NEW HETEROGENEOUS CATALYSTS FOR TRANS-ESTERIFICATION OF TRIGLYCERIDES

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ABSTRACT

This paper describes preliminary work done towards the development of new metallic heterogeneous catalysts to be used in the transesterification reaction of triglycerides, which is of considerable interest in the production of biodiesel. Biodiesel, is a mixture of mono-alkyl esters of fatty acids, and is currently manufactured by transesterification of triglycerides with methanol using NaOH or KOH as liquid base catalyst. Catalysts as such are corrosive to the equipment, and as these catalysts are in liquid phase must be neutralized after the completion of the reaction, typically using HCl, thus producing salt streams. Moreover, due to the presence of free fatty acids it reacts to form soaps as unwanted by-products, hence requiring more expensive separation processes. Therefore, there is a great need on the development of industrial processes for biodiesel production using solid acid catalysts. The key benefit of using solid acid catalysts is that no polluting by-products are formed and the catalysts do not have to be removed since they do not mix with the biodiesel product.

Keywords: Biodiesel, heterogeneous catalysis, efficiency, transesterification

INTRODUCTION

Biofuels are all the fuel substances produced from Biomass and includes the Biodiesel (single alkyl ester of fatty acids), bioethanol and biogas (a mixture of methane and CO_2). The highway transports activity, in a global level, is 98% oil dependent. In the EU, this activity is responsible by more than 20% of total CO_2 emissions and, more than 50% of these emissions concerns to the individual

transport, which increase 22% since 1999. The climate changes, the increase of crude prices and the supply energetic security leads to the growing interest about biofuels potential as substitutes of oil fuels, like gasoline's and diesel (OE, 2007).

Nowadays, biodiesel is obtained essentially, from oleaginous plants by the transesterification process (as described in figure 3), which involves, as reactants, alcohol, essentially, methanol (CH_3OH) and a catalyst, preferably alkaline, liquid phase (NaOH, KOH, sodium methoxide). This process occurs with homogeneous catalysis. The main raw materials, which are the mentioned oils from oleaginous plants, previously refined, are, in majority, of colza, sunflower and soy. It can be done, also, by other plants, such as palm. Chemically, biodiesel is described as a mixture of methyl ester's of fatty acids, where, through the transesterification process, are produced those ester's (single, double and triple triglycerides), and produces also, Glycerine as co-product reaction (OE, 2007), (BPR, 2004).

The quality of biodiesel must comply with several specifications in order to ensure a final product with good quality, main issue to guarantee his suitably introduction in the market. Naturally, the oil quality has significantly influence in the labour process qualification and in the biodiesel final specifications. It's important, also, refer that, to ensure those specifications, the production process has to be controlled, either at the reaction control level, either, basically, at the purification process level, where occurs the biodiesel/methanol, biodiesel/catalyst and biodiesel/water separation steps, through the washing of biofuel. One of the most important control parameters of biodiesel is the maximum proportion of total glycerine, which is 0,25% in the European and American technical standards, in order to avoid the formation of particles in the combustion chamber and, also, to avoid the production of higher

percentages of acrolein on the automobile combustion gases (BPR, 2004). Other important parameters are the viscosity, the water content, the iodine index, the proportion of single, double and triple triglycerides, the methanol proportion, the sulphur proportion, ashes, carbon residue, total contamination and cetane number. The biodiesel specifications currently available and used are described on the EN 14214 standard. The table 1 presents the goals stipulated by the EU to the incorporation of biofuels in the fuel oils until 2010, which includes the incorporation of biodiesel on the diesel fuel [3]. Figure 1 shows the process diagram of biodiesel production and figure 2 shows a generic flowsheet of the same process.

