

New High-Throughput Reactor for Biomass Valorization †

Irene Malpartida ^{1,2,*}, Pedro Maireles-Torres ², Valentin Lair ¹, Samy Halloumi ¹, Julien Thiel ¹ and François Lacoste ¹

¹ Deasyl S.A., Chemin du Pont-du-Centenaire 109, 1228 Plan-les-Ouates, Geneva, Switzerland; v.lair@deasyl.ch (V.L.); s.halloumi@deasyl.ch (S.H.); j.thiel@deasyl.ch (J.T.); f.r.lacoste@wanadoo.fr (F.L.)

² Departamento de Química Inorgánica, Cristalografía y Mineralogía, Universidad de Málaga, 29071 Málaga, Spain; maireles@uma.es

* Correspondence: i.malpartida@deasyl.ch

† Presented at the 1st International Electronic Conference on Catalysis Sciences, 10–30 November 2020; Available online: <https://eccs2020.sciforum.net>.

Published: 9 November 2020

Abstract: The development of an innovative and sustainable high-throughput reaction platform allows optimizing a wide range of chemical processes (materials synthesis and catalysis, among others) to tackle the Green Deal. This tool unifies, for the first time, the benefits of mechanical energy, thermal and pressure activation in continuous flow with an induction in situ heating system, facilitating the incorporation of inputs (liquids, solids and gases) with controlled pressure. As a result of the synergistic effect of this simultaneous activation, this technology will: (i) shorten reaction times; (ii) decrease temperature; (iii) improve reactions kinetics as mass transfer limitations are reduced; (iv) minimize the use of solvents; (v) decrease the reaction steps; (vi) increase the volume treated, enabling a real scale-up; and (vii) enhance the yields and/or selectivity. This new high-throughput reactor is used for the synthesis of calcium diglyceroxide (CaDG), minimizing the reaction steps and cost, to obtain a pure CaDG. This heterogeneous catalyst is used for biodiesel production and valorization of the glycerol generated as a by-product. An efficient synthesis protocol of CaDG has been developed, requiring shorter time, without heating, and no need for a solvent. This new process facilitates oil–methanol mixing in the transesterification process, thus minimizing the mass transfer limitations associated with the immiscibility of reactants. In addition, this process has been optimized by using CaDG as a solid catalyst.

Keywords: biomass; biodiesel; biofuel; calcium diglyceroxide; heterogeneous catalysis; glycerol valorization

1. Introduction

Depletion of fossil fuels constitutes, nowadays, one of the most critical problems in all the scientific agendas of the world, including the European Green Deal and Sustainable Development Goals of the United Nations. Looking forward, in order to avoid a crisis of chemical and fuel supplies, without affecting current living standards, biorefinery has emerged as an outstanding alternative to replace the petro-based industry. The use of biomass residues, as feedstock for biorefinery, represents an inexpensive option that also promotes environmental sustainability and helps with the transition to climate neutrality. Biomass valorization is also an opportunity with economic benefits, especially for companies generating biomass waste, boosting the integration of a circular economy and green chemistry principles [1].

However, traditional methods for their synthesis are neither atom-efficient nor sustainable [2]. Therefore, the development of greener pathways is highly necessary. The use of renewable biomass

feedstock for sustainable processes must also consider the use of catalysis, the reduction of solvents and additional reagents, the decrease in reaction times, minimization of energy requirements and scalable processes.

In this context, mechanochemistry represents an environmentally friendly strategy, which still requires a lot of efforts for its establishment as a consolidated approach for organic synthesis. After decades of study, mechanochemistry has demonstrated to be able to: (i) simplify work-up protocols, (ii) allow safer processes and (iii) reduce waste, improving energy and cost efficiencies. Mechanochemical methods could certainly contribute to re-thinking organic chemistry from a greener perspective and translate it into a more sustainable chemical industry [3].

