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STUDY OF HETEROGENEOUS CATALYSTS IN TRANSESTERIFICATION FOR BIODIESEL PRODUCTION

ESTUDO DE CATALISADORES HETEROGÊNEOS NA TRANSESTERIFICAÇÃO PARA PRODUÇÃO DE BIODIESEL

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ABSTRACT

Studies for clean fuels are interesting for the development of research through the processing of oils and fats, consisting of fatty acids, with high energy power and capable of conversion to esters (biodiesel), in transesterification or esterification reactions with homogeneous, heterogeneous catalysis, enzymatic. Basic homogeneous catalysis is the most widely used way of obtaining biodiesel, however it requires refined raw material and is free of water. In addition, the commonly used catalysts (NaOH, KOH, etc.) are aggressive to the environment and require a neutralization step. Heterogeneous catalysts have been shown to be efficient in transesterification reactions, because in addition to being reusable and not requiring a neutralization step after the reaction, they also have great economic viability. The considerations reported demonstrate the potential of heterogeneous catalysts in transesterification reactions, highlighting economic, technological and environmental aspects; and reinforce the need for incentives and research.

Keywords: transesterification. heterogeneous catalysts. biodiesel.

RESUMO

Estudos para combustíveis limpos são interessantes para o desenvolvimento de pesquisas por meio do processamento de óleos e gorduras, constituídos por ácidos graxos, com alto poder energético e capazes de conversão em ésteres (biodiesel), em reações de transesterificação ou esterificação com catálise homogênea, heterogênea, enzimática. A catálise homogênea básica é a forma mais utilizada de obtenção de biodiesel, porém necessita de matéria-prima refinada e é isenta de água. Além disso, os catalisadores comumente utilizados (NaOH, KOH, etc.) são agressivos ao meio ambiente e necessitam de uma etapa de neutralização. Os catalisadores heterogêneos têm se mostrado eficientes em reações de transesterificação, pois além de serem reutilizáveis e não necessitarem de uma etapa de neutralização após a reação, também apresentam grande viabilidade econômica. As considerações relatadas demonstram o potencial dos catalisadores heterogêneos em reações de transesterificação, destacando aspectos econômicos, tecnológicos e ambientais; e reforçam a necessidade de incentivos e pesquisas.

Palavras-chave: transesterificação. catalisadores heterogêneos. biodiesel.

1. INTRODUCTION

Energy sources for the production of fossil fuels (coal, oil and natural gas) are not sustainable due to the depletion of natural reserves and serious environmental damage caused by their use. Therefore, studies aimed at finding sources of “green energy” that satisfy economic needs and are environmentally friendly have gained prominence (Cremonez *et al.*, 2015).

Biofuels are one of the alternatives that can generate a quantity of energy with the potential to produce less environmental impact. According to law nº 9,478, of 1997 (Kuss *et al.*, 2015), biofuel is defined as a fuel derived from renewable biomass for use in internal combustion engines or, according to regulation, for another type of energy generation that may partially or totally replace fuels. of fossil origin, one of them being biodiesel.

Biodiesel has advantageous characteristics when compared to petroleum-derived fuels, such as: being free of sulfur and compounds aromatics; high cetane number; average oxygen content; higher flash point; lower emission of particles, CH_4, CO and CO_2; non-toxic and biodegradable, in addition to coming from renewable sources (Jasper *et al.*, 2010). This biofuel is highly adaptable to diesel cycle engine technology and can be obtained by the transesterification of vegetable

oils or animal fats and the esterification of free fatty acids (Cordeiro *et al.*, 2011). Biodiesel is composed of alkyl esters of long-chain fatty acids. Fatty acid esters are generally obtained through the transesterification and/or esterification reaction of vegetable oils or animal fats with short-chain alcohols, preferably in the presence of a catalyst. Among the various species of catalyst, there are alkali metal alkoxides, hydroxides, sodium carbonates, potassium and strong acids, enzymes, zeolites and ionic liquids (Sivasamy *et al.*, 2009).