DEVELOPMENT OF NEW HETEROGENEOUS CATALYSTS FOR BIODIESEL PRODUCTION

The transesterification reaction is considered the process with more technical effectiveness and with higher efficiency for biodiesel production using large scale, with minimization of co-products. Nevertheless, it's essential that, the raw materials (vegetable oils) keep a minimum level of quality, which can be achieved in the presence of acids, alkaline or enzymatic catalysts, simples or supported. The use of acid catalysts, like sulphur acid, leads to a reaction kinetic much lower when compared with alkaline catalysts. Other disadvantage in the utilisation of these kinds of catalysts is concerned with biodiesel separation from the process, in order to prevent possible damages to the engines structures, caused by the acid catalyst.

On the opposite side, basic catalysts are faster and, in many cases, the steady-state is achieved at 15-30 minutes and leads to higher biodiesel yields, generally higher than 50%. However, they have the inconvenient of being sensible at the presence of

water and free fatty acids. These last ones consume the catalyst and conducts to the formation of gels and soaps. These demands difficult the utilisation of used fried oils. On another hand, the enzymatic catalysts offer some advantages when compared with acids and alkaline catalysts, like, for instance, less sensibility to water presence, more catalyst recovery and more efficiency in the biodiesel separation steps. However, their utilisation implies higher costs (BPR, 2004).

Other way in catalyst utilisation is the employment of heterogeneous catalysts in the biodiesel production, in order to replace the conventional homogeneous alkaline or acids catalysts, to eliminate the difficulties founded in the current biodiesel/catalyst separation. These new catalysts are solid. By another hand, these alternative and innovative solutions in the biodiesel production system allowed, more economic profitability and competitiveness to the process and, brings also, more environmental compatibility, when compared with the conventional processes. In this last issue, the use of heterogeneous catalytic systems in the transesterification of triglycerides implies the elimination of several washing/recovery biodiesel/catalyst process steps, in order to ensure a higher efficiency and profitability of the process, lowering the production costs. There is, also, the strong possibility of being implemented in a continuous way, with the construction of a fixed bed catalytic reactor.

The utilisation of heterogeneous catalysts implies higher lifetimes, because there is no need in their recirculation to the initial step (mixture), since the catalyst utilisation time is higher than the homogeneous catalytic processes. This means less catalyst replacements on the fixed bed catalytic reactor, which leads to a higher quality of the final product and, also, to the co-product, the glycerine. However, either the reaction

conversion, either the *turnover number*, in order to keep constants, there is the necessity of optimize the operating conditions in the reactor.

A literature search about these subjects was already done and the main results and contributions of several authors are synthesized in table 2.

The optimization process at an industrial scale needs, to perform a previous study, at laboratory scale, which concerns to perform several modifications of concentration ratios, temperature, catalyst structure and composition and time residence, in a fixed bed catalytic reactor. After that, we intend to optimize the biodiesel process production with heterogeneous catalysis, performing the scale-up in a pilot unit and quantify his composition, according to the EN 14214 standard specifications. Figure 4 shows a possible *flow-sheet* for biodiesel production process with heterogeneous catalyst.

CONCLUSIONS

As a first approach, it was possible to conclude that, the main advantages of replacing the actual homogeneous catalysts by heterogeneous catalytic matrices (solids structures), concerns with the establishment of surplus-values in a process, economic and environmental points of view, in which this last one depends of minimization of waste solid and liquid production on the labour process. On another hand, it's possible affirm that, through the experimental results searched on the performed bibliographic research that, either the catalytic activity, either the biodiesel yields obtained, either the biofuel quality (fulfilment of the control quality parameters stipulated in the EN 14214 standard) were maximized with supported metallic catalysts matrices, mostly the ZrO_2/SO_4 heterogeneous catalyst matrix, for several

temperatures, preferably, the higher ones, in the gap between 65 and 70ºC, with large quantities of methanol, six times higher that the vegetable oil quantity and with percentages rounded 1% of catalyst comparatively with the vegetable oil used in the transesterification process.