The development of an innovative high-throughput reaction platform will allow uniquely optimizing a wide range of chemical processes to contribute to tackling the European Green Deal [4]. This tool will unify, for the first time, the benefits from mechanical energy, thermal and pressure activation in continuous flow. In addition to taking advantage of the powerful synergy obtained from this innovative combination, a tailored in situ heating system will allow the incorporation of inputs (liquids, solids and gas) with controlled pressure. This innovative reaction platform will allow efficiently carrying out a large variety of processes, providing a ground-breaking sustainable, versatile and scalable alternative to currently available technologies, and helping with the transition to climate neutrality and a circular economy. Several catalyst preparations and heterogeneous catalytic processes have limitations, thus the new high-throughput reactor will help to solve them. Traditional methods for synthesis are neither atom-efficient nor sustainable [2] and most of the studies are developed at laboratory scale. The processing routes for biomass valorization still do not meet the requirements for industrial needs. The development of new production technologies in an environmentally and energy-friendly way is still missing [5]. The breakthrough processes opened by the high-throughput reactor will allow studying new tools of activation hitherto unexplored in catalysis, which could facilitate the discovery of new chemical reactions and/or new regio-, chemo- and stereo-selectivity patterns, challenging the current paradigms of conventional organic chemistry and catalysis. Among all target products selected, mechanical energy-assisted synthesis has never been used for their preparation to the best of our knowledge.

In this challenging scenario, biodiesel production needs an effort to develop new technologies to reduce its cost and improve energy efficiency, as well as promote the use of second-generation feedstock, not competing with food supply [6,7]. The main challenge must be focused on the change from a homogenous to heterogeneous process. The use of a solid catalyst will allow a better separation, reduce the post-treatment needs, reduce the use of water in washing steps, minimize the formation of soaps and produce better quality of both biodiesel and glycerol [8,9]. The second difficulty lies in the immiscibility of vegetable oil and alcohol, which generates mass transfer limitations, decreasing the reaction rate. A new method that allows a better mixing of the reactants with scalable opportunity is still missing. In this sense, the new high-throughput reactor seems a good opportunity, firstly, for the synthesis of a solid catalyst and, secondly, for the heterogeneous transesterification of triglycerides with methanol to produce biodiesel.

2. Materials and Methods

2.1. Preparation of Heterogeneous Catalyst: Calcium Diglyceroxide

CaO and glycerol were mixed in a batch reactor, before pumping to the mechanochemical reactor. This equipment possesses a chamber containing yttrium-doped zirconia beads and microbeads that occupies 55–70% of the total volume, and it works with a continuous input flow (between 4 and 150 L/h). Experimental variables, such as methanol/vegetable oil molar ratio, reaction temperature and time, were optimized. The solid catalyst prepared was characterized by several techniques, such as X-ray diffraction, scanning electron microscopy and thermal analysis.

2.2. Heterogeneous Transesterification Reaction with Methanol

The optimized calcium diglyceride was tested in the transesterification reaction of vegetable oil with methanol. Kinetics of fatty acid methyl esters (FAME) yield was analyzed by HPLC, comparing the conventional batch reactor, based on the use of a 3-neck reactor at laboratory scale (60 mL of total volume), and the high-throughput reactor (H-TR) at 50 °C, a methanol/oil molar ratio of 4:1 and 1.5% of weight percentage of the catalyst by oil weight.

3. Results

3.1. Synthesis Optimization of Calcium Diglyceride

Calcium diglyceride is a suitable candidate for the transesterification of triglycerides in heterogeneous conditions; even more, some studies showed that CaO needs to be transformed to CaDG during the reaction to be active [10,11]. Some synthesis protocols have been published, but in a batch reactor and with some hours of residence time [12], so an industrial approach has to be developed and the high-throughput reactor is a good candidate to obtain this objective.

Several reaction conditions were tested in order to optimize the CaDG production, such as CaO/glycerol molar ratio, stirring time and temperature (Table 1). Even more, the effect of the water presence (10 wt.%) in glycerol was also evaluated. The percentage of crystalline CaDG formed was quantified by using the Rietveld method. An XRD study was conducted for all samples and the nominal composition from the structure obtained in the peak identification step was carried out by a Rietveld study. The best fit and convergence of the refinement were obtained taking into account sample displacement, background, peak profile parameters and the scaling of each phase. The percentage of CaDG is shown in Figure 1.

Table 1. Experimental conditions used in the optimization of the synthesis of CaDG.

