USE OF ETHANOL IN TRANSESTERIFICATION

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Due to the unrestrained energy consumption associated with growing environmental concern, research is being encouraged in many diverse areas, to search for alternative resources, which were neglected until recently, principally renewable energy resources such as wind, tides and biomass.

Among these energy resources, biomass has received special attention because due to the large number of applications e.g. ethanol and biodiesel, which are the object of great interest in the world economy.

They can be burned directly or used indirectly after chemical, biological or thermochemical transformations. Among these are the transesterification of vegetable oils, fatty acids esterification, pyrolysis, gasification, extractions with supercritical fluid, anaerobic digestion and fermentation. These processes can use various feedstocks such as agricultural wastes, which otherwise would cause serious environmental problems if left in the fields as it is the case of sugarcane bagasse (MARCINIUK, 2007).

In addition, the use of biomass reduces pollution, because its main components are formed from carbon dioxide and water, using sunlight as a source of energy. This gives biomass a strategic position for the solution of problems related to global warming. If you consider that during combustion of biomass, carbonic gas emitted to the atmosphere is absorbed by photosynthesis during growth, the mass balance for CO_2 is more favorable than zero. However, for this becoming a reality, a sustainable consumption of biomass is needed, without

reduction of its availability over the years, as it is presently happening in most developing countries (GARCIA, 2006).

As readily available sources, vegetable oils have been gaining in importance in current energy programs. They provide a decentralized energy generation, bringing benefits to more distant locations and less affluent regions. Its production also means supporting family farming and enhancing regional development (RAMOS, 2003).

Several researchers propose the direct use of vegetable oils as alternative fuels for petroleum-based such as diesel oil. However, despite being vegetable oils energetically favorable due to their high calorific value, their direct use may prejudice operations and durability of diesel engines, increasing their maintenance costs (MACEDO, 2004).

This is due to the high viscosity of these oils, approximately 11 to 17 times greater than diesel fuel, low volatility and high molecular weight because of the large chain of triacylglycerides. These factors may prevent their complete combustion, leading to the formation of carbon deposits inside the engine and obstruction of oil filters and injection systems. Furthermore, the thermal decomposition of glycerol, present in vegetable oils, can lead to the release of acrolein, a highly toxic and carcinogenic substance (TEIXEIRA, 2006).

Several processes have been studied which would allow to obtain renewable fuels with physicochemical properties similar to diesel oil, without requiring engine modifications or additional technology investment. An example is the use of biodiesel, which can be obtained from vegetable

oils or other sources of fatty materials, such as animal fats or waste oils, by transesterification with short-chain alcohols. The fuel compatibility with conventional diesel has characterized it as the most appropriate alternative which can be used in fleet of most diesel vehicles existing on the market (XIE *et al.*, 2006).

When compared to mineral diesel, biodiesel has as major advantages such as the reduction of emissions, biodegradability, higher flash point and increased lubrication.

The term "transesterification" (or alcoholysis) describes an important class of organic reactions in which an ester is transformed into another through the exchange of their alkoxide groups. In this reaction, the triacylglycerides present in vegetable oils, react with an alcohol in the presence of a catalyst producing a mixture of monoalkyl esters of fatty acids and glycerol, as shown in Figure 1.

Various alcohols can be used in such reactions, however, only methanol or ethanol will produce biodiesel. Both can be obtained from renewable sources such as dry distillation of wood and fermentation of sugarcane, respectively.

According to the technical aspects of transesterification, the use of methanol (methanolysis) is advantageous because it allows the spontaneous separation of glycerol and as a consequence the reduction of the number of process steps. Moreover, it gives a high conversions using homogeneous catalysts in basic or acidic conditions. On the other hand, this alcohol has a high toxicity.

The use of ethanol (ethanolysis), even anhydrous, creates problems in the separation of glycerin from the reaction mixture. The power consumption of a plant that produces ethylic biodiesel is higher when compared to methylic biodiesel. However, for Brazil, from the economic point of view, the use of ethanol is more advantageous, since the country is considered to be the second largest producer.

The transesterification of vegetable oils is a reversible reaction, whose kinetics is governed by the principle of Le Chatelier. Thus, the conversion of the reaction depends on shifting the chemical equilibrium towards the formation of products through the optimization of the variables such as temperature, concentration of catalyst, its acidic or basic strength and the amount of reagents.