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Table 1: Targets of biofuels incorporation on oil fuels (Pelkmans, 2007)

2005	2006	2007	2008	2009	2010
2%	2,75%	3,5%	4,25%	5%	5,75%

Table 2: Used heterogeneous catalysts, experimental conditions and respective results obtained, found in literature research, for biodiesel production

Authors (year)	*Catalysts tested and their properties*	*Experimental conditions and obtained results*
Kiss *et al* , 2006	Zeolites Y, β and ZSM-5, Cationic Resins Amberlite-15 and Nafion-50, metallic oxides such as ZrO_2/SO_4^-, TiO_2/SO_4^{2-} and SnO_2/SO_4^{2-} and $Cs_{2,5}H_{0,5}PW_{12}O_{40}$.	Good results in the reaction conversion and yield for ZrO_2/SO_4^-, in a large gap of temperatures.
Rosa *et al* , 2005	Butilestanoic acid ($(C_4H_9)SnO(OH)$), Dibutyltin oxide ($(C_4H_9)_2SnO$) and Dibutyl dilaurat of tin ($(C_4H_9)_2Sn(C_{12}H_{23}O_2)_2$).	Soya oil transesterification. Molar ratio oil/ methanol/ catalyst: 100/400/1, 10 h of residence reaction time. Higher conversion (35%) for dibutyltin oxide.
Srivastava *et al* , 2006	Supported catalysts Fe-Zn in cyanidric complexes, with and without ter-buthanol (complex agent) and with a co-polymer ($EO_{20}PO_{70}EO_{20}$).	Higher activity and selectivity with complex agent in the catalytic matrix
Perin *et al* , 2006	SiO_2/H_2SO_4, SiO_2/KOH e Al_2O_3/KOH, SiO_2/HCl, $SiO_2/ZnCl_2$, $SiO_2/AlCl_3$ e Al_2O_3/H_2SO_4,	Mamona and Soya oil transesterification, with methanol, temperatures of 25ºC and 65ºC, ratio support/catalyst of 50% (w/w), ratio oil/methanol of 1:6, mass ratio of 5 g oil/0,25 g of catalyst. Best results for supported alumina catalysts for alkaline catalysis, whilst the silica catalysts showed best results for acid catalysis.
Rosa *et al* , 2006	K_2CO_3, Na_2CO_3 e $CaCO_3$	Mamona oil transesterification with methanol, ratio oil/ methanol/ catalyst of 100/600/1, reaction time of 10 h. K_2CO_3 showed best catalytic activity and higher yields in biodiesel production. $CaCO_3$ do not show any catalytic activity.
Brito *et al* , 2007	Zeolite Y	Employment of used fried oils. Good results regarding biodiesel yield.
West *et al* , 2007	ZrO_2/SO_4^{2-},	Good results at catalyst activity and in the biodiesel yield production.
Santos *et al,* 2007	Hydrotalcytes of Mg and Al (ratio Mg/Al of 3), modified with Zn, Sn, Ba, Mn, Ce and Ca, with 5% catalyst (%w/w)	Soya oil transesterification with methanol, 70ºC, reaction time of 3 h, ratio methanol/oil of 9:1. Good results regarding biodiesel yield and product quality.

