PRODUCING ESTER DERIVATIVES OF SATURATED TRIGLYCERIDES BY GLYCEROLYSIS - HYDROLYSIS IN SUPERCRITICAL CO_2

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Abstract. The application of supercritical carbon dioxide as a reaction medium for the production of monoglycerides (MG) and diglycerides (DG) from hydrogenated triglycerides was studied. An experimental design was used to study the effect of the process operating variables (temperature, pressure, reagents ratio and water quantity) on the yield of MG and DG. Processing conditions resulting in product concentrations similar to those obtained by conventional catalytic processes were determined. In particular, the influence of temperature and initial concentrations of water and free fatty acids (FFA) on the final product composition was determined, demonstrating that temperature is the operating variable with the most important impact on the process. The results also show that it is technically feasible to produce these ester derivatives when the corresponding reactions take place in supercritical carbon dioxide and in the presence of water, thereby avoiding the use of catalysts that are commonly used.

1. Introduction

Derivatives esters of triglycerides, such as monoglycerides (MG) and diglycerides (DG) are important products from the fats and oils industry, and are used mainly as emulsifiers by the food, pharmaceutical and cosmetic industries [1,2]. Industrially, these products are produced by glycerolysis of triglycerides (TG) at high temperature (503 – 533 K) in the presence of a catalyst. After 5 h of processing, a final product with a MG concentration near to 50 wt% is usually obtained. Subsequently, this product is subjected to molecular distillation to achieve MG concentrations of about 90% [3]. The use of a solid catalyst requires a fast cooling step to prevent reversion [3] of the reaction, and a neutralization step in order to prevent the formation of undesirable odors and colors in the final product [4].

In an effort to find better operating conditions for this reaction, the use of supercritical fluids as reaction media has been studied. The use of a supercritical fluid prevents the use of a solid catalyst and eliminates the steps needed for its elimination by the inclusion of water in the reaction mixture. In an early application, Kochar and Bhatnagar [5] reported that a product with 91% MG was obtained from castor oil when the reaction was conduced in CO_2 after 2 h of reaction at 4.8 – 5.2 MPa and 503 – 513 K. However, despite the high MG concentration reached, this process has not been applied in industry. Temelli, et al. [6] studied the effect of temperature, pressure, glycerol/oil ratio and water concentration on the glycerolysis of soybean oil in SC-CO_2 . They achieved a maximum MG concentration of 49.2% at 523 K, 20.7 MPa, a glycerol/oil ratio of 25 and 4% water after 4 h, and found that temperature is the variable that affects the most the extent of reaction, and that pressure has an adverse effect when it increases above 20 MPa. Supercritical fluids have also been applied in the glycerolysis of soybean oil [7] and canola oil [8], considering kinetic aspects that includes hydrolysis reactions. Kinetics of glycerolysis – hydrolysis of hydrogenated canola oil (HCO) in SC-CO_2 was studied using a model based on equilibrium reactions that takes into account the catalytic effect of free fatty acids (FFA) [9], showing the catalytic role that such acids play in the reaction.

In order to develop a technically feasible process, it is necessary to study the effect of the operating variables on the product composition. Such study will allow one to determine the operating conditions that maximize the concentration of either MG or DG. Thus, the objectives of this study were to investigate, using statistical techniques, the effect of temperature, initial water content ,and initial FFA concentration, on the conversion of hydrogenated canola oil to MG and DG by glycerolysis – hydrolysis reactions in SC-CO2 .

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2. Materials and methods

2.1 Materials

The reagents were hydrogenated canola oil, which was generously donated by Canbra Foods Ltd. (Lethbridge, AB, Canada), 99.5% enzymatic grade glycerol from Fisher Bioreagents (Morris Plains, NJ, USA), 97% reactive grade stearic acid from Fisher Scientific (Somerville, NJ, USA) and deionized distilled water. Experiments were performed using 99.8% bone dry carbon dioxide (CO_2) from Praxair Canada Inc. (Mississauga, ON, Canada).

Supercritical fluid chromatography analyses were performed using >99.998% chromatography grade CO_2 , ultrahigh purity grade (99.999%) hydrogen, 4.8 pp nitrogen, 4.5 pp Helium and extra dry air from Praxair Canada Inc. (Mississauga, ON, Canada) as well as HPLC-GC/MS grade dichloromethane from Fisher Scientific (Napean, ON, Canada). Docosane (99%) from Acros Organics (Morris Plains, NJ, USA) was used as internal standard. Finally, reference standards (>99%) for tristearin, monostearin, distearin and stearic acid were obtained from Nu-Chek Prep Inc. (Elysian, MN, USA).

