

Microwave-Assisted Continuous Flow for the Selective Oligomerization of Glycerol †

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Abstract: The continuous oligomerisation of glycerol for the production of polyglycerol was carried out for the first time under microwave activation. Using potassium carbonate, a homogeneous commercial catalyst, various parameters like temperature, flow rate and residence time were studied. The main linear and branched-chain diglycerol and triglycerol regioisomers were characterized and the proportions of the different oligomers were quantified. A cyclic mode process was developed and short distance distillation allowed the mixture to be enriched with glycerol digesters and thus to obtain the following mixture: glycerol dimer (50.2 % by weight), glycerol trimer (22.1 wt%), glycerol tetramer (9.5 wt%) and glycerol pentamer (4.3 wt%).

Keywords: biomass; continuous flow; microwave; polymer

1. Introduction

Considering the programmed decrease in oil resources, chemical industry gives increasing attention to the concept of biorefinery [1–5]. In particular, the use of vegetable oils opens promising ways to valorize biomass and reach ecological future objectives [6–8]. Among the oilseed chemicals, glycerol is an outstanding example with great potential for conversion into valuable products. Glycerol has two primary hydroxyl groups and a secondary hydroxyl group with an axial symmetry. Hydroxyl groups have similar pKa and therefore close acid-base reactivity. Several chemical modifications obtained by esterification, etherification, oxidation, dehydration, hydrogenolysis, and oligomerization of glycerol have led to the production of many value-added chemicals. The products derived from that renewable resource had proven interesting in application fields like polymer, agrochemical and pharmaceutical industries [9–11].

Recently, alternative intensification processes such as continuous flow [12,13] and microwave [14,15] have been used and improved with the aim to develop sustainable and green processes. Among these, microwave-assisted continuous organic synthesis [16,17] as a hybrid technology offers significant processing advantages over traditional batch chemistry like thermal control, conversion and mixture control, safety, adaptability to different reaction conditions, waste reduction, energy efficiency, continuous heterogeneous catalysis, easy scalability, and multi-step synthesis. The present work focuses on the efficient oligomerization of glycerol in a continuous microwave flow process.

2. Experimental

2.1. Reagents

Glycerol was obtained from Fisher chemicals. Bis(trimethylsilyl)acetamide (BSA) and potassium carbonate were obtained from Acros. No further purification was performed for all materials before utilization. Distilled water was used for oligomerization. Linear diglycerol, linear triglycerol and linear tetraglycerol were synthesized following synthesis previously described in the literature,[18,19] and used as standard for analysis.

2.2. Microwave-assisted continuous oligomerization of glycerol

A mixture of 240 g of glycerol (2.61 mol) and 10.0 g of potassium carbonate (72.4 mmol) was magnetically stirred and heated in a 250 mL glass beaker until the basic catalyst is completely dissolved. A 2.45 GHz microwave equipment, Miniflow 200SS manufactured by Sairem SAS (France) was, used with a Watson Marlow 520 peristaltic pump. The homogeneous mixture was into the coiled reactor (54 mL) including an irradiation cell (20 mL). The pump is set to appropriate flow rate and the target temperature of irradiation cell to 238 °C. After the beginning of collection an equilibration time is needed to reach a stationary regime (35 min at 1 mL min⁻¹, 70 min at 0.5 mL min⁻¹, 140 min at 0.25 mL min⁻¹). Glycerol oligomers were quantified by gas chromatography analysis ~~with~~ using calibration curves obtained from synthesized standards.

In cyclic mode, the reactor output was linked to the feeding beaker. After 250 min, the reactor output was collected.

