

Heterogeneously-Catalyzed Glycerolysis of Fatty Acid Methyl Esters: Reaction Parameter Optimization

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The synthesis of monoglycerides by glycerolysis of methyl oleate, an unsaturated fatty acid methyl ester, was studied on strongly basic high surface area MgO as an alternative to the current commercial technology that uses liquid base catalysts. Initially, the reaction conditions such as catalyst particle size and stirring rate required for operating the four-phase reactor under a kinetically controlled regime were determined. Then, the optimization of the reaction parameters for achieving high monoglyceride yields was performed. Results showed that glycerolysis of methyl oleate on MgO compares favorably with the corresponding homogeneously catalyzed process. In fact, when using high reaction temperatures (493–523 K), glycerol/methyl oleate molar ratios between 2 and 6, and catalyst/reactant ratios of about 30 g/mol, glycerolysis of methyl oleate on MgO yields up to 77% monoglycerides in 2 h, a much higher value than those usually obtained via the liquid-base-catalyzed homogeneous process (40–60%).

1. Introduction

During biodiesel synthesis by oil or fat transesterification, glycerol (Gly) is obtained as the main coproduct, representing ~10% of the biodiesel production. The increasing production of biodiesel around the world generates a Gly surplus that is becoming a matter of economic and environmental concern since the drop of the Gly price has forced the producers to burn or sell Gly without even refining it. Thus, new applications intended to convert glycerol into value-added chemicals are highly desirable not only to improve the economics of biodiesel production but also for ecological reasons.

Due to its structure and properties Gly participates in the formulation or synthesis of many compounds such as food products, cosmetics, pharmaceuticals, liquid detergents, and antifreeze.¹ Gly can also be used in the synthesis of hydrogen,² liquid fuels,³ fuel additives,⁴ and chemicals.^{1,5} Among the latter, monoglyceride (MG) synthesis by Gly esterification or transesterification is an attractive option to transform this biomass-derived compound into fine chemicals.

Monoglycerides, the glycerol monoesters of fatty acids, are molecules consisting of a hydrophilic head and a hydrophobic tail having surfactant and emulsifying properties that help hydrophilic and lipophilic substances mix together. Because of these properties, monoglycerides increase the stability and improve the viscosity and shelf life of many substances. They are biodegradable and can be used as food additives because of their good sensorial properties. They can be found in bakery products, instant and low-fat foods, dairy products, and sauces. They also have antimicrobial activity and improve skin permeability. For these reasons, MGs are widely employed in food, cosmetics, pharmaceuticals, and plasticizer and detergent formulations.^{5,6}

Application of enzymes as catalysts for the production of MG from oils and fats has been extensively investigated lately. For instance, several patents and reports study the enzymatic triglyceride alcoholysis and enzymatic glycerol esterification with fatty acids.⁶ However, these processes are difficult to set

up and expensive and not very efficient because of enzyme reusability issues.

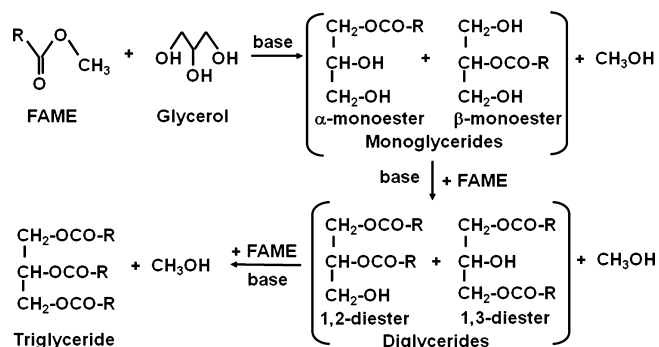
On the other hand, there are two main homogeneously catalyzed synthesis routes to produce MG from glycerol: (i) esterification of fatty acids (FA) catalyzed by strong mineral acids such as sulfuric and phosphoric acids at temperatures in the range of 363–393 K; (ii) glycerolysis (transesterification) of triglycerides (TG) or fatty acid methyl esters (FAME) promoted on strong liquid bases such as Ca(OH)₂ and KOH at 393–533 K. In the transesterification of FAME, one Gly molecule reacts with one FAME molecule to produce one MG molecule and one methanol molecule (Scheme 1).

In all the homogeneously catalyzed processes, the reaction products contain only 40–60% MG, the rest being DG and TG. Several purification steps are required to obtain food- or pharmaceutical-grade MG, such as neutralization of the reaction media and discoloration followed by expensive molecular distillation.^{5,6}

The use of solid catalysts for MG synthesis presents not only the known environmental and practical advantages but also provides the opportunity to increase the MG yield by developing a catalyst with tunable structural, surface acid–base, and textural properties specifically designed to promote the reaction.

Furthermore, the base-catalyzed MG synthesis from Gly using FAME instead FA or TG has several advantages, e.g., FAME

Scheme 1. Monoglyceride (MG) Synthesis via Transesterification (Glycerolysis) of FAME with Gly and Consecutive Reactions to Diglycerides (DG) and Triglycerides (TG)



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is less corrosive than FA, has lower hydrophobic character than TG, and exhibits higher miscibility with glycerol; therefore, the process can be carried out at lower temperatures (393–503 K) than TG transesterification (≈ 533 K).⁶ The reaction route from FAME allows the production of MGs with a definite acyl group composition (FAMEs are easier to separate by fractional distillation than FA) whereas in TG glycerolysis the products contain the acyl group distribution of the oil or fat.⁷ Also, no water forms, and because methanol is highly volatile, it can be easily removed from the reactor to drive the reaction forward. However, industrial implementation of a heterogeneously catalyzed process for FAME glycerolysis using a solid basic catalyst able to replace the current technology using liquid bases with similar performance is still a challenge.

