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Valorisation of glycerol by new mechanochemical processes

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PURPOSE OF THE ABSTRACT

Mechano-chemistry deals with the induction of chemical and physico-chemical transformation of matter by the effect of mechanical energy, which allows the activation of chemical processes and structural changes in solids, as well as the reduction of particle size. Among the benefits of the application of mechano-chemistry to chemical reactions, the homogenization of particle sizes and renovation of surfaces are two key effects. Mechano-chemistry transfers energy to reagents via impacts from milling media, increasing the reactivity and selectivity. Energy can be transferred to reagents independently of the state-of-matter, so it is not limited to just solid-state, reactions in liquid-phase and even gas-phase are also feasible. Possible synthesis at room temperature and the reduced need for solvents result in less waste generation, thus allowing to overcome drawbacks associated to diffussional problems, as the rate-controlling process [1-3].

Currently, much attention is being paid to the valorisation of glycerol, the by-product of biodiesel production, as a main to get a more sustainable chemical process, from both economical and environmental viewpoints. The search for new applications of glycerol, as a chemical platform from which a broad spectrum of new valuable derivatives can be obtained, is ongoing [4-5]. In the present communication, a new mechano-chemical reactor is used for the valorisation of glycerol, and some examples of potential chemical processes by using mechano-chemical energy will be provided in order to reduce the residence time, to minimize the use of solvents or to decrease the temperature.

In this sense, the mechano-chemical 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 could be used as heterogeneous basic catalyst, in order to valorise the glycerol produced during the transesterification process. Several calcium precursors, the glycerol:calcium molar ratio, the use of solvent for washing, among other experimental conditions have been evaluated and the resulting CaDG have been characterized (XRD, SEM, TG-DTA and N2 sorption). Finally, a new and more efficient mechano-chemical synthesis of CaDG has been achieved, requiring short synthesis time without heating and no need of solvents. The stability of this catalyst is studied under presence of free fatty acids and water, compounds presents in waste oils that decrease the yield to fatty acid methyl ester (FAME) during the reaction. Moreover, the transesterification reaction of used and refined vegetable oils with methanol has also been studied and optimised in the presence of CaDG as basic solid catalyst, using the same mechano-chemical reactor that promotes the oil-methanol mixing, minimizing the mass transfer problems associated to the immiscibility of reactants [7]. Low methanol:oil ratios and low temperature can be used with promising results using a mechanical reactor even with used oils and in plant pilot scale under flow conditions.

Glycerol carbonate is a green chemical glycerol derivative with several industrial applications (solvents, pharmaceutics, detergent, adhesives, lubricants, beauty, among others) [8]. The transesterification of dimethyl

carbonate with glycerol to produce carbonate of glycerol has already been studied under batch conditions using basic solid catalyst, at 60 to 120 ºC during 3 up to 13 h [9-10]. Preliminary tests using a mechano-chemical reactor under continuous flow conditions shows the possibility to reduce the time of reaction to 1h and lowering the temperature.

Finally, the production of Zn glycerolate (good candidate for the tire industry) is also studied. Bibliography shows high conversion (? 100%) in batch reactor, with acid acetic catalyst at 125 ºC after 4-5 hours [11].]. Mechano-chemical synthesis is an alternative for attaining a more sustainable process, reducing time and reaction temperture.

FIGURES

Process	Transesterification Dimethyl carbonate	Calcium diglyceroxide	Biodiesel	Production of Zn glycerolate
Products	Carbonate de glycerol	Calcium diglyceroxide	FAME	Zn glycerolate
Reactor	Batch	Batch	Batch	Batch
Catalyst	CaO, KF-Hydroxyapatite, Mg/Al/Zr mixed oxides	-	KOH, NaOH, CaO, CaDG...	Acide acetique
Temperature (°C)/ Pression (bar)	60 – 120 ºC	220ºC	60 – 120 ºC	120-130ºC
Reaction Time	3 – 13 h (DMC/Glyc = 1/2.5; 1/3.5)	6h	2 – 3 h	4 -5 h
Conversion or selectivity		80 glycerol conversion, S = 40%	90 – 99 %	100%
Test MMR	60º C, reaction time ≤ 1h	100% conversion, r.t. during few minutes	90 – 100% 25º – 50ºC	high conversion, at 100ºC, time ≤ 1h

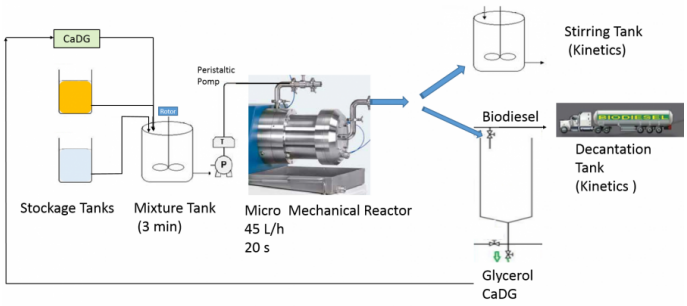

FIGURE 1

Green chemical processes running under mechano-chemical conditions

Reactions parameters used in bibliography are described and expectatives using a mechano-chemical process.

FIGURE 2

Scheme reactivty system with mechano-chemical reactor

Scheme for biodiesel green production

KEYWORDS

Valorisation of glycerol | Mechano-chemical reactor | Calcium diglyceroxide | Biodiesel production

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