One of the most important variables that affect the conversion to esters is the vegetable oil to alcohol molar ratio. Using an excess of alcohol, the equilibrium is shifted towards the product, however, an excessive increase will also favor the solubility of glycerol in biodiesel, making its separation difficult (GARCIA, 2006). According to the literature, vegetable oil to alcohol molar ratios are normally in the range of 1:6 to 1:30. In the case of ethanol, ratios of 1:6 and 1:12 show satisfactory results.

ENCINAR *et al.* (2002) have studied the ethanolysis of *Cynara* oil by varying the oil to ethanol molar ratio from 1:3 to 1:15. The best results were obtained for reactions carried out with the molar ratio between 1:9 and 1:12. The reactions employing molar ratios below 1:6 were incomplete and problems in the glycerol separation step were found when using a molar ratio of 1:15. The temperature and reaction time also influence these reactions. High temperatures al-
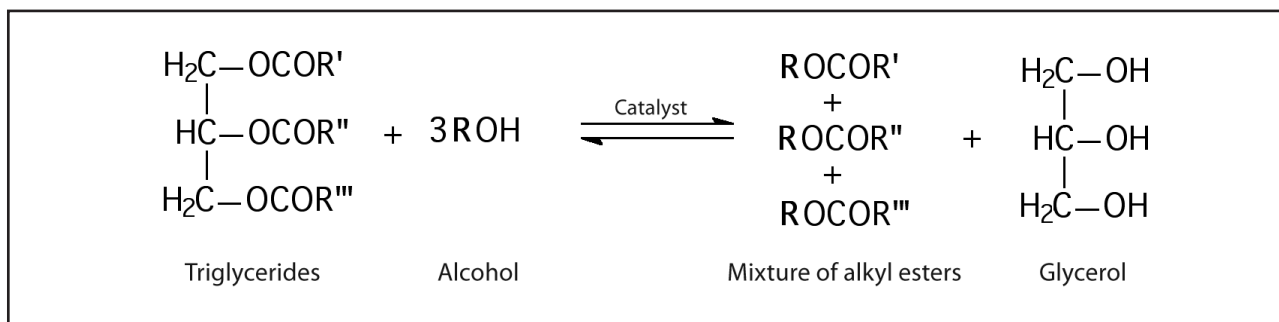
FIGURE 1   Transesterification of a triacylglycerides.

low higher conversions in shorter reaction times. However, it is necessary to evaluate whether the energy expenses used for heating do not exceed the economic gains.

Methanol and ethanol are not miscible with vegetable oils at room temperature. To increase the reagents' miscibility, transesterification reactions are largely promoted at temperatures between 60 ºC and 70 ºC under vigorous stirring in order to promote the phase transfer. These conditions usually cause the formation of an emulsion which, in the case of methanolysis, is rapidly broken with the interruption of agitation, leading to the separation of glycerol. In ethanolysis, these emulsions are much more stable and sometimes difficult to brake (MEHER *et al.*, 2006).

The emulsions formed during transesterification are partly due to the presence of diacilglycerides (DAG) and monoacilglycerides (MAG), intermediaries in the alcoholysis of triacylglycerides (TAG), which are good surfactants. In the alcoholysis process the base catalyst is dissolved in the alcohol and, after its complete dissolution, is mixed with the triacylglyceride. The reaction is initially controlled by phase transfer, however, in the course of the reaction the concentration of intermediaries decreases, reaching a critical level at which the formation of emulsions is favored. When the concentrations of MAG and DAG in the reaction medium reach very low values, the emulsion is broken. However, the emulsion formed in the course of ethanolysis provides a large contact of glycerol with the ethyl esters, thus making the phase separation more difficult (GARCIA, 2006). The presence of glycerol in the reaction medium shifts the equilibrium of the reaction towards the reactants. Consequently, the conversion is decreased and intermediate surfactants will remain in the system in concentrations that enable their performance as emulsion stabilizers.

Another important aspect for the reaction is the agitation speed. After homogenization of the system, vigorous agitation may cause glycerol droplets to disperse in the reaction medium, making its separation longer. This variable is much more important in ethanolysis, in which the agitation should be vigorous only in the first minutes of

reaction; after this period it is preferable that the reaction is conducted under milder agitation. This procedure reduces the dispersion of glycerol droplets and thus shortens the glycerin coalescence at the end of the reaction.