The catalyst used in the transesterification reaction can be homogeneous, heterogeneous or enzymatic, having acidic or basic properties. Most of the biodiesel currently produced is through homogeneous catalysis using the bases KOH and NaOH, this is because its cost is low when compared to other catalysts (Santos, 2010). However, the use of heterogeneous catalysts has advantages over homogeneous catalysts, which are: ease of purification, recovery, reuse, high selectivity, high reactivity and low volatility.

Some examples of heterogeneous catalysts are potassium compounds deposited on different supports such as zeolites, oxides and inorganic salts, coordination compounds, ion exchange resins, ionic liquids, organic acids and bases, hydroxy salts and lamellar carboxylates (Ramos *et al.*, 2011).

In this context, this work aims to carry out a bibliographical review of the use of heterogeneous catalysts via transesterification for biodiesel production, mainly addressing the advantages and disadvantages, as well as the perspectives of the use of heterogeneous catalysts in biodiesel production.

2. METODOLOGY

A literature search was carried out for scientific works and data on the use of heterogeneous catalysts via transesterification for biodiesel production. Only publications that discuss the advantages, disadvantages and perspectives of using heterogeneous catalysts via transesterification in biodiesel production were considered. Furthermore, data from the National Petroleum, Natural Gas and Biofuel Agency (ANP) were used.

3. MAIN RAW MATERIALS FOR BIODIESEL PRODUCTION

Biodiesel is produced from several different raw materials. All compounds that have triglycerides in their composition can be used in the production of biodiesel. Vegetable oils are natural products made up of triglycerides, and to a lesser extent mono- and diglycerides (Lotero *et al.*, 2005), and may also contain free fatty acids. Triglycerides are found in vegetable oils and animal fats (usually tallow). Among the animal fats with potential, beef tallow, fish oils, mocotó oil, lard, among others, stand out as examples of animal fats with potential for biodiesel production. Residual oils and fats resulting from domestic, commercial and industrial processing can also be used as raw materials (BIODIESELBR, 2018). Frying oils represent a great supply potential. A primary survey of the supply of residual frying oils, which can be collected, reveals a potential supply in Brazil of more than 30 thousand tons per 10 years.

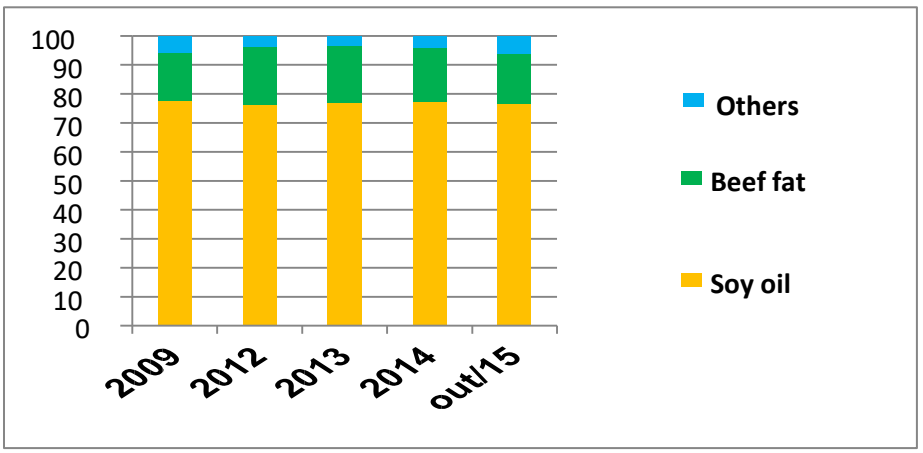

Figure 1. Participation of raw materials in biodiesel production in Brazil. Source: MME, 2016.