2.3. Gas chromatography analysis

PerkinElmer Gas Chromatography (Autosystem XL GC) apparatus is used to perform Gas chromatography analyses. We used an Altech AT HT column. FID detector temperature is set to 300 °C, injector temperature at 340 °C, and a constant flow of nitrogen of 1 mL min⁻¹ is applied. The temperature profile of the column is a preheating 150 °C for 2 min, followed by an increase to 350 °C at 15 °C min⁻¹, this temperature being maintained for 4.67 min. Before injection, each sample is derivatized to decrease boiling points of oligomers. 0.5 mL of Bis(trimethylsilyl)acetamide (BSA) (~~0.5 mL~~) were added to 40 mg of sample (~~40 mg~~) and the mixture is heated for 30 min at 50 °C. 1 mL of ethyl acetate is added to the solution and 1 mL of the final solution ~~was~~ is injected in the injector. We used Glycerol, linear diglycerol, triglycerol and tetraglycerol as standard samples.[20]

3. Results and discussion

Oligomerisation of glycerol has been widely described through the use of different basic or acidic, homogeneous or heterogeneous catalysts. Continuing our previous work, K₂CO₃ as a homogeneous basic catalyst and glycerol (PG1) were chosen as this protocol can easily be carried out continuously. Oligomerisation was carried out using a continuous microwave intensification process using a commercial equipment (Sairem). A brief temperature study (200 °C – 238 °C) with a constant flow of 1.0 mL min⁻¹ showed that a temperature lower than 230 °C did not allow an interesting conversion of glycerol and 238 °C is the higher temperature allowed by the equipment.

Based on these results, variation of the flow (0.25 – 1.0 mL min⁻¹) was studied at 238 °C (Table 1). In our hands, significant oligomerization is observed, particularly at low flow (0.25 *vs* 1.0 mL min⁻¹), with formation of many regioisomers (PG2 and PG3) and cyclic products (cPG2). However, the conversion of glycerol (PG1) remains low because of a small reaction volume (20 mL) and consequently a short residence time. However, the longer the residence time the better the glycerol (PG1) conversion and the higher the yields of diglycerol (PG2), triglycerol (PG3) and tetraglycerol (PG4). With a reaction time four times longer, glycerol (PG1) conversion and diglycerol (PG2) yield are increased from 16% to 41% and from 12% to 22%, respectively. Obviously, mixtures of dimer, trimer and tetramer include the corresponding regioisomers (PG2: α,α -diglycerol, α,β -diglycerol, β,β -diglycerol; PG3: α,α,α -diglycerol, α,α,β -diglycerol, $\alpha,\alpha,\alpha,\beta$ -diglycerol, $\alpha,\beta,\alpha,\beta$ -diglycerol, $\beta,\alpha,\alpha,\beta$ -diglycerol, $\alpha,\alpha,\beta,\beta$ -diglycerol, β,α,β,β -diglycerol...) (Figure 1).

Table 1. Microwave-assisted continuous oligomerization of glycerol with peristaltic pump (GC analysis).¹

Entry	Flow [mL min ⁻¹]	Residence time [min]	PG1 [wt%]	PG2 [wt%]	PG3 [wt%]	PG4 [wt%]	Other [wt%]
1	1.0	20	84.0	12.1	2.4	0.2	0.4
2	0.5	40	70.3	19.5	6.3	1.0	2.0
3	0.25	80	59.1	22.1	9.3	4.4	5.0

¹ Reaction conditions: 240 g of glycerol (2.61 mol), 10.0 g of K₂CO₃ (72.4 mmol), 238 °C, microwave in continuous flow.