2.2 Experimental procedure and sample analysis

The experimental runs were performed in a high pressure-high temperature 200 mL batch reactor, which was electrically heated and was equipped with a magnetic stirrer and a sampling system. A detailed description of this apparatus and the experimental procedure has been previously reported [8,9]. For this work, we only considered the data obtained after 6 h of reaction. All the compositions were reported as mole fraction in the lipid phase. These were determined using a Lee Scientific Series 600 SFC/GC supercritical fluid chromatograph (SFC) (Dionex Inc., Salt Lake City, UT, USA) equipped with a flame ionization detector (FID) operated at 350 °C. A SB-octyl-50 column (50% n-Octyl, 50% methylpolysiloxane, 10 m × 50 µm i.d., 0.25 µm film thickness, Selerity Technologies, Inc., Salt Lake City, UT, USA) and a timed-split injection valve (500 nL injection loop, Valco Inc., Houston, TX, USA), which was held open for 1 s. The carrier gas was CO_2. A complete description of the procedure used in this chromatographic analysis is available in the literature [9].

2.3 Experimental design and statistical analysis

A three level Box-Behnken experimental design [10] was used. The design consists of eight factorial points, four axial points and three central points to estimate the experimental error. To generate the response factor, the variables were coded using the following expressions:

$$x_1 = \frac{T-210}{30} \quad x_2 = \frac{W-4}{4} \quad x_3 = \frac{R-1}{1} \tag{1}$$

where T is the reaction temperature (K), W is the initial percentage of water (w/w of glycerol) and R is the initial FFA / TG molar ratio. Other operating conditions such as pressure and initial glycerol / TG molar ratio, were kept constant at the best conditions that were previously reported [6,7,8]. Thus, a pressure of 10 MPa and a glycerol / TG molar ratio of 34 were chosen. The original levels for each variable for each experiment are presented in Table 1.

The experimental data and the coded variables were fitted to a second order polynomial equation:

$$y_i = a_0 + a_1 x_1 + a_2 x_2 + a_3 x_3 + a_4 x_1 x_2 + a_5 x_1 x_3 + a_6 x_2 x_3 + a_7 x_1^2 + a_8 x_2^2 + a_9 x_3^2 \tag{2}$$

The regression analysis, statistical significance and analysis of variance (ANOVA) were performed using the statistical toolbox available in MATLAB [11]. Additional programs were developed to calculate the optimal values using the Nelder-Mead algorithm available in the optimization toolbox in MATLAB [11].

3. Results and discussion

Table 1 shows the experimental results for the concentrations of FFA, MG, DG and TG in the lipid phase obtained by glycerolysis – hydrolysis after 6 h of reaction at 10 MPa and an initial glycerol/TG molar ratio of 34. Note the repeatability of Runs 13, 14 and 15 which were performed at the same experimental conditions. This indicates a low experimental error. The highest experimental MG concentration was 56% and was achieved at 513 K with and 4% initial water (w/w of glycerol) and highest fatty acid / triglyceride selected from the experimental design. The highest experimental DG concentration (41%) was obtained at the same temperature, an initial molar FFA / TG equal to 1 and without initial water.

Table 1. Experimental molar fraction after 6 h for FFA, MG, DG and TG on glycerolysis – hydrolysis of HCO in SC-CO2. A three level Box-Benhken experimental design with original variables: Temperature (T, K), initial water content (P, w/w of glycerol) and initial FFA / TG molar ratio (R).

	Variable			Molar fraction in lipid phase			
Run	**T**	**P**	**W**	**FFA**	**MG**	**DG**	**TG**
1	453	0	1	0.317	0.215	0.259	0.209
2	453	8	1	0.283	0.198	0.279	0.240
3	513	0	1	0.073	0.362	0.410	0.154
4	513	8	1	0.212	0.371	0.336	0.081
5	453	4	0	0.094	0.075	0.106	0.725
6	453	4	2	0.404	0.147	0.272	0.177
7	513	4	0	0.118	0.521	0.264	0.098
8	513	4	2	0.111	0.563	0.269	0.057
9	483	0	0	0.051	0.131	0.235	0.583
10	483	0	2	0.139	0.427	0.324	0.110
11	483	8	0	0.178	0.162	0.295	0.365
12	483	8	2	0.345	0.253	0.299	0.103
13	483	4	1	0.139	0.436	0.319	0.106
14	483	4	1	0.147	0.439	0.313	0.101
15	483	4	1	0.162	0.435	0.310	0.094

3.1 Response surface models

The experimental data for MG and DG were fitted to a second order polynomial which was then used to determine the operating conditions which maximized their production. Table 2 shows the coefficients of the statistical model that were obtained for MG and DG mole fractions in the lipid phase, as well as the correlation coefficient for the model. For MG, the linear coefficient related to the temperature is the only significant value at $p < 0.05$, while the linear coefficient for FFA initial concentration and the quadratic coefficient for initial water content were at $p < 0.1$. For DG, the linear coefficients related with temperature and FFA initial ratio, and the quadratic coefficients for initial water and FFA concentration, are significant at $p < 0.05$ and when this level was increased to 10%, the only coefficient that had not statistical significance was the linear coefficient for initial water content.