Nevertheless, several researchers have investigated the Gly transesterification with FAME under heterogeneously catalyzed conditions and reported that the nature and strength of catalyst surface basic sites as well as the pore structure are crucial in the MG synthesis on solid catalysts. Bancquart et al. tested MgO, CeO₂, La₂O₃, and ZnO in Gly transesterification with a saturated FAME, stearic acid (C18:0) methyl ester, and found that the more significant the intrinsic basicity, the more active the catalyst.⁸ Corma et al.⁶ studied the Gly transesterification with an unsaturated FAME, oleic acid (C18:1) methyl ester, and used among other solid basic catalysts, Mg–Al hydroxycarbonates of hydrotalcite structure after rehydration or calcination. They found that rehydrated hydrotalcites with Brønsted basicity were more active and selective than calcined hydrotalcites. They also showed that strong Lewis bases were more active but less selective than the Brønsted bases. On the other hand, Barrault et al.⁹ investigated the use of mesoporous materials such as Mg/MCM-41 in Gly transesterification with saturated FAMEs such as lauric (C12:0), myristic (C14:0), and stearic acid methyl esters. They found that pore size reduction increased MG selectivity in methyl laurate glycerolysis.

The purpose of this work is to study the Gly transesterification with an unsaturated FAME, oleic acid (C18:1) methyl ester, under heterogeneously catalyzed conditions. High surface area MgO was chosen as the solid base catalyst because of its well-known basic properties and good catalytic performance in other base-catalyzed reactions.^{10–12} The reaction was carried out in a slurry four-phase reactor, and results were compared with the homogeneously catalyzed process. A systematic study of the effect of several variables influencing the catalytic performance was carried out. Our goals were to implement this reaction under kinetically controlled conditions and to optimize the reaction parameters for maximum MG yield. Therefore, the effect of the stirring rate and catalyst particle size was investigated in order to rule out diffusional limitations. Moreover, the effect of reaction temperature, Gly/FAME ratio, and catalyst load on the MG yield was also studied.

2. Experimental Section

2.1. Catalyst Preparation. Magnesium oxide was prepared by hydration with distilled water of low surface area commercial MgO (Carlo Erba 99%; 27 m²/g). Then, the resulting Mg(OH)₂ was decomposed and stabilized in a N₂ flow for 1 h at 373 K, then for 1 h at 623 K, and finally for 18 h at 773 K to obtain high surface area MgO.¹³ The catalyst was ground, sieved, and separated into three different lots before decomposition in N₂. The resulting average particle size lots were the following: <100; 100–177; 177–250 μm .

2.2. Catalyst Characterization. The BET surface area and pore size distribution were determined by N₂ physisorption at

77 K in a NOVA-1000 Quantachrom sorptometer. The structural properties of MgO were determined by X-ray diffraction (XRD) using a Shimadzu instrument XD-D1 equipped with Cu K α radiation and a Ni filter.

Catalyst base site density (n_b) was measured by temperature-programmed desorption (TPD) of CO₂ preadsorbed at room temperature. The sample was pretreated in situ in a N₂ flow at 773 K, cooled down to room temperature, and then exposed to a flowing mixture of 3% of CO₂ in N₂ until surface saturation was achieved (5 min). Weakly adsorbed CO₂ was removed by flushing with N₂. Finally, the temperature was increased to 773 K at a ramp rate of 10 K/min. Desorbed CO₂ was converted in CH₄ on a methanation catalyst (Ni/Kieselghur) and then analyzed using a flame ionization detector (FID).

2.3. Catalytic Tests. The transesterification of methyl oleate (Fluka, technical grade, 86% total C18 + C16 esters as determined by gas chromatography, the rest being C12, C14, and C20 esters) with glycerol, Gly (Aldrich, 99.0%), was carried out at 473–523 K in a seven-necked cylindrical glass reactor with mechanical stirring equipped with a condenser to remove the methanol generated during reaction.

Gly/FAME molar ratios in the range of 1–6 and a catalyst/FAME ratio ($W_{\text{cat}}/n_{\text{FAME}}^0$) of 9–30 g/mol were used.

The reactor was operated in a batch regime for the solid and liquid phases at atmospheric pressure under flowing N₂ (35 mL/min). A bubbling N₂ flow was used to remove methanol from the reactor and to provide an inert atmosphere to avoid degradation of reactant and products. First, the liquid reactants were introduced and the reactor was flushed with nitrogen, and then, they were heated to reaction temperature under stirring (400–700 rpm). Catalyst was pretreated ex-situ at 773 K for 6 h to remove adsorbed water and carbon dioxide and kept overnight at 373 K in flowing N₂ until used and, then, quickly transferred to the reactor without exposing it to air to start the reaction. In the reactor both liquid phases were assumed to be perfectly mixed.

For the homogeneously catalyzed experiment, a 25 wt % sodium methoxide (NaMeO) solution was prepared by reacting NaOH with methanol under stirring.¹⁴

2.4. Sample Analysis and Quantification. Reaction products— α - and β -glyceryl monooleates (MGs), 1,2- and 1,3-glyceryl dioleates (diglycerides, DGs), and glyceryl trioleate (triglyceride, TG)—were analyzed by gas chromatography (GC) after silylation to improve compound detectability.¹⁵ For quantification, glyceryl trioleate (Sigma, 65.0%) and a commercial mixture of glyceryl mono- and dioleate of known composition (Fluka, 71.5% MG and 25.3% DG) were used as analytical standards.