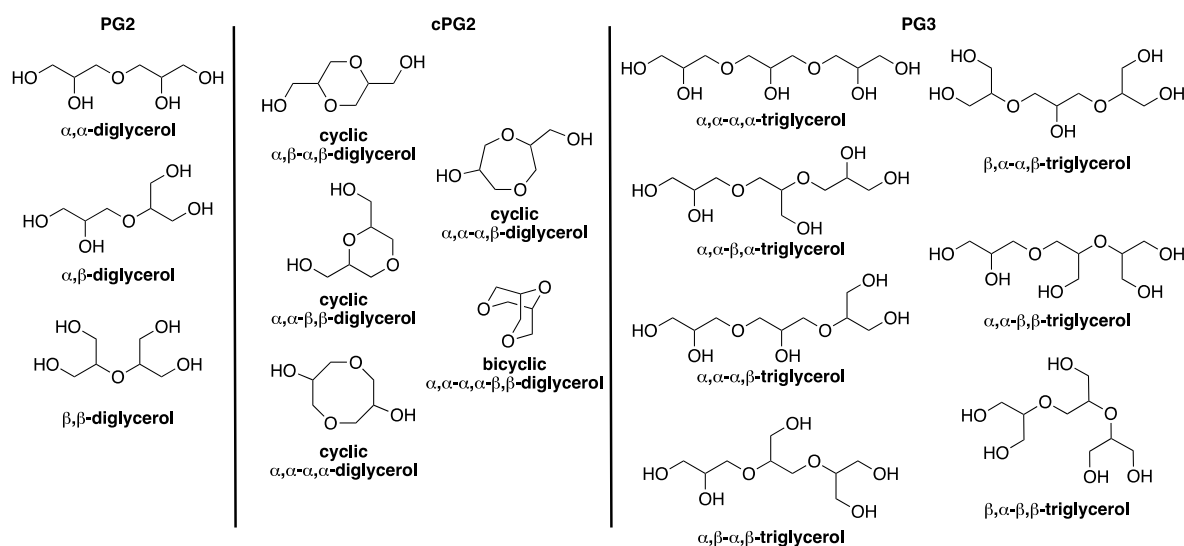


Figure 1. Different isomers of diglycerol (PG2) and triglycerol (PG3).

In order to increase the residence time while keeping the same equipment and specially the same reactor, the reaction mixture was re-injected to simulate a system with reactors in serial mode. These results suggest that while residence time controls glycerol conversion (Table 1), flow influences the distribution of oligomers with high flow favoring glycerol dimer over larger oligomers (Table 2).

Table 2. Microwave-assisted continuous oligomerization of glycerol with peristaltic pump in serial mode (GC analysis).¹

Entry	Flow [mL min ⁻¹]	Residence time [min]	PG1 [wt%]	PG2 [wt%]	PG3 [wt%]	PG4 [wt%]	Other [wt%]
1	0.25	80	59.1	22.1	9.3	4.4	5.0
2	0.5 x 2	40 x 2	58.4	26.0	9.3	3.5	2.8

¹ Reaction conditions: 240 g of glycerol (2.61 mol), 10.0 g of K₂CO₃ (72.4 mmol), 238 °C, microwave in continuous flow.

To extend the result obtained in serial mode and to obtain better selectivity of the dimer (PG2), the process was used in cyclic mode (Figure 2). In these experimental conditions, there is no steady state as the composition of the solution changes at any time. Due to the variation in volume in our system (loss of water during the reaction), it is not possible to quantify the cycles. Therefore, only the reaction time was taken as a parameter to study the evolution of the composition of the solution during the reaction cycles (Table 3). With a flow rate of 0.5 mL min⁻¹, the modification of the oligomer distribution is confirmed and a better selectivity of the dimer PG2 (26.4% after 250 min vs 12.3% after 50 min) has been obtained for a higher glycerol conversion. However, higher glycerol (PG1) conversion and higher diglycerol (PG2) formation as well leads to increased trimer (PG3) and tetramer (PG4) formation.