Vegetable oils, in addition to being consumed directly in food, constitute an important raw material for the chemical, pharmaceutical and food industries. In biodiesel production, the biggest challenge lies in the high cost added to pure vegetable oils, which represent 70 – 85% of the total production cost. Furthermore, the use of these oils has a negative impact on the environment, as it requires large amounts of available agricultural land (Ferrari *et al.*, 2004; Guabiroba *et al.*, 2008).

Therefore, a constant search for new alternative sources for production is necessary.

Figure 1 shows the raw materials most used in the production of biodiesel in Brazil in 2015, where it is possible to observe that the most used triglycerides are soybean oil and beef fat. However, there are oilseed species that are still little explored, such as jatropha, forage turnip, camelina and crambe.

Public policies such as the National Biodiesel Program have encouraged the production of oilseed plants for the production of biodiesel. Among the species commercially exploited, the most notable are fodder turnips, soybeans, castor beans and some palm trees, such as macaúba and oil palm. Soy has been widely used for the production of biodiesel, with around 90% compared to oilseeds throughout the country, according to reports from the ANP (ANP, 2018).

4. TRANSESTERIFICATION REACTION

Transesterification, also called alcoholysis, is the reaction that occurs between an ester and an alcohol, usually methanol or ethanol, to form an ester (biodiesel) and glycerin as a co-product of the reaction (Fangrui *et al.*, 1999). This process has been widely used to avoid the high viscosity of triacylglycerides. In the transesterification reaction of vegetable oils, a triglyceride reacts with an alcohol in the presence of a catalyst (enzymatic, strong acid or base), producing a mixture of esters and glycerol. The stoichiometric reaction requires 1 mole of a triglyceride and 3 moles of alcohol, resulting in the production of 3 moles of esters and 1 mole of glycerol (Meher *et al.*, 2006), as shown in Figure 2. However, an excess of alcohol is used to increase the yields of esters.

Several aspects, including the type of catalyst (enzymatic, alkaline or acid), molar ratio between alcohol/vegetable oil, temperature, purity of reagents (mainly water content) and free fatty acids affect the reaction rate (Schuchardta *et al.*, 1998).

The synthesis of biodiesel using heterogeneous catalysts presents a series of advantages. Unlike homogeneous catalysis, the heterogeneous catalyst is more easily separated from the final products of the reaction, there is a possibility of recovery and reuse of the catalyst, necessary in continuous production regimes,

and it does not favor saponification and corrosion. Transesterification in a heterogeneous medium for biodiesel production aims to improve the effectiveness of its production and the final quality of the reaction products.