Twelve samples of the reaction mixture were extracted and analyzed during the 8-h catalytic run. Reaction samples were centrifuged at room temperature at 3000 rpm; then, 10 μL of “fatty phase” (FAME-rich phase) were measured with a Tomos micropipet, weighted, and placed in test tubes. Known amounts of pyridine solution of *n*-hexadecane (Sigma, >99.0%) and cholesterol (Aldrich, 95.0%) were added as internal standards of the silylation reaction. Then, the reaction products were converted to trimethylsilyl ether derivatives with *N,O*-bis(trimethylsilyl) acetamide (BSA, Fluka, >95%) and trimethylchlorosilane (TMCS, Fluka, >98%). Hexane solutions of the resulting mixtures were then analyzed by GC in a SRI 8610C gas chromatograph equipped with a flame ionization detector (FID) set at 623 K, on-column injector port at 323 K and an HP-1 Agilent Technologies 15 m \times 0.32 mm \times 0.1 μm capillary column. The column was ramped from 323 to 373 K at 50

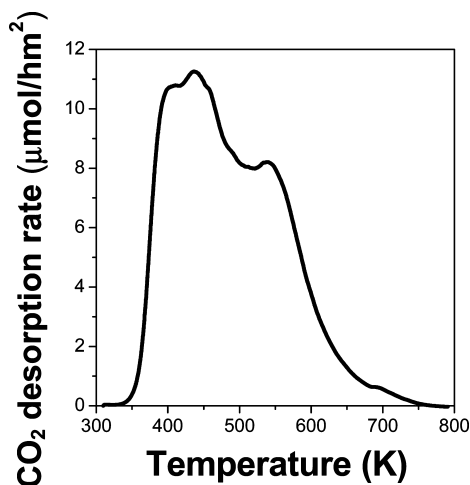


Figure 1. TPD profile of CO₂ on MgO.

K/min, and then consecutively to 403 at 20 K/min, to 443 at 6 K/min, to 463 at 20 K/min, to 523 at 10 K/min, to 558 at 35 K/min, to 583 at 20 K/min, and finally to 623 at 4 K/min; the column temperature was maintained at 623 K until elution of all the components. The method precision was evaluated by consecutively analyzing a sample six times. Data of standard deviations and relative standard deviations (RSD) for Gly, FAME, MG, DG, and TG compounds were in all cases lower than 10%, except for TG (13%).

Conversion (X_{FAME} , referred to the total content of esters in the reactant), selectivity (S), and yield (Y) were calculated through the following equations (n_j , mol of product j ; n_{FAME} , mol of unreacted FAME; MG = monoglycerides (both isomers), DG = diglycerides (both isomers), TG = triglyceride):

$$X_{\text{FAME}}(\%) = \frac{n_{\text{MG}} + 2n_{\text{DG}} + 3n_{\text{TG}}}{n_{\text{MG}} + 2n_{\text{DG}} + 3n_{\text{TG}} + n_{\text{FAME}}} \times 100$$

$$S_{\text{MG}}(\%) = \frac{n_{\text{MG}}}{n_{\text{MG}} + 2n_{\text{DG}} + 3n_{\text{TG}}} \times 100$$

$$S_{\text{DG}}(\%) = \frac{2n_{\text{DG}}}{n_{\text{MG}} + 2n_{\text{DG}} + 3n_{\text{TG}}} \times 100$$

$$S_{\text{TG}}(\%) = \frac{3n_{\text{TG}}}{n_{\text{MG}} + 2n_{\text{DG}} + 3n_{\text{TG}}} \times 100$$

$$Y_j(\%) = X_{\text{FAME}} S_j \times 100$$

3. Results and Discussion

3.1. Structural, Textural, and Acid–Base Properties of MgO. After hydration of commercial MgO and subsequent decomposition at 773 K, the BET surface area increased from 27 to 192 m²/g. MgO had a pore volume of 0.38 mL/g and a mean pore diameter of about 30 Å.

XRD analysis of MgO revealed that a single phase of MgO periclase (ASTM 4-0829) was present. A MgO crystallite size of 69 Å was determined using the Scherrer equation.

The TPD of CO₂ experiment in Figure 1 shows the CO₂ desorption rate vs temperature obtained on MgO. The total amount of CO₂ desorbed (base site density, n_b) was calculated by integration of the TPD curve and the resulting value was 3.4 μmol/m². CO₂ was adsorbed with different binding energies on MgO as indicated by the presence of several desorption peaks in Figure 1, thereby revealing that the MgO surface is

