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An efficient and sustainable biodiesel production in a mechanochemical pilot reactor under heterogeneous catalysis

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Introduction

Fatty acid methyl esters (FAME) produced from vegetable oils or animal fats by transesterification, or from the esterification of fatty acids, with methanol, is labeled as ‘‘Biodiesel”. Current industrial processes for biodiesel production are mainly based on homogeneous catalysis, in presence of an alkali hydroxide or methoxide dissolved in methanol, a large excess of methanol (methanol:oil molar ratio > 6), a temperature around 60 ºC and 1-2 h of reaction [1]. However, this process suffers from different drawbacks, mainly related with the generation of large amount of wastewater associated to the washing and neutralization steps, the non-recovery of the homogeneous catalyst, or the formation of stable emulsions difficult to separate. These problems cause an increase of the overall biodiesel production cost. To overcome them, different approaches have been proposed, such as the use of heterogeneous catalysis, CO_2 under supercritical conditions or enzymes, coupled to microwave and ultrasonic systems as alternative to conventional heating [2].

In this sense, unlike homogeneous catalysts, heterogeneous ones are environmentally benign and can be reused and regenerated. However, higher catalyst loading and alcohol:oil molar ratio are required for biodiesel production in the presence of solid catalysts [3-5].

In the present communication, a new mechanochemical reactor is used for the transesterification reaction that promotes the oil-methanol mixing, minimizing the mass transfer problems associated to the immiscibility of reactant mixtures. Moreover, in order to achieve a more sustainable biodiesel production process, a new heterogeneous basic catalyst is prepared from calcium oxide and glycerol, the by-product of biodiesel industry.

Results and Discussion

Mechanosynthesis could be easily used at industrial scale, with high input flow, allowing production from 30 to >5m^3/h of reaction mixture. The methanol:oil molar ratio has been optimised in order to minimize the excess of methanol, because its recovery by distillation is costly. Thus, values between 3.5:1 (very close to stoichiometric value) and 6:1 have been tried, whereas the mixture has been incorporated at room temperature or 60ºC, at different flow values for varying the residence time. This new mechanochemical reactor allows to attain more than 90% weight of FAME using mixtures of methanol and vegetable oil close to the stoichiometric ratio (4:1), at room temperature during less than one minute of residence time in the reactor [5].

On the other hand, mechanochemical synthesis of calcium diglyceroxide (CaDG) from glycerol and CaO has been optimised to minimize the number of reaction steps, and cost, to obtain a pure CaDG. This CaDG could be used as heterogeneous basic catalyst, in order to valorise the glycerol produced during the transesterification process. Different glycerol:calcium precursor ratios, nature of CaO precursor ($CaCO_3$, commercial CaO, a modified-CaO, $Ca(OH)_2$) and conditions reactions have been evaluated, and the resulting CaDG have been characterized by XRD, SEM, TG-DTA and N_2 sorption at -196ºC. Finally, a new and more efficient mechanochemical synthesis of CaDG has been achieved, requiring a very short synthesis time (just few seconds), room temperature [6], which is much quicker and more efficient than other synthesis proposed in literature [7].

Therefore, a new smart and efficient process for biodiesel production has been developed without waste production (no water, nearly no excess of methanol), with glycerol valorisation in the catalyst synthesis, under very low energy consumption conditions: room temperature and less than 1 minute of residence time in reactor.

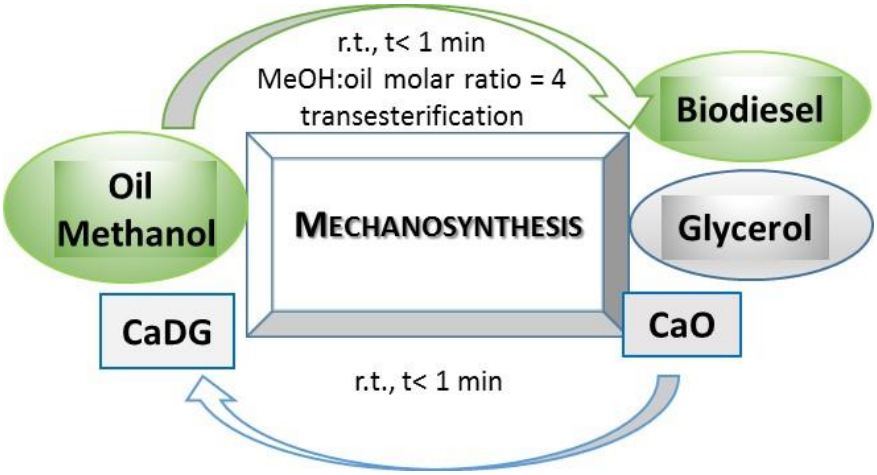

Figure 1: Scheme of the sustainable biodiesel production and heterogeneous catalysis synthesis.

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