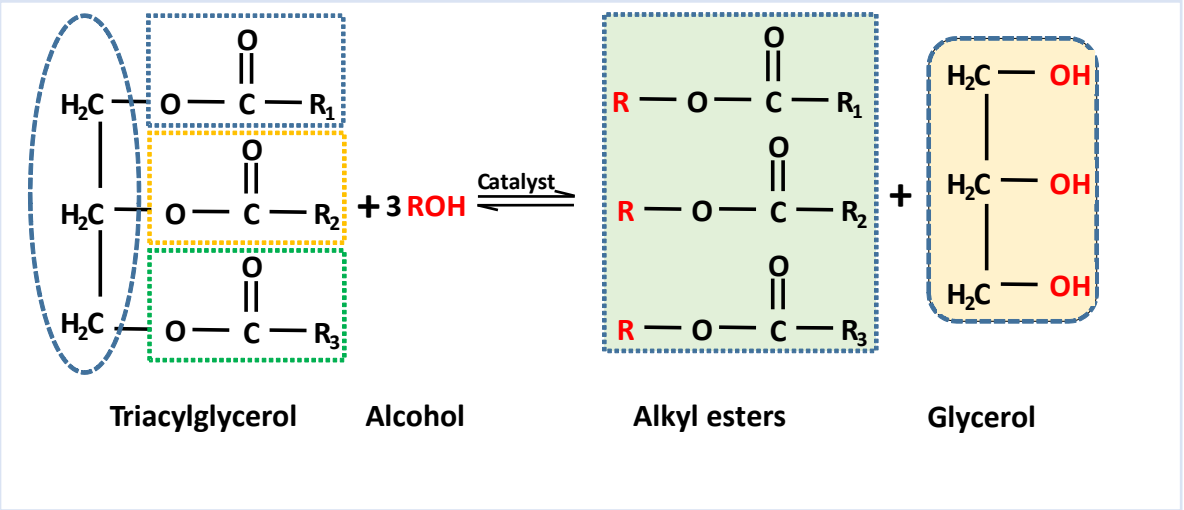

Figure 2. Representation of the triglyceride alcoholysis reaction.

4.1 Important factors for transesterification

Transesterification reactions are influenced by the following factors: type of alcohol, alcohol:oil molar ratio, water and free fatty acid content, reaction temperature, reaction time, and type of catalyst (Issariyakul *et al.*, 2014).

4.1.1 Type of alcohol

Methanol is the most used alcohol, as it offers the best cost-benefit. Its disadvantages are that it is obtained from fossil sources and has low solubility in triacylglycerols. This low solubility causes the beginning of the reaction to have a mass transfer limitation between the oil and alcohol phases. Some ways to reduce this mass transfer resistance between phases can be: rigorous mechanical agitation, addition of a cosolvent, supercritical reaction conditions and techniques such as microwaves and ultrasound (Ma, *et al.*, 1999). Other alcohols such as ethanol, propanol and butanol have already been tested to improve mass transfer between phases. If ethanol is used, biodiesel is obtained from completely renewable sources, which is a great advantage; however, the reaction with ethanol is slower

than with methanol. When esterification occurs through homogeneous alkaline catalysis, alkoxides are formed, which are the true catalysts of the reaction. If ethanol is used instead of methanol, its longer carbon chain reduces nucleophilicity and, consequently, reduces the reactivity of ethoxide in relation to methoxide. The lower polarity of ethanol presents advantages and disadvantages for the transesterification process, with the reduction of the mass transfer limitation existing at the beginning of the reaction and, consequently, the increase in the initial reaction rate being highlighted as an advantage; As a disadvantage, the miscibility between the ester and glycerol increases and makes it difficult to separate the phases at the end of the process. Thus, the speed at which saponification and soap formation occurs when ethanol is used is greater than when methanol is used (Issariyakul *et al.*, 2014).

4.1.2 Alcohol: oil molar ratio

The molar ratio is one of the most important variables that affect the yield of fatty acid esters in the transesterification reaction. The stoichiometric ratio is 1:3 (one mole of triglyceride for three moles of alcohol) with the product being three moles of alkyl esters of fatty acids and one mole of glycerin. However, the transesterification reaction is an equilibrium reaction, which requires an excess of alcohol to drive the formation of esters. For greater conversion into esters, it is necessary to exceed the molar ratio, which must be greater than or equal to 1: 614. However, care must be taken with increasing this molar ratio, as a very high increase may increase the solubility of the glycerin, interfering with its separation from the final product (Albuquerque *et al.*, 2008). In the methanolysis reaction, it forms emulsions that disappear easily and quickly form a lower phase rich in glycerin and an upper phase rich in methyl esters. When it comes to the ethanolysis reaction, emulsions are more stable and more difficult to separate, complicating the purification of esters (Zhou *et al.*, 2003).

4.1.3 Water and free fatty acid content

The presence of water and free fatty acids can significantly affect the yield of the reaction to obtain biodiesel when the alkaline catalysis route is used. All raw materials such as vegetable oil, alcohol and catalyst must be anhydrous. Still regarding the alkaline catalyst, prolonged contact with atmospheric air must be avoided, as the presence of humidity and carbon dioxide reduce its efficiency. In relation to free fatty acids, vegetable oils must contain a maximum of 0.5% free fatty acids (Ma, *et al.*, 1999), as the greater the acidity of the oil, the lower its conversion into biodiesel, as part of the alkaline catalyst will be consumed by the reaction. with free fatty acids. If there is a significant presence of free fatty acids in the vegetable oil, extra amounts of alkaline catalyst will be necessary for neutralization and, consequently, the formation of soap and water will occur, that is, saponification.