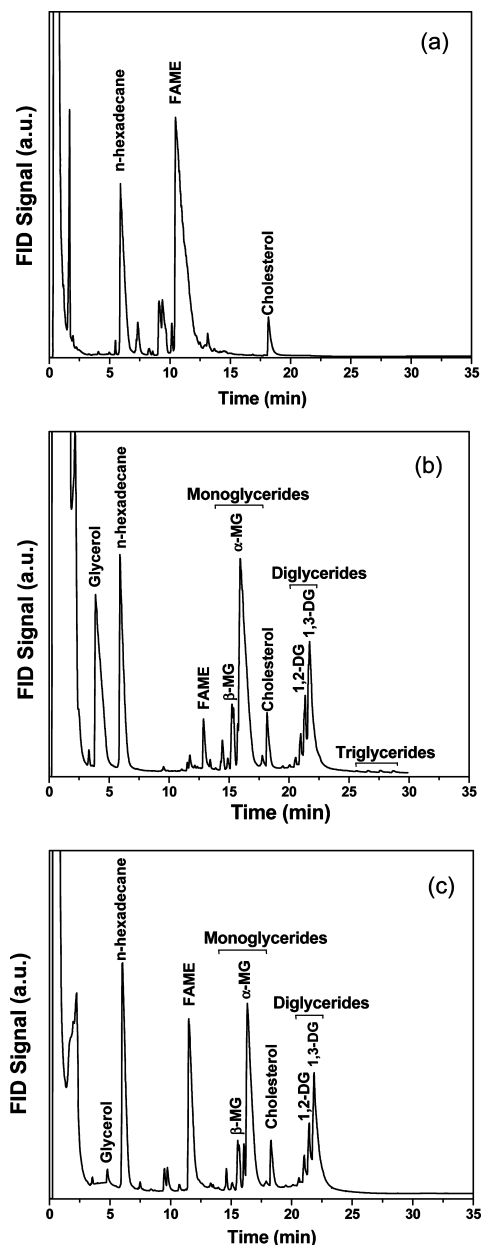


Figure 2. Typical chromatograms of the FAME-rich phase [arbitrary units (au)]: (a) before introducing the catalyst; (b) from homogeneously catalyzed reaction experiment; (c) from heterogeneously catalyzed reaction experiment.

nonuniform and contains CO₂ surface adsorption sites of different basic strength with a high contribution of strongly basic surface sites desorbing CO₂ at more than 500 K.

3.2. Preliminary Catalytic Tests. Previous to the heterogeneously catalyzed experiments, a homogeneously catalyzed reaction was performed. On the basis of literature data,^{16,17} the reaction was carried out at 408 K with a Gly/FAME = 2 (molar ratio) and a stirring rate of 550 rpm. The catalyst was sodium methoxide (NaMeO) in a ratio of $W_{\text{cat}}/n_{\text{FAME}}^0 = 5.5$ g/mol which represents a 0.1 mol of basic species/mol of FAME.

Figure 2 shows typical chromatograms of the FAME-rich phase before reaction (Figure 2a) and during the reaction experiment (Figure 2b). Gly is not observed in Figure 2a because of the low solubility of Gly in FAME.¹⁸ Formation of the glycerides during reaction and the presence of the NaMeO–methanol catalyst solution increase the Gly solubility⁶ as shown in Figure 2b that corresponds to a FAME conversion of 90%. Figure 3a shows the time evolution of FAME conversion and

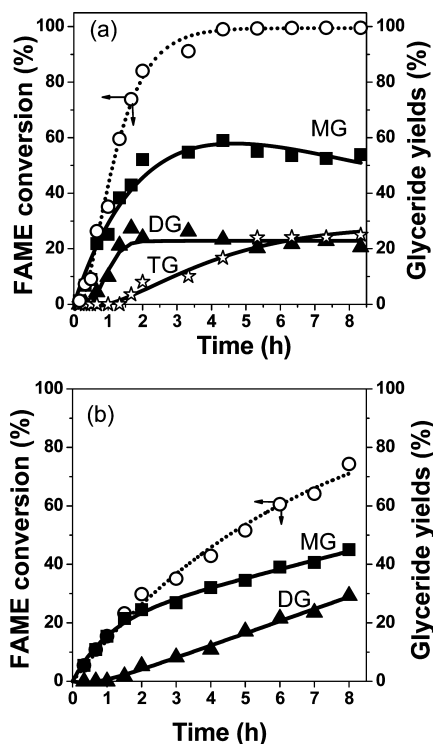
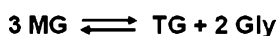
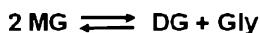


Figure 3. FAME conversion and glyceride yields. Gly/FAME = 2: (a) catalyst Na methoxide, $T = 408$ K, 0.1 mol basic species/mol FAME; (b) catalyst MgO, $T = 493$ K, 0.007 mol basic species/mol FAME.

Scheme 2. DG and TG Formation by Disproportionation Reactions



MG, DG, and TG yields. After 5 h, a FAME conversion of $\approx 100\%$ was achieved with a maximum MG yield of 59%, a DG yield of 24%, and a TG yield of 17%. After FAME has been almost completely consumed, the decrease of MG and DG yields is probably due to the competitive formation of DG and TG by the disproportionation reactions of Scheme 2.

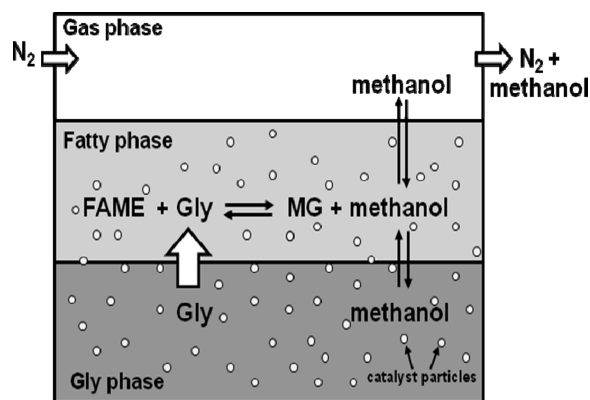
Two MgO-promoted preliminary blank tests were carried at 493 K by loading the reactor first with pure glycerol and then with pure methyl oleate. No conversion was detected in any of the experiments.