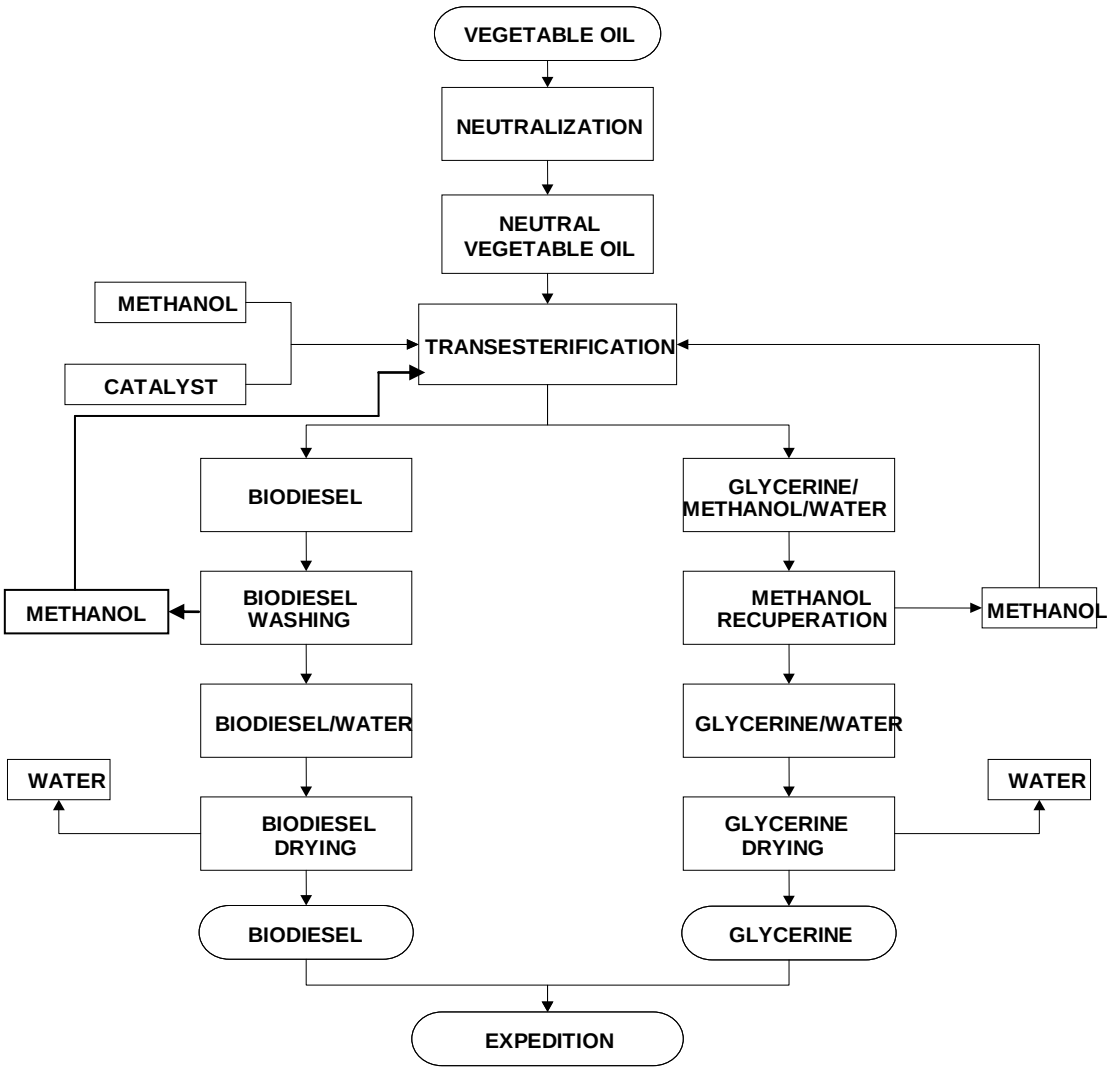

Figure 1: Schematic process diagram of Biodiesel production process

