solute to the active site.

As can be seen in Table 1, methanol was the alcohol most used in the reactions, first due to its low cost and second because it is more reactive when compared to ethanol, but it has the disadvantage of being toxic and water miscible, representing a danger to the environment [81] and from non renewable sources.

Another factor to note is that high conversions were obtained using high FFA oils such as cooking oils. Heterogeneous catalysts do not have sensitivity to FFA, once they are adsorbed by the heterogeneous catalyst and there is no soap formation, reducing the biodiesel purification steps [42,11,30,48,65].

It was also observed that faster reactions were obtained when using small amounts of catalyst. For the catalysts based on hydrotalcites, when high temperatures and high molar ratios were used, the conversions were not good enough for the studied conditions.

Mild temperatures were used by ion exchange resins, which is limited by their manufacturer's specification. The highest temperature used was 65℃ for Amberlyst-A26 OH. Normally, times longer than 6 h were required to obtain high conversions.

For situations where high pressure and temperature conditions were used [55,44,43,59,60], high conversions were observed, which may also be due to the high molar ratio values used, except for the case of hydrotalcites.

5. Conclusions

Optimum conditions were shown for each type of heterogeneous catalyst, such as temperature, amount of catalyst, alcohol: oil molar ratio, stirring speed and reaction time. The reaction mechanisms of the catalysts were also presented and explained. Finally, it was possible to arrive at the conclusions that the adsorption of alcohol is the first step for the reaction of transesterification using heterogeneous catalysts, the anion exchange resins presented better performances for biodiesel production in relation to the other catalysts and, for the calculation of the molar ratio of alcohol:oil, the alcohol used in the pretreatment of the resin must be taken into consideration.

In addition, different kinetic models can be used to adjust parameters to the experimental data. The pseudo-first order, pseudo-second order, ER and LHHW models were the most used to describe the transesterification reactions with heterogeneous catalysts. The LHHW and ER models were also used to explain the adsorption of alcohol or triacylglycerol on the catalyst surface.

It was also confirmed that these catalysts lack sensitivity to FFA presence. In the case of anion exchange resins, specifically Amberlyst A26 OH, besides producing biodiesel, it can be used to remove FFA from the mixture and, as observed in the kinetic models, these FFA can favor the transesterification reaction. Although, further studies are needed to confirm this hypothesis.

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