A typical heterogeneously catalyzed test was performed with MgO at 493 K with a Gly/FAME = 2 (molar ratio) and 700 rpm using a $W_{\text{cat}}/n_{\text{FAME}}^0 = 11$ g/mol. Figure 3b shows that monoglycerides can be obtained with reasonable MG yields (45%) in 8 h using MgO. Initially, only MG formation was observed. Then, as the reaction proceeded, MG concentration raised and a second transesterification took place forming diglycerides (DG) from MG and FAME (Scheme 1). At the end of the run, the DG yield was 29%. No TGs were observed at any reaction time under heterogeneously catalyzed conditions.

In both the homogeneously and the heterogeneously catalyzed experiments, the main MG isomer was the α -glyceryl monooleate (Scheme 1) resulting from participation of the two primary OH groups of Gly in the glycerolysis reaction. Similarly, 1,3-glyceryl dioleate was the main DG isomer.

The solid base-promoted reaction system is outlined in Scheme 3. Under solid base-catalyzed conditions, no glycerides were found in the glycerol phase because the reaction occurs in the fatty phase where Gly is hardly soluble. Therefore, Gly

Scheme 3. Four-Phase Reactor for the Heterogeneously-Catalyzed Monoglyceride Synthesis



is not detected in that phase at short reaction times because as Gly is transferred from the more hydrophilic glycerol phase it is immediately consumed in the fatty phase. Nevertheless and similarly to the homogeneous reaction, as FAME conversion increases and glycerides are formed, the Gly solubility in the fatty phase increases. Figure 2c shows a chromatogram of the experiment with MgO at 75% FAME conversion showing the incipient Gly peak and the absence of TGs.

From CO₂ adsorption experiments on MgO (n_b value) and surface area measurements, the basic sites/FAME ratio in the reactor during the catalytic test was determined as 0.007 mol of basic sites/mol of FAME, i.e., 14 times lower than in the experiment with NaMeO. Therefore and considering the different amount of active species in the experiments using MgO and NaMeO, we compared for both experiments the initial MG formation rates (R_{MG}^0) per unit basic site; from the data of Figure 3, we determined the R_{MG}^0 values in inverse hours by calculating the initial slopes according to $R_{\text{MG}}^0 = (n_{\text{FAME}}^0/n_{\text{BS}})[dY_{\text{MG}}/dt]_{t=0}$, where n_{BS} is the molar amount of basic species in the catalyst load, n_{FAME}^0 is the initial molar amount of FAME, and Y_{MG} is the MG yield. The $n_{\text{BS}}/n_{\text{FAME}}^0$ values were 0.1 and 0.007 mol of basic species/mol of FAME for the homogeneous and heterogeneous experiments, respectively. When reaction rates were compared on an active species molar basis, a much higher value of 7.4 h⁻¹ was determined for MgO in contrast to 3.5 h⁻¹ for the experiment with NaMeO. This result opens a good perspective for the use of solid catalysts to replace the current technology using liquid bases.

3.3. Evaluation of Diffusional Limitations. Under heterogeneously catalyzed conditions, as sketched in Scheme 3, the reactor contains four phases: the solid phase; the bottom layer formed by the Gly phase; the fatty phase containing FAME and the glyceride products located on top of the latter, and the gas phase containing N₂ and methanol. Therefore, operative conditions to rule out diffusional limitations had to be determined. Only mass-transfer limitations were investigated since transesterification reactions are known to have low reaction enthalpies.^{19,20} In the present case of the transesterification of Gly with methyl oleate toward glyceryl monooleate and methanol, the calculated standard reaction enthalpy (ΔH_{R}^0) was 0 kJ/mol, thereby confirming reaction thermoneutrality.

In the reaction system of Scheme 3, several mass interfacial gradients can occur such as those at the liquid–liquid (Gly phase–fatty phase interface) and liquid–solid (mass transfer resistance around the catalyst particles in the fatty phase) boundaries as well as those inside the catalyst pores. If the overall reaction rate were controlled by the reactant diffusion rate through the liquid–liquid or liquid–solid interfaces, then

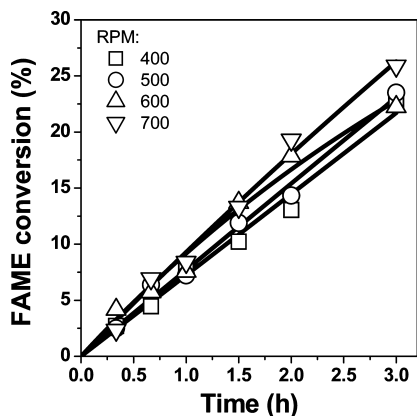


Figure 4. 3-h catalytic tests varying stirring rate: $T = 493$ K; Gly/FAME = 4.5; $W_{\text{cat}}/n_{\text{FAME}}^0 = 9$ g/mol; particle size < 100 μm ; catalyst MgO.

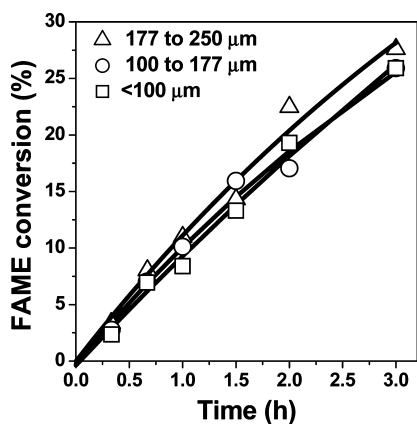


Figure 5. 3-h catalytic tests varying catalyst particle size: $T = 493$ K; Gly/FAME = 4.5; $W_{\text{cat}}/n_{\text{FAME}}^0 = 9$ g/mol; stirring rate = 700 rpm; catalyst MgO.