4.1.4 Reaction temperature

The increase in temperature favors the direct transesterification reaction and increases the ester production yield. In the initial phase controlled by mass transfer, the higher temperature takes the molecules to a higher energetic state that can be transformed into a higher molecular vibration with greater translational movement, which makes the molecules more likely to collide. with each other accelerating the reaction speed. Furthermore, increasing the temperature decreases the viscosity of the vegetable oil involved in the reaction and also decreases the reaction time (Issariyakul *et al.*, 2014).

4.1.5 Reaction time

Transesterification yield and conversion increase with increasing reaction time. The reaction begins with two distinct phases of alcohol and oil and as intermediate products (diacylglycerols and monoacylglycerols) are formed, they act as surfactants allowing a faster mass transfer from the oleic phase to the alcoholic phase (Issariyakul *et al.*, 2014). Normally, the maximum reaction yield is obtained in less than 90 minutes and remains relatively constant for additional reaction times (Leung *et al.*, 2010). Furthermore, very high reaction times will lead to a decrease in

yield, as the reverse reaction will take precedence if there is no phase separation, resulting in a decrease in the esters formed and the formation of free fatty acids that will cause the formation of soap.

4.1.6 Type of catalyst

Most transesterification reactions are conducted in the presence of homogeneous catalysts. The most used for this purpose are basic, acidic or enzymatic (Albuquerque *et al.*, 2008). Basic catalysts have been shown to be more efficient compared to acid catalysis, with alkoxides being the most efficient. Some recent works propose heterogeneous catalysis in biodiesel synthesis, as it makes the process simpler and cheaper, as the catalyst is easily separated from the product and can be subsequently reused (Alba-Rubio *et al.*, 2007).

5. USE OF HETEROGENEOUS CATALYSTS IN BIODIESEL PRODUCTION

The heterogeneous catalysis route, if further studied and developed like the homogeneous one, can produce biodiesel in a much more viable economic way, as the use of a solid as a heterogeneous catalyst offers advantages such as: ease of separation and purification of the biofuel, recovery of the catalyst, recovery of excess alcohol by distillation, separation of glycerin from biofuel by decantation, absence of parallel reactions such as, for example, soap production, possibility of reusing the catalyst in new reactions (Ramos *et al.*, 2016). Heterogeneous catalysts can be grouped into acidic character and basic character. Dantas (2017) states that heterogeneous catalysts have physical and chemical characteristics, such as acidic and basic, Lewis and Brönsted sites and a favorable surface area for carrying out biodiesel conversion reactions.

Albuquerque *et al.* studied the production of biodiesel by heterogeneous catalysis, as the process is simple and more financially viable, as it is easily separated from the product and the heterogeneous catalyst can be reused. Heterogeneous catalysts are usually used by industries, as most of these solids are robust at high temperatures, enabling a range of operations. Another reason for using this type of catalyst is that it is not necessary to use extra steps to separate it from the phases, this is a great advantage when compared to homogeneous

catalysts (Atkins, 2008). Solid heterogeneous catalysts can be grouped into seven groups, according to Sivasamy *et al.*: metal oxides, mixed and doped metal oxides, supported catalysts, zeolites, lamellar double hydroxides, organic bases, anionic resins.