Figure 1 shows the influence of temperature on the final MG and DG concentrations. Temperature was the most influential variable in MG production ($p<0.008$), which is in agreement with the literature [6]. This is evident from the linear coefficients in both models. Also, temperature had no interaction with the other variables under study; this is observed by the low values of the cross-products coefficients involving temperature. The final DG mole fraction increased with temperature ($p<0.002$), but this increase was less important at higher temperatures. At 453 K without initial water and FFA, the model predicted no conversion of TG to MG and DG. This is consistent with previous studies which show that it is necessary to conduct such reactions at high temperature to increase the solubility of TG in glycerol. For both MG and DG, the maximum level was achieved when the reaction was conducted at the highest temperature level tested (513 K).

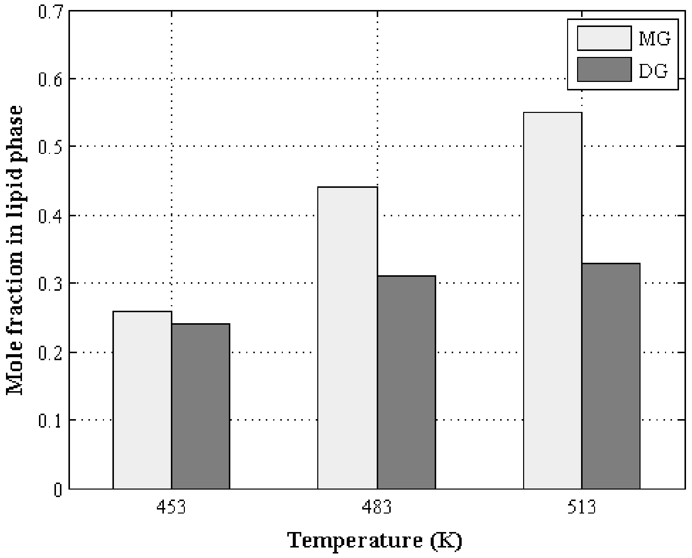

Figure 1. Effect of temperature on MG and DG mole fraction at initial water content of 4 w/w of glycerol and initial FFA / TG molar ratio of 1.

Table 2. Coefficients for polynomial regression for MG and DG molar fraction after 6 h on glycerolysis – hydrolysis of HCO in SC-CO_2.

Coefficient	MG	DG
a_0	0.4367 (1)	0.3140 (1)
a1	0.1477 (1)	0.0454 (1)
a_2	-0.0189	-0.0024
a_3	0.0626 (2)	0.0330 (1)
a_4	0.0065	-0.0235 (2)
a_5	-0.0075	-0.0403 (2)
a_6	-0.0512	-0.0213 (2)
a_7	-0.0335	-0.0267 (2)
a_8	-0.1167 (2)	0.0338 (1)
a_9	-0.0767	-0.0595 (1)
R^2	0.8565	0.9636

(1) Significant at 5% confidence level

(2) Significant at 10% confidence level

Figure 2 shows the effect of water initial content on the final MG and DG concentrations. For MG, the initial water content had the highest quadratic coefficient ($p<0.07$) and its cross-product coefficient with the initial FFA concentration is considerable. MG mole fraction reached a maximum at ~4% for the complete temperature range at 513 K. A maximum is reached at 3.42% water and 1.5 initial FFA/TG molar ratio. For DG, the initial water content had the lowest linear coefficient, which means that its effect was purely quadratic ($p<0.03$). A moderate amount of water has a positive effect on MG production but the presence of water has a negative effect on DG production.

Figure 3 shows the effect of initial concentration of FFA on MG and DG final mole fractions. For all the temperatures considered in this study, the concentration of monoglyceride increased with the initial FFA content ($p<0.1$). At constant temperature, the MG mole fraction reached a maximum and this trend did not vary with the initial water content. For DG, the effect of the initial content of FFA varied with temperature ($p<0.01$) and this variation was more important at lower temperatures. At constant temperature of 513 K the final concentration of DG reached a maximum at R of 1.8 when no water was initially added to the reactor and this trend did not change with a change in the initial water content.