GARCIA (2006) found that the yield of esters in transesterification reactions of soybean oil with ethanol at 70 ºC in the presence of potassium hydroxide was directly proportional to the amount of catalyst used, however, the formation of a transparent and thermodynamically stable microemulsion was observed, which does not allow the coalescence of the glycerol, reducing the amount of ethyl esters isolated and increasing the difficulty to purify the product. On the other hand, the alcoholysis at 25 ºC, catalyzed by sodium methoxide or by sodium or potassium hydroxide, resulted in systems that allowed the complete separation of glycerin which was observed immediately after switching off the agitation. For all three reactions total conversion was observed.

Since methanolic solutions of sodium or potassium methoxide are now commercially available, the problems of the ethyl esters and glycerin separation are reduced, so that the water content of ethanol is now a major variable causing problems in the separation of the products. This should not be higher than 0.2%. Although the use of these commercial catalysts has bypassed much of the problem of the separation of glycerin, the time required for full separation is larger for the production of biodiesel with ethanol compared to that with methanol.

LIMA *et al.* (2006) reported the production of biodiesel from babassu (Orbingnya species) oil with methanol or ethanol at room temperature for 30 min, using sodium hydroxide as catalyst. The yields were 71.8% and 62.2% (by mass) which was attributed to the formation of soap, since the alcohols used were not anhydrous. FERRARI *et al.* (2005) used the ethylic route in the transesterification of neutral soybean oil in the presence of sodium hydroxide to demonstrate the rapid conversion into ethyl esters after 5 min. at 45 ºC. This reaction time is sufficient for the full conversion into esters, as verified by the sudden darkening of the mixture which then returned to the original

color (confirmed by gas chromatography). After the reaction, 600 g of glycerin were added to the system in order to accelerate the formation of the lower phase, facilitating the separation of biodiesel and glycerol.

As can be seen, the appearance of the reaction mixture during the reaction is very relevant. The beginning of the transesterification of vegetable oils is characterized by changes in the color of the reaction system. This change of color ceases in methanolysis, regardless of the reaction temperature, and the reaction system becomes opalescent. In ethanolysis, carried out between 60 and 70 ºC, the reaction mixture becomes clear and transparent, as if a solution had been formed. In ethanolysis at room temperature, the end of color change is followed by a loss of transparency of the reaction mixture and coalescence of glycerol, which starts immediately after interruption of agitation (GARCIA, 2006).

Most of the implications cited are consequences of the use of homogeneous catalysts in the transesterification of vegetable oils, which requires the steps of washing and purification of the products. The attempt to recover the catalysts that are dissolved in the reaction medium will lead to a series of environmental problems since large amounts of solvents and energy are used (DOSSIN *et al.*, 2006). Furthermore, the use of homogeneous basic catalysts can lead to the production of soap by secondary reactions, such as the neutralization of free fatty acids and saponification of triglycerides and/ or mono-esters formed. These reactions are undesirable because they consume part of the catalyst and make the separation of glycerin more difficult. This means higher costs of ester production and possible damage to the environment (LIU *et al.*, 2007).

However, the basic homogeneous catalysis still prevails as the common technology used by industry, because it is a simple process and the catalysts are more easily manipulated and less corrosive than acid catalysts for industrial plants (BUNYAKIAT *et al.*, 2006). It provides very high conversions to esters, even at room temperature, and allows a faster reaction when compared to acid catalysis. The catalysts used are the hydroxides or alkoxides of sodium or potassium (SCHUCHARDT *et al.*, 1998).

Heterogeneous catalysis, on the other hand, has several advantages over homogeneous catalysis, considering the ease of catalyst recovery and reuse, as long as the catalyst does not leach to the reaction medium. Furthermore, a purer fraction of glycerin and an easy recovery of alcohol are obtained. The catalysts allow a continuous process, using a fixed bed reactor, and thus a decrease in production costs (MARCINIUK, 2007). Moreover, the transformation of a homogeneous catalyst into a heterogeneous catalyst and the development of alternative solid catalysts are of great importance for organic synthesis, because the catalytic activity is closely related to the surface used in the absorption of the reagents (BAZI *et al.*, 2006).