A considerable number of heterogeneous catalysts have been reported in the literature to promote the transesterification reaction, such as Kawashima *et al.*, who used oxides to promote the biodiesel production reaction from rapeseed oil; their catalytic activities were tested at 60 °C, with a methanol: oil molar ratio of 6:1 and a reaction time of 10 hours. Under these conditions, the catalysts $CaTiO_3$, $CaMnO_3$, $Ca_2Fe_2O_5$, $CaZrO_3$ and $CaO\text{-}CeO_2$ showed approximately 90% yield of methyl esters. Liu *et al.* used calcium methoxide to promote the transesterification of soybean oil, under conditions of 2 hours of reaction at 65 °C, using 2% (m/m) of catalyst and a 1:1 oil volume ratio: methanol obtaining an ester yield of 98%. Yang and Xie used alkaline earth metal doped in zinc oxide as a heterogeneous catalyst for the transesterification of soybean oil, with the highest catalytic activity being obtained with ZnO impregnated with 2.5 mmol of $Sr(NO_3)_2$/g, followed by calcination at 600 °C for 5 hours. The transesterification reaction was carried out in methanol reflux at 55 °C, oil: methanol molar ratio of 1:12, using 5% catalyst, obtaining a conversion of 94.7% into biodiesel. Furthermore, when tetrahydrofuran was used as a co-solvent, the conversion reached 96.8%.

The use of heterogeneous chemical catalysts in the alcoholysis reaction of vegetable oils reduces the difficulties in separating the products and the catalyst, resulting in less effluent generation (Silva *et al.*, 2009). The literature indicates the use of different acid and basic catalysts (Antunes *et al.*, 2008; Park *et al.*, 2008; Trakarnpruk *et al.*, 2008), which can be reused in the process. Alkaline transesterification occurs approximately 4000 times faster than acid transesterification and is the most commonly used commercially, as it allows obtaining high conversions in low reaction times, as reported by studies in the literature (Freedman *et al.*, 1986; Noureddini and Zhu, 1997; Faccio, 2004).

Although chemical transesterification, employing alkaline catalysis, results in high conversion rates of triglycerides into their respective esters, when it comes

to costs, reaction times, there are some drawbacks or disadvantages (MADRAS *et al.*, 2004).

- Has high energy costs;
- Glycerol recovery is difficult and time-consuming;
- Removal of the catalyst is necessary;
- Requires treatment of alkaline waste water;
- Substrates/reagents must have low water concentration and free fatty acids.

6. NATURAL HETEROGENEOUS CATALYSTS FOR BIODIESEL PRODUCTION

Several works are reported in the literature regarding heterogeneous catalysts used to produce biodiesel obtained from natural sources. The heterogeneous catalysts most used for biodiesel production are based on calcium oxide. Among them, derivatives of natural or waste materials stand out, which in addition to presenting intrinsic advantages related to heterogeneous catalysis, reduce biodiesel production costs. Many heterogeneous basic catalysts have been used in the synthesis of biodiesel, with CaO being part of a group of natural catalysts that do not harm the environment (Viriya-Empikul *et al.,* 2010). Generally, $Ca(NO_3)_2$ or $Ca(OH)_2$ are the precursors in the production of CaO. Furthermore, there are natural sources of calcium that can be obtained from waste, such as: crab shells, eggshells and mollusk shells.

7. CONCLUSIONS

Through this work it was possible to deepen knowledge in the area of raw materials for biodiesel production, as well as the use of heterogeneous catalysts in biodiesel production. Biodiesel can totally or partially replace petroleum diesel oil in automotive diesel cycle engines such as trucks, tractors, vans, automobiles, or stationary engines such as electricity and heat generators.

Biodiesel is made up of biomass from the use of fresh vegetable oils. It is a biodegradable, renewable and environmentally friendly fuel, obtained through the transesterification process.

Heterogeneous catalysts have advantages in the production of biodiesel, according to research reported in the literature, when applied in the transesterification reaction they have several advantages: easy separation of the reaction medium, possibility of recovery and reuse in reaction cycles, in addition to high percentages of conversion to biodiesel. These advantages make the catalysis process heterogeneous, environmentally and technically viable. In this context, the considerations reported in this article reinforce the need for incentives and research regarding the study of heterogeneous catalysts for the production of biodiesel, given the great potential and advantages that are both economic, technological and environmental.

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