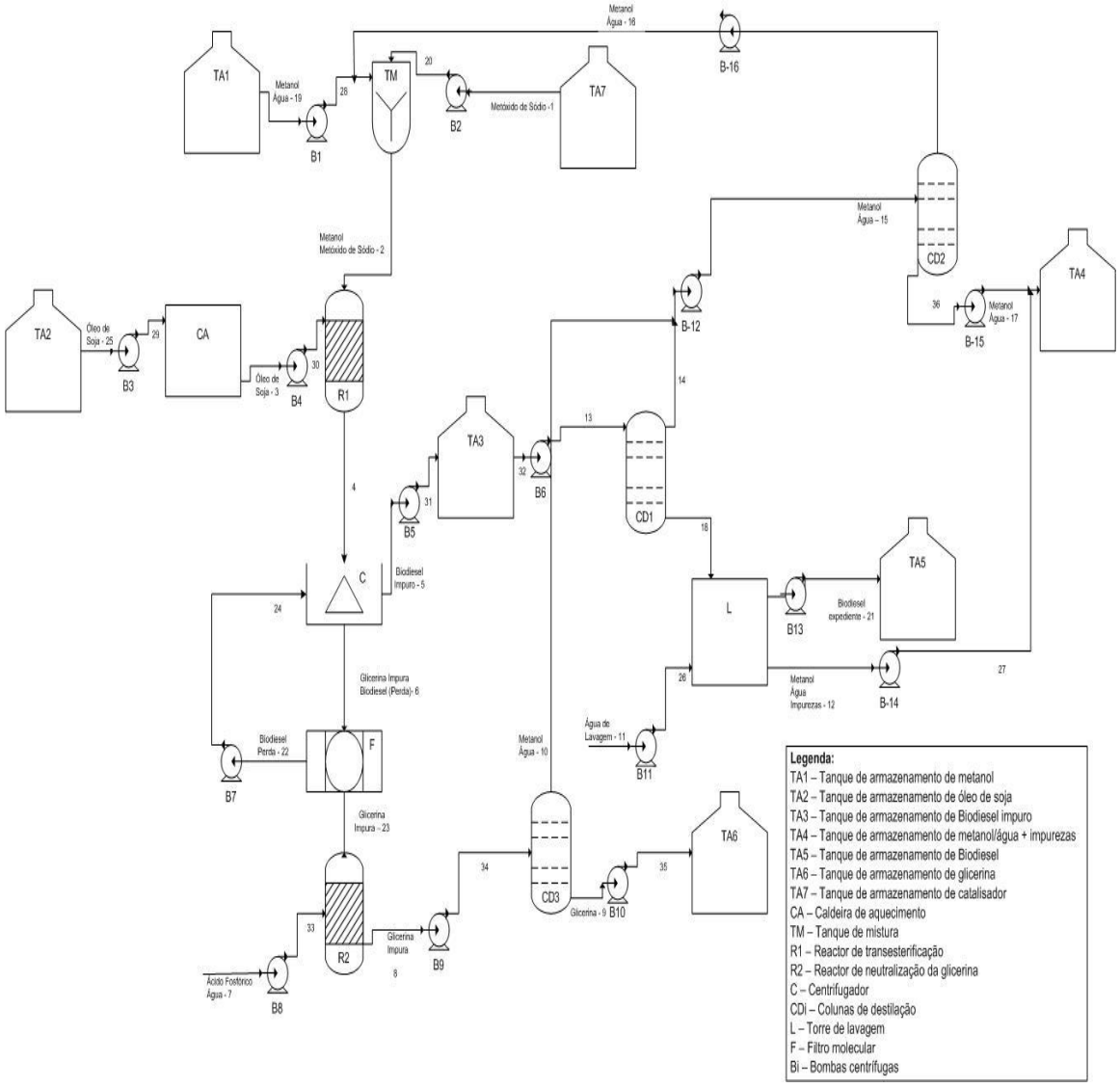

Figure 2: Conventional process flowsheet using homogeneous catalysis for biodiesel production