FAME conversion would increase by increasing the stirring rate as indicated by the number of revolutions per minute (rpm). To investigate the effect of the stirring rate on the reaction kinetics, several 3-h catalytic tests were carried out on MgO using stirring rates in the range of 400–700 rpm, without changing any other operational parameter (Figure 4). Results in Figure 4 show that FAME conversion was not significantly changed by increasing the stirring rate from 400 to 700 rpm.

Although the experiment at 700 rpm shows a slightly higher conversion at 3 h, this variation is within the analytical error. It is concluded then that the reaction is neither liquid–liquid nor liquid–solid diffusion-controlled under the present experimental conditions, and we adopted the highest stirring rate (700 rpm) for performing the following experiments.

On the other hand, the reactant diffusion rates at the liquid–solid interface and inside the catalyst particle (intraparticle mass-transfer diffusion) are increased by diminishing the catalyst particle size. Thus, if the overall reaction rate were controlled by the reactant diffusion around or inside the catalyst particle, then FAME conversion would increase when decreasing the catalyst particle size.

In order to investigate the effect of the MgO particle size on FAME conversion, we carried out several 3-h catalytic tests using three different particle size ranges (< 100 , 100–177, and 177–250 μm), without changing any other reaction parameter (Figure 5). Only small differences could be observed during the 3-h tests. The two catalytic tests with the smallest particles show slightly lower FAME conversions than the experiment with the largest size. This result is the opposite of that expected in the presence of diffusional limitations and can be attributed

to a “flotation effect” of the smallest particles in the presence of the foam caused by the surfactant MG that probably places the catalyst surface far from the glycerol phase thereby decreasing the FAME conversion.

To verify the absence of internal mass transfer limitations, the Weisz–Prater criterion²¹ for a first-order reaction and for spherical catalyst particles was used: $\Phi = 0.28 (R^2 r_{\text{FAME}}^0 \rho_p) / (C_{\text{FAME}}^0 D_{\text{eff}}) \ll 1$, where Φ is the dimensionless Weisz–Prater modulus, R is the radius of the largest catalyst particle (1.25×10^{-4} m), r_{FAME}^0 is the initial FAME conversion rate (0.01344 mol/h·g), ρ_p is the catalyst particle density (2460 kg/m³), C_{FAME}^0 is the initial FAME concentration (1400 mol/m³), and D_{eff} is the effective diffusion coefficient (4×10^{-10} m²/s). A value of 0.25 was calculated for Φ , which corresponds to a Thiele modulus of 0.17 and an effectiveness factor of 0.99. This result confirms the absence of pore diffusion limitations.

Then, no diffusional limitations seem to be present under typical reaction conditions and the reaction takes place under kinetic control. Therefore, for practical reasons and to avoid flotation of small particles, we adopted the largest particle size range for the following catalytic experiments.

3.4. Reaction Parameter Optimization. 3.4.1. Effect of the Gly/FAME Ratio. The stoichiometry of the MG reaction synthesis (Scheme 1) requires a glycerol to FAME (Gly/FAME) molar ratio of 1:1. However, from the thermodynamics point of view, MG yield may be enhanced by increasing the Gly/FAME ratio to higher values than the stoichiometric ratio, i.e., a glycerol excess would shift the reaction equilibrium to the right and increase the FAME conversion. On the other hand, the effect of the glycerol excess on the reaction kinetics is hard to predict since glycerol is more dense than the fatty phase and more hydrophilic than FAME. Therefore, Gly is probably strongly adsorbed on the surface. In addition, Gly has to be transferred to the fatty phase where the reaction takes place, and therefore, the Gly/FAME ratio can affect the Gly solubility in the reaction zone.

In order to investigate the effect of the Gly/FAME ratio on the MG yield, 8-h catalytic tests were performed using MgO at 493 K with Gly/FAME molar ratios of 1 (stoichiometric), 2, 3, 4.5, and 6. These experiments were carried out at a constant $W_{\text{cat}}/n_{\text{FAME}}^0$ of 11 g/mol and at variable molar amounts of Gly. Results are shown in Figure 6. From the data of Figure 6, we determined the initial MG formation rate (r_{MG}^0 , mmol/g·h) by calculating the initial slopes according to $r_{\text{MG}}^0 = (n_{\text{FAME}}^0 / W_{\text{cat}}) [dY_{\text{MG}}/dt]_{t=0}$, where W_{cat} is the catalyst weight. The r_{MG}^0 values plotted in Figure 7 slightly varied in the range of 13.0–14.7 mmol/g·h what suggests that under initial conditions the MG formation rate is independent of the Gly excess. This can be observed also in Figure 6, since at the beginning of the reaction there was no difference between the tests at increasing Gly/FAME ratios.

However, as shown in Figure 6, at higher reaction times, the catalytic tests with Gly/FAME > 1 showed higher FAME conversions and MG yields. Contrarily, for the lowest Gly concentration (Gly/FAME = 1), a maximum in the MG yield curve was found because of the rapid transformation of MG in DG. This maximum is explained by a faster Gly consumption in the reaction zone. In fact, as predicted by reaction stoichiometry calculations, Gly conversion increased with decreasing the Gly/FAME ratio and for the stoichiometric reactant ratio (Gly/FAME = 1), the Gly transfer rate to the reaction zone was not rapid enough to replenish the Gly consumed in the FAME–Gly reaction. As a consequence, the Gly–FAME reaction stops and MGs initially formed keep reacting with another FAME