Entry	Glycerol Quality (wt.% H ₂ O)	Stirring Time (min)	Glyc/CaO MR *	Temperature (°C)	% CaDG (XRD)
1	0	5	30	25	15.40
2	0	5	30	50	18.30
3	0	5	50	25	18.10
4	0	5	50	50	84.30
5	0	30	30	25	91.20
6	0	30	30	50	99.30
7	0	30	50	25	99.50
8	0	30	50	50	55.50
9	10	5	30	25	82.60
10	10	30	50	50	100

* The glycerol/CaO molar ratio is multiplied by 10.

The synthesis was always conducted with a bead size of 0.5 mm, 50 wt% of methanol as the solvent and without water. We can observe that after 30 min of stirring time, the high-throughput reactor is needed to achieve nearly 100% of CaDG (entries 6 and 7). Then, if a glycerol/CaO molar ratio of 3 is used, the temperature must be increased up to 50 °C. At room temperature, an excess of glycerol is mandatory (entry 7). Moreover, the influence of the presence of water was tested (10 wt% water in the glycerol phase was added), and it was observed that a similar purity of CaDG is attained (entry 10). Finally, taking into account these preliminary results and with the objective of decreasing the percentage of methanol used to reduce the viscosity of the mixture, the size of beads was shifted to 1 mm, and it is demonstrated that no methanol was needed to maintain a similar high yield.

Therefore, for the first time, a mechanochemical synthesis protocol under flow conditions is described to obtain CaDG in a scalable process to meet industrial needs. The high-throughput reactor, using a flow between 4 and 150 L/h, allows the synthesis without the need of a solvent, at low temperature, even in the presence of water [13].

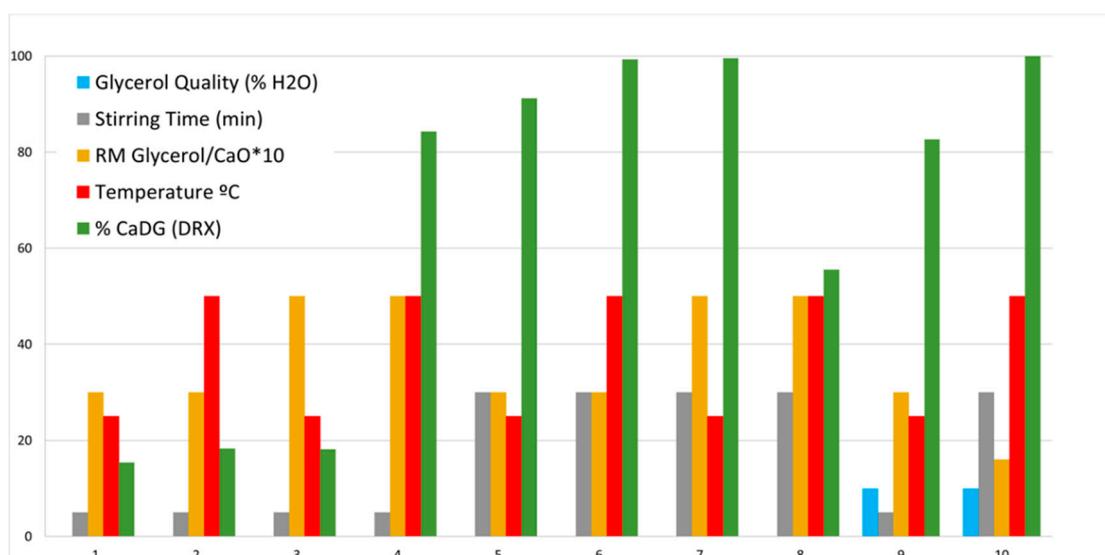


Figure 1. Experimental conditions and percentage of CaDG, as calculated by the Rietveld method.