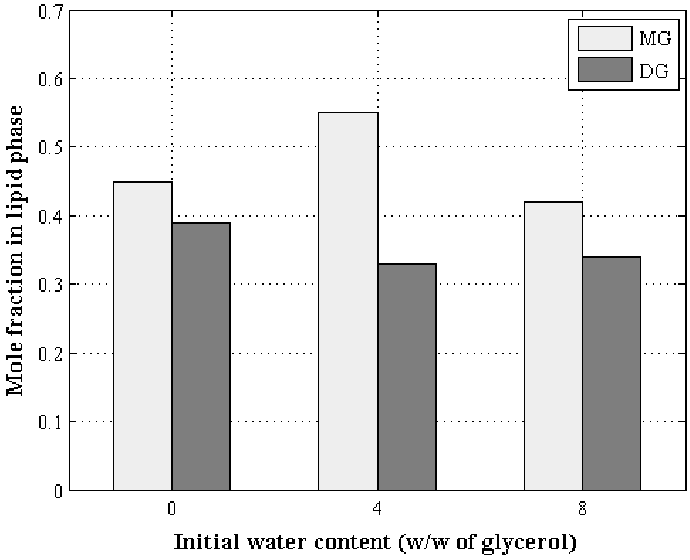

Figure 2. Effect of initial water content on MG and DG mole fraction at 513 K and initial FFA / TG molar ratio of 1.

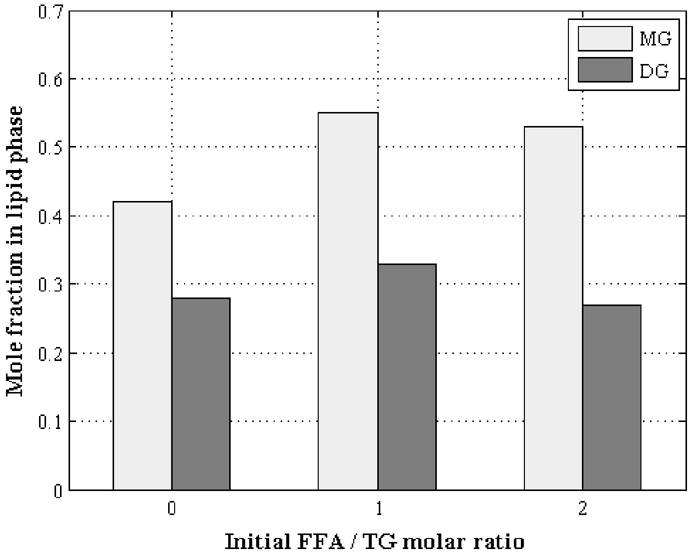

Figure 3. Effect of initial FFA / TG molar ratio on MG and DG mole fraction at 513 K and initial water content of 4 w/w of glycerol.

The FFA acted as a catalyst and autocatalyzed the glycerolysis-hydrolysis reactions as suggested earlier [12]. Such effect is clear at low temperatures where the reaction did not proceed without the addition of FFA. The effect of FFA concentration was also strongly dependent on the initial water content. The use of a supercritical fluid allows one to implement post-separation stages where the MG and DG can be concentrated and where FFA can be recovered and reused. The feasibility of this kind of process has been previously considered [13,14].

4. Conclusions

The findings demonstrate the feasibility to conduct glycerolysis – hydrolysis reactions of hydrogenated canola oil in SC-CO2 media without the use of a non-lipid catalyst. The optimal temperature, initial concentration of water and initial FFA content were established. At 513 K, 3.4% of water (w/w of glycerol) and an initial FFA / TG molar ratio of 1.4 produced a maximum MG content of 56% (mole percent). A maximum DG molar concentration of 39% was obtained at the same temperature and using an initial FFA / TG molar ratio of 1.12 in the absence of water.

The conversion of TG by glycerolysis – hydrolysis to MG and DG increased with temperature. The initial water content and initial FFA concentration had a joint effect that mutually affected the conversion of TG to MG and DG. The use of FFA as a catalyst in glycerolysis – hydrolysis reactions not only causes an increase in conversion, but also it does not require any specialized separation technique or bleaching process. In addition, the completion of the reaction in supercritical media could favor the coupling of a unit separation such as a fractionator, which has proven to be effective in separating and purifying glycerolysis products.

Acknowledgments

The authors express their gratitude to *Departamento Admnistrativo de Ciencia, Tecnología e Innovación de Colombia* (COLCIENCIAS) and to the Natural Sciences and Engineering Research Council of Canada for their financial support.

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