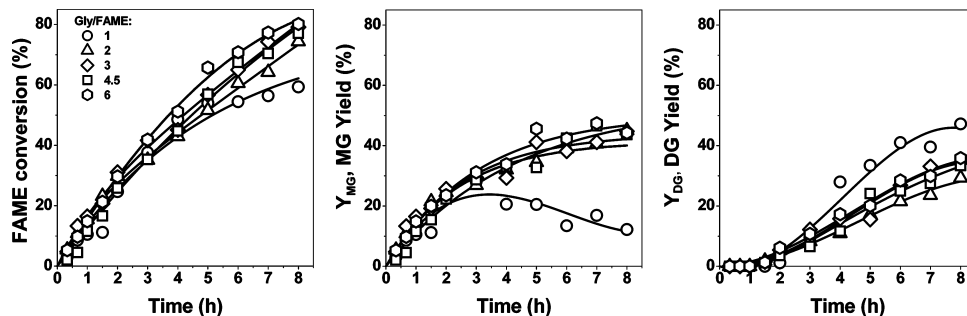


Figure 6. Effect of the Gly/FAME ratio on FAME conversion and MG and DG yields: $T = 493$ K; $W_{\text{cat}}/n_{\text{FAME}}^0 = 11$ g/mol; particle size 177–250 μm ; stirring rate = 700 rpm; catalyst MgO.

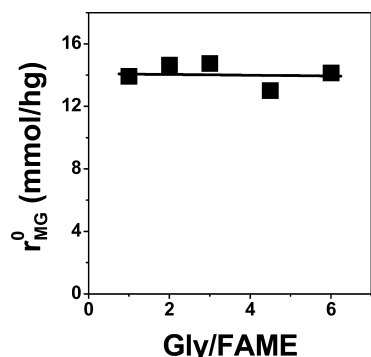


Figure 7. Effect of the Gly/FAME ratio on MG initial formation rate (r_{MG}^0): $T = 493$ K; $W_{\text{cat}}/n_{\text{FAME}}^0 = 11$ g/mol; particle size 177–250 μm ; stirring rate = 700 rpm; catalyst MgO.

molecule to form DGs preferentially (Scheme 1) that are the main reaction products at high reaction times.

As a conclusion, Gly/FAME ratios higher than the stoichiometric one have to be used in order to selectively obtain MG.

Gly/FAME ratios in the range of 2–6 gave similar results probably suggesting Gly surface saturation and a zeroth reaction order with respect to Gly in the overall kinetics. Therefore, Gly/FAME ratios as low as 2 can be used without significantly affecting the MG yield.

3.4.2. Effect of the Catalyst Load. Under heterogeneously catalyzed conditions, the reaction occurs on the catalyst surface. Thus, an increase of the area available for the reaction, i.e., an increase of the catalyst load, is expected to increase the reactant conversion.

To investigate the effect of the catalyst load, catalytic tests were conducted on MgO at 493 K with catalyst/FAME ratios ($W_{\text{cat}}/n_{\text{FAME}}^0$) of 11, 17, and 30 g/mol.

Results shown in Figure 8 indicate that as expected when no diffusional limitations are present, the FAME conversion was almost duplicated when the $W_{\text{cat}}/n_{\text{FAME}}^0$ ratio was increased from 17 to 30 g/mol, reaching 100% in ≈ 7 h. Similarly, MG formation was enhanced as the catalyst load increased; an MG yield of 73% was attained in 8 h for the experiment with $W_{\text{cat}}/n_{\text{FAME}}^0 = 30$ g/mol. In spite of the fact that the amount of basic

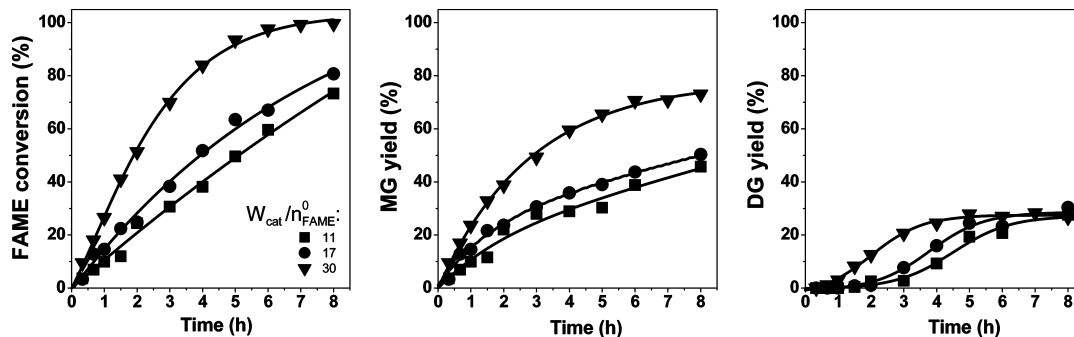


Figure 8. Effect of the catalyst load on FAME conversion and MG and DG yields: Gly/FAME = 4.5 (molar ratio); $T = 493$ K; particle size 177–250 μm ; stirring rate = 700 rpm; catalyst MgO.