LÓPEZ *et al.* (2008) reported the synthesis of three modified zirconia: SZ, WZ and TiZ (sulfated zirconia, tungstated zirconia and titania zirconia, respectively), calcined at temperatures of 400 ºC to 900 ºC. The catalytic activity of the different zirconia was evaluated as a function of the calcination temperature in the reaction of tricaprylin with ethanol at 75 ºC for 8 h. Although the sulfated zirconia SZ is the most active in this reaction, its catalytic activity is not easily recovered, even when recalcinated at 500 ºC. The TiZ was more active than the WZ, due to the presence of basic sites, according to the authors. The yields of ethyl caprylates were, however, only in the order of 10%. The WZ catalyst proved to be most active in the esterification of oleic acid, giving a yield of 100% at 120 ºC after 8 h and of 80% at 75 ºC after 22 h of reaction (LÓPEZ *et al.*, 2008).

SHIBASAKI-KITAKAWA *et al.* (2007) used a variety of ionic resins in the transesterification of triolein with ethanol. The anionic resins showed greater activity than the cationic. The ethyl oleate was obtained with a conversion of 98.8% using a triolin: ethanol molar ratio of 1:20, 4% (w/w) of catalyst at 50 ºC for 1 h of reaction.

MARCINIUK (2007) evaluated the catalytic activity of various phosphates of trivalent metals for the production of esters. The catalysts were shown to be very efficient in the transesterification of vegetable oils and in the esterification of free

fatty acids, giving more than 95% yield of methyl and ethyl esters. The reactions conditions were 2 h in methanolysis and 1.5 h in ethanolysis, 175 ℃, molar ratio of oil: methanol of 1:12 and oil: ethanol of 1:9 and 5% (w/w) catalyst.

It was found that these catalysts do not lose their catalytic activity in the presence of water, allowing the use of hydrated ethanol in the reactions. This can be demonstrated by the yield of esters of 90% and 97% for the reactions of soybean oil with ethyl alcohol containing 20% and 5% (w/w) water, respectively. In addition, the solids can be recycled, however, a loss of their catalytic activities from the second re-use is observed, due to leaching of phosphate groups (SCHUCHARDT *et al.*, 2006).

GARCIA (2006) synthesized the sulfated zirconia S-ZrO_2, through an alternative route without solvents and precipitation, and SZ, through a different precipitation method. In addition, non-sulfated zirconia (ZrO_2) was used. The catalytic activity of zirconia was evaluated in the methanolysis and ethanolysis of soybean oil at 120 ℃ and 1 h reaction time using 5% (w/w) of catalyst. The results show that the non-sulfated zirconia (ZrO2) is not active in the methanolysis of soybean oil. The sulfated zirconia (SZ) showed a low catalytic activity (8.5% conversion), compared to the very active S-ZrO_2 (98.6% yield of methyl ester and 92% yield of ethyl ester).

The performance of the sulfated zirconia (S-ZrO_2) and a commercial niobium catalyst (niobic acid supported on graphite) was compared in the esterification of oleic acid with methanol and transesterification of soybean oil. The sulfated zirconia as well as the niobium catalyst converted oleic acid into methyl oleate, however, the niobium catalyst was not active in the transesterification of soybean oil (GARCIA *et al.*, 2008).

RATNASAMY *et al.* (2006) developed bimetallic cyanides (Fe-Zn) which were shown to be highly active in both transesterification of vegetable oils and esterification of free fatty acids. These catalysts have acid sites which are resistant to the presence of water, probably due to the hydrophobic characteristic of their surface, and can be reused several times without significant loss of their activity. Conversion of vegetable oils increased with the amount of catalyst used, resulting in yields of methyl esters of 99% at 170 ℃. As expected, an increase of conversion with increasing oil:ethanol molar ratio was observed, giving 100% yield at a molar ratio of 1:15 (RATNASAMY *et al.*, 2006).

The largest biodiesel factory in Latin America, Naturoil Combustíveis Renováveis S.A., is being constructed in Ourinhos (São Paulo) which will produce 227 million liters per year. French technology (Esterfip-H) will be employed, using zinc aluminate ($ZnAl_2O_4$) as a catalyst for the transesterification of different vegetable oils and tallow.

In addition to all the advantages of heterogeneous catalysis, the great difference in using a heterogeneous acid catalyst for transesterification is the easy separation and recovery of the catalyst, the elimination of washing steps and the possibility of using vegetable oils with high levels of free fatty acids which are typically found in the north and northeast of Brazil, in waste oils and animal fats.

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