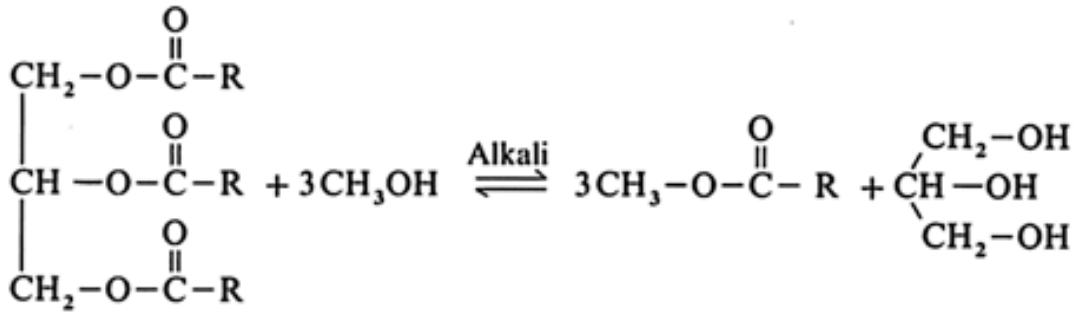

Figure 3: Transesterification reaction for biodiesel production

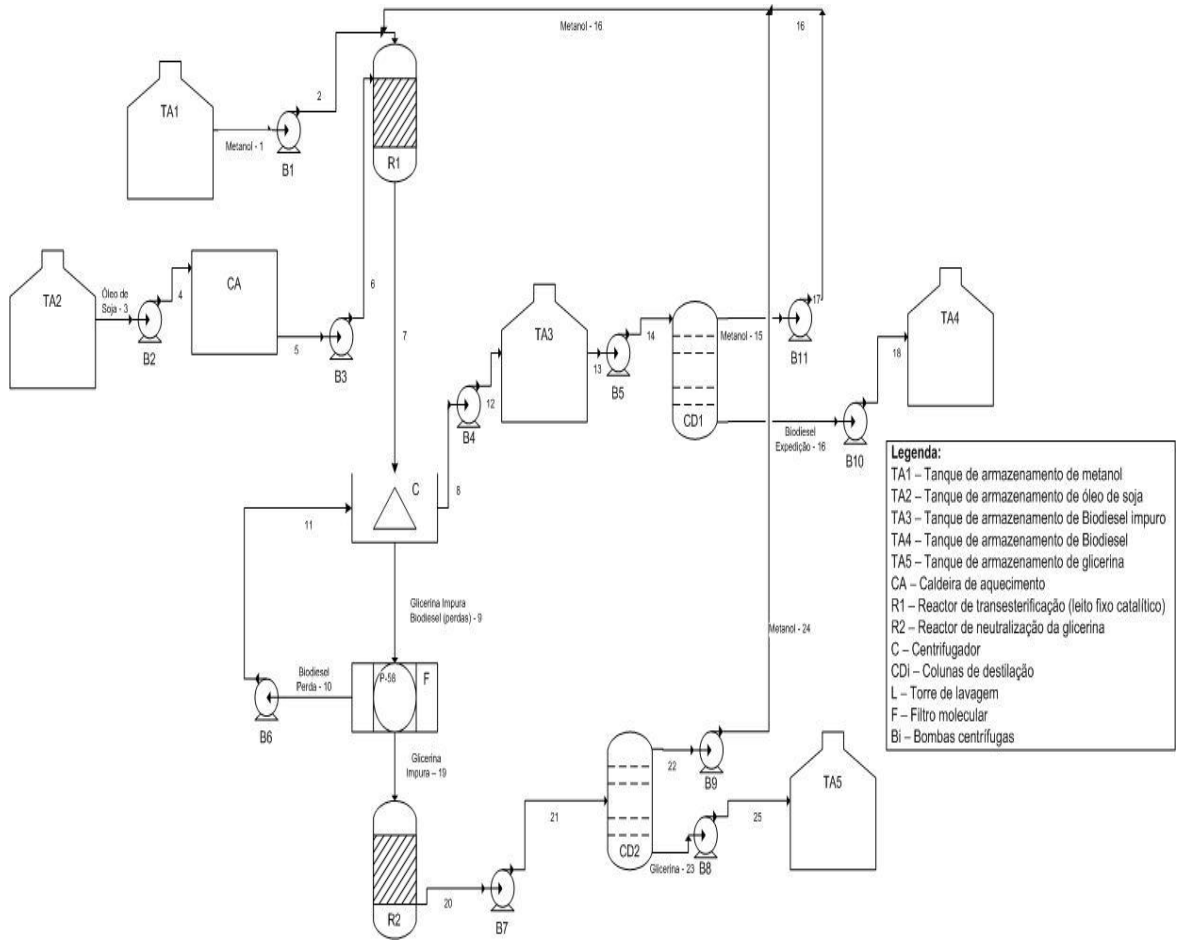

Figure 4: Previewed f*lowsheet* for biodiesel production using heterogeneous catalysis