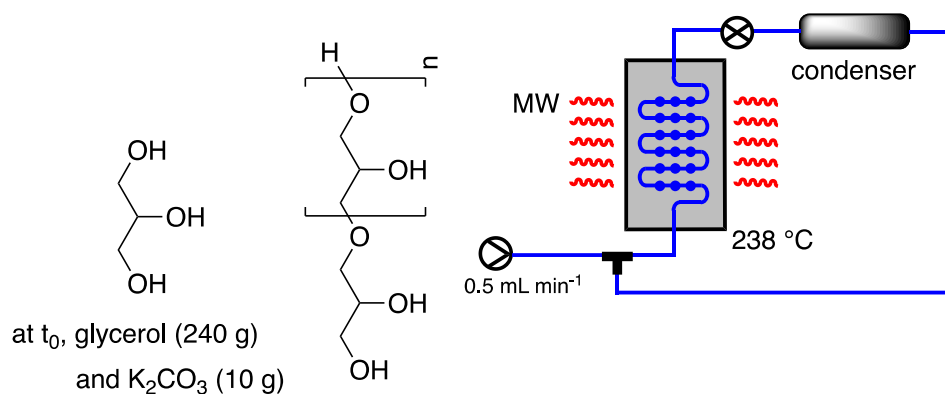


Figure 2. Cyclic microwave-assisted continuous oligomerization of glycerol.

Table 3. Microwave-assisted continuous oligomerization of glycerol with peristaltic pump in cyclic mode (GC analysis).¹

Entry	Time [min]	PG1 [wt%]	PG2 [wt%]	PG3 [wt%]	PG4 [wt%]	Other [wt%]
1	50	85.9	12.3	1.5	0.2	0.1
2	100	71.8	20.6	5.2	1.2	1.2
3	150	62.1	25.5	7.9	2.3	2.2
4	250	55.1	26.4	10.0	3.7	4.8
5	250	55.2	24.2	9.2	3.4	7.4

¹ Reaction conditions: 240 g of glycerol (2.61 mol), 10.0 g of K_2CO_3 (72.4 mmol), 238 °C, microwave in cyclic continuous flow.

In order to obtain a mixture of oligomers with a minimum amount of glycerol (PG1) and a maximum amount of diglycerol (PG2), short path evaporation has been performed at 150 °C under 0.1 mbar (Table 4). The sample obtained after 250 min of cyclic microwave-assisted reaction at 238 °C and 0.5 mL min⁻¹ was evaporated and glycerol (PG1) and cyclic dimer (cPG2) were completely removed and no trace was detected in the residual fraction (Table 4, entry 3). Furthermore, an oligoglycerol enriched mixture containing 50% diglycerol (PG2) is obtained.

Table 4. Short path evaporation of the crude product obtained after cyclic microwave-assisted oligomerization of glycerol (GC analysis).

Entry	Fraction	PG1 [wt%]	cPG2 [wt%]	PG2 [wt%]	cPG3 [wt%]	PG3 [wt%]	PG4 [wt%]	PG5 [wt%]	PG6 [wt%]	Other [wt%]
1 ¹	Crude	55.2	1.6	24.2	0.7	9.2	3.4	1.5	0.6	3
2 ²	Distillate	90	2.2	6.3	0.2	0.5	-	-	-	0.8
3 ²	Residue	-	-	50.2	2.0	22.1	9.5	4.3	2.0	7.4

¹ Reaction conditions: 240 g of glycerol (2.61 mol), 10.0 g of K_2CO_3 (72.4 mmol), 238 °C, microwave in cyclic continuous flow.

4. Conclusion

Microwave-assisted continuous oligomerization of glycerol was developed in cyclic mode using commercial equipment (Sairem). Glycerol conversion is controlled by the residence time, the continuous flow has an impact on the distribution of oligomers, with smaller oligomers being obtained for higher flow. The optimized conditions (240 g of glycerol (2.61 mol), 10.0 g K_2CO_3 (72.4 mmol) at 238 °C under microwaves for 250 min, 0.5 mL min⁻¹) afforded a glycerol conversion of 45% and a diglycerol selectivity higher than 26%. After purification by short-distance evaporation, a 50% enriched dimer mixture is obtained without trace of glycerol and cyclic diglycerol. Further research

with a larger reactor and higher power would allow more selective enriched oligoglycerol mixtures to be obtained.

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