3.2. Heterogeneous Transesterification Reaction with Methanol

In order to overcome the main drawback in biodiesel production associated with the immiscibility of vegetable oils and methanol which decreases the reaction rate, alternative processes to the conventional batch system using a homogeneous catalyst have been previously reported, for instance, by using enzymatic catalysis, supercritical conditions, ultrasound reactors or microwaves [14,15]. However, most of these technologies still have limitations in being upscaled. Taking into account these previous assumptions, a methanol/oil molar ratio of 4:1 was used, as well as a low reaction temperature (50 °C) and a catalyst loading of 1.5 wt.%. Figure 2 displays the kinetics of the reaction with both systems. The best performance is reached by using the high-throughput reactor, since, after 1 h of reaction time, the FAME yield increases from 20 until 60 wt.% after passing the reaction mixture by the new reactor.

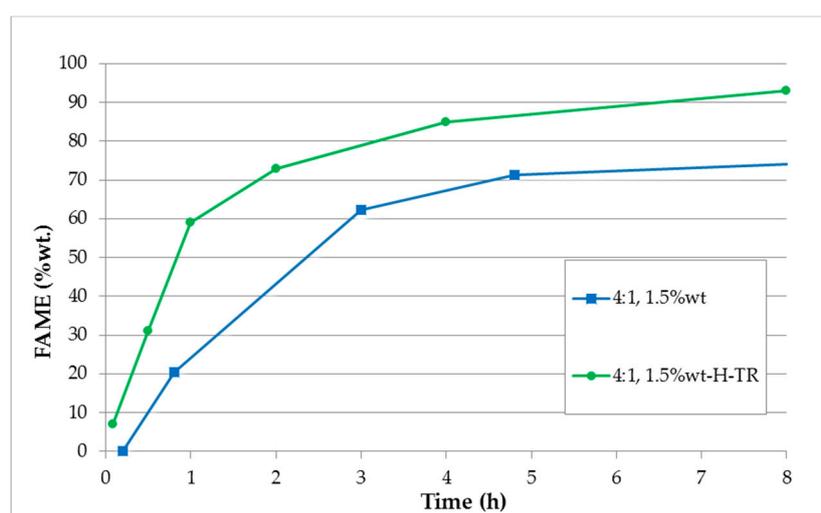


Figure 2. Kinetics of FAME yield under conventional and high-throughput reactors (H-TR) at 50 °C, 4:1 methanol/oil molar ratio and 1.5% of weight percentage of the catalyst by oil weight.

Most of the continuous biodiesel production methods reported so far in the literature require the use of a high reaction temperature and pressure, which means working with very low flow rates [16], so the use of the high-throughput reactor is very promising, since both a low temperature and methanol/oil molar ratio have been used [17].

4. Conclusions

In particular, this breakthrough technology will open new opportunities for greener and more efficient chemical processes, as it is demonstrated in biodiesel production and catalyst preparation to: (i) shorten reaction times (from h to min) as a result of the activation by mechanical energy; (ii) decrease the reaction temperature, since mechanical activation takes place under non-equilibrium conditions; (iii) improve reactions' kinetics as mass transfer limitations are reduced, while the collision between beads and reactants increases the probability of contact between them; (iv) minimize the use of reactants (methanol); (v) increase the volume treated (from mL to L), enabling a real scale-up; and (vi) enhance the yields and/or selectivity, as regeneration of the catalyst surface takes place simultaneously to the reaction.

In this sense, the high-throughput reactor allows optimizing the synthesis protocol of calcium diglyceroxide in flow conditions, with no use of a solvent and no needs stemming from the temperature. In addition, the results for the vegetable oil transesterification process are promising, since at a lower temperature, they show better biodiesel performance than the conventional batch reactor.

5. Patents

Patent new biodiesel process—WO2018002559: Method for producing fatty acid esters and glycerol at low temperature.

Patent CaDG synthesis—PCT/FR 2017 052675: Procédé de fabrication de diglyceroxide de calcium.

Author Contributions: I.M.: writing—original draft, investigation, data curation. P.M.-T.: writing—original draft, conceptualization, project administration. S.H.: investigation, data curation. V.L.: investigation, data curation. J.T.: project administration, resources, supervision. F.L.: funding acquisition. All authors have read and agreed to the published version of the manuscript.

Acknowledgments: We thank the technical support of the Central Research Services of the University of Málaga.

Conflicts of Interest: The authors declare no conflict of interest, as well as the funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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