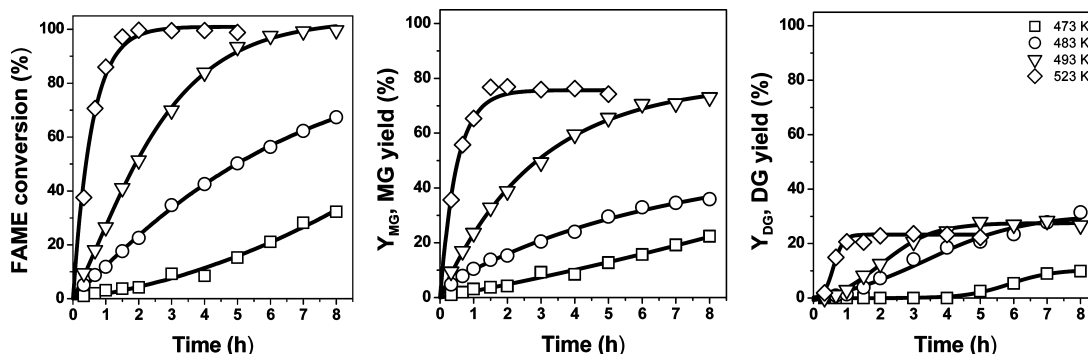


Figure 9. Effect of the reaction temperature on FAME conversion and MG and DG yields: Gly/FAME = 4.5 (molar ratio); $W_{\text{cat}}/n_{\text{FAME}}^0 = 30$ g/mol; particle size 177–250 μm ; stirring rate = 700 rpm; catalyst MgO.

sites in the reactor for this experiment (0.02 mol basic sites/mol FAME) was 5 times lower than in the experiment with NaMeO (0.1 mol basic species/mol FAME), the 73% MG yield was much higher than the one measured during the experiment with NaMeO (Figure 3a) and than the value typically obtained in commercial homogeneously catalyzed MG synthesis (40–60%).^{5,6}

3.4.3. Effect of the Reaction Temperature. Considering that diffusional limitations have been ruled out (Figures 4 and 5), variations of the reaction temperature would affect mainly the reaction kinetics not only in what concerns the overall kinetic rate constant as predicted by the Arrhenius equation ($k = Ae^{-E_d/RT}$) but also reactant solubility since FAME is not soluble in Gly and Gly is barely soluble in the fatty phase where the reaction occurs. Therefore, the reaction will proceed faster as glycerol solubility in the fatty phase increases, which has been shown to occur at increasing temperatures.^{22,23} Therefore, an increase of the reaction temperature is expected to improve the catalyst activity, i.e., the FAME conversion. However, the reaction cannot be performed at temperatures higher than 533 K because on basic catalysts, polyglycerol formation cannot be avoided.²³

The effect of the reaction temperature was investigated by carrying out the catalytic tests on MgO at 473, 483, 493, and 523 K (Figure 9) and using a Gly/FAME of 4.5. As expected, FAME conversions significantly increased with the reaction temperature so that complete conversion was achieved in 2 h at 523 K in contrast to 51% reached in 2 h at 493 K, 23% at 483 K, and 4% at 473 K. Similarly, Gly conversions after 2 h of reaction were 1% at 473 K, 4% at 483 K, 10% at 493 K, and 20% at 523 K. At the lowest reaction temperature (473 K), the initial slope of the FAME conversion curve, Figure 9, suggests a strong adsorption of reactants and products on the catalyst surface causing partial catalyst deactivation and therefore inhibiting reactant conversion.

Results showed that MG yield was enhanced by increasing the reaction temperature. This is due not only to the increasing conversion but also to the fact that the selectivity to MG improved at higher reaction temperatures at the expense of DG selectivity when compared at similar FAME conversion levels. Thus, an enhanced MG/DG ratio was found at higher temperatures. In a kinetically controlled consecutive reaction system such as that for MG and DG formation (Scheme 1), this result is consistent with a higher activation energy for the MG synthesis step compared to that of DG.²⁴ In fact, from the results of Figure 9 at 483–523 K, the r_j^0 values were calculated as explained previously and the apparent activation energies for MG and DG formation were determined using an Arrhenius-type function ($r_j^0 = \varphi e^{-E_d/RT}$, where φ is a constant containing the pre-exponential factor and initial reactant concentrations) by plotting $\ln r_j^0$ values as a function of $1/T$. As predicted, the calculated values were 26 and 19 kcal/mol, for MG and DG formation, respectively.

In summary, as a result of the combined effect of temperature on FAME conversion and MG selectivity, MG yields as high as 77% can be obtained at 523 K in just 2 h on MgO without thermal degradation of reactants or products.

4. Conclusions

The synthesis of glycerol monoesters (monoglycerides) by fatty acid methyl ester glycerolysis is efficiently achieved on MgO catalyst, thereby offering an alternative technology to the current commercial processes that use environmentally unfriendly liquid bases. Our results show that on MgO, the heterogeneous monoglyceride synthesis is a four-phase reaction that may be conducted in kinetically control regime provided that appropriate operative

conditions are used, namely, relatively high stirring rates (500–700 rpm) and mean catalyst particle sizes of up to 250 μm .

High monoglyceride yields can be obtained using temperatures between 493 and 523 K and glycerol/fatty acid methyl ester ratios higher than 1. In particular, oleic acid methyl ester glycerolysis on MgO at 523 K gives monoglyceride yields of 77% in 2 h, a value higher than those typically obtained via the homogeneously catalyzed process (40–60%). The increase of the reaction temperature in that range improved the monoglyceride yield without product degradation. A glycerol/oleic acid methyl ester ratio of 1 (stoichiometric ratio) shifts the reaction pathway toward diglyceride formation (consecutive reaction) whereas a glycerol excess in the reactant mixture increases monoglyceride yield and gives similar results for glycerol/oleic acid methyl ester ratios of 2–6, suggesting a zeroth reaction order with respect to glycerol in the overall kinetics.

Regarding the heterogeneous process selectivity, the α -isomer is the main monoglyceride isomer obtained under the reaction conditions noted above. Moreover, no triglycerides are formed with the 1,2- and 1,3-diglycerides being the only reaction byproducts.

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Supporting Information Available: Additional experimental details on the silylation reaction. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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