

# Glycerolysis of Fatty Acid Methyl Esters: 1. Investigations in a Batch Reactor

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**Abstract** The present work focused on the glycerolysis of fatty acid methyl esters. The aim was to develop and test a kinetic model that could be used to reliably simulate different process alternatives for this reaction. A prerequisite was the identification and characterization of the factors that affect the reaction kinetics. Experiments were carried out in a batch reactor with and without forced removal of methanol, which is one of the reaction products. Concentrations of all components in the two-phase system were measured. It was found that the methanol concentration has a strong effect on the reaction rate and equilibrium conversion. Near-complete conversions were obtained by stripping methanol with an inert gas. The glycerol concentration in the ester phase was found to increase as the reaction proceeds, which also accelerates the reaction. Effects of mass transfer on the reaction rate were not found to control the reaction rate under well-agitated conditions. A semi-empirical model was used to simulate the reaction. The results from the semi-empirical model show good agreement with experimental results.

**Keywords** Diglycerides · Fatty acid methyl esters · Glycerolysis · Liquid–liquid reaction · Monoglycerides · Transesterification

Monoglycerides are important chemicals mainly used as emulsifiers in food industry [1]. Other important uses have been discussed by Meffert [2]. The most popular method of producing monoglycerides has been the base-catalyzed glycerolysis of fats (triglycerides). Compared to fat glycerolysis, an energy-saving but less frequently investigated process is the glycerolysis of fatty acid methyl esters (FAMES) [3]. This process also provides a way to “design” the monoglycerides by selecting a FAME of the desired chain length. A process for monoglyceride production based exclusively on FAME glycerolysis has also been patented in recent years [4]. The methanolysis of fats, which is the main reaction used to produce biodiesel, is the reverse of the FAME glycerolysis reaction.

The glycerolysis of fats, fatty acids and fatty acid methyl esters is a liquid–liquid two-phase reaction where the law of mass action cannot be simply applied on the basis of total concentrations. The kinetics of fats and fatty acid glycerolysis have been investigated by quite a number of researchers [3, 5, 6], but there are still open questions regarding the reaction kinetics in these systems, and differences can be found between the information available. The effect of mixing has been investigated by some authors [7, 8], but knowledge of mass transfer processes in these complex reaction systems is still far from complete. Moreover, it is not known where exactly the reaction takes place (i.e., at the interface or in one or both the phases, in bulk or in film or both). The number of possibilities may be large, and an exact description can be quite complicated. To our knowledge, such aspects have not been thoroughly studied, and most authors have not taken the presence of two phases into consideration while investigating the kinetics. An interesting fact

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about glycerolysis and methanolysis of fats is that the conversion of the limiting reactant, which is mostly the oil phase, can generally be described by an “S” shape. This means that the reaction is slow in the beginning, gets faster thereafter and slows down again at the end. Several investigators have reported this fact [5, 9–11], and some of them have also provided explanations for this behavior [5, 9, 10]. Freedman et al. [9] suggested kinetics with a combination of pseudo-first-order or second-order and fourth-order shunt mechanisms. Nouredini and Zhu [10] suggested a regime change, beginning with a mass-transfer-limited regime and changing into a kinetically controlled regime later. Bossaert et al. [5] gave the credit to the emulsifying properties of monoglycerides (for fat glycerolysis), which in principle, would also indicate an initial mass-transfer-limited regime.

In our studies on FAME glycerolysis, we also found that reaction rates changed, and that the glycerol concentration in the ester phase increases with conversion, which gives rise to a faster reaction rate after a slow start.

## Experimental

### Materials

The reactants used for the glycerolysis reaction were: glycerol (>99%, Sigma, Munich, Germany) and methyl oleate (>75%, Lancaster, Frankfurt am Main, Germany). The analysis of the technical-grade methyl oleate supplied showed that the actual methyl oleate (C18:1) content was  $85 \pm 1\%$  and the overall content of C18 (C18:0–C18:3) was  $97 \pm 1\%$ . Sodium methoxide (30 wt% in methanol, Fluka, Munich, Germany) was used as catalyst. The samples were analyzed by gas chromatography. For sample preparation, 1,4-dioxane (>99.8%, Roth, Karlsruhe, Germany) was used as solvent. *N,O*-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) (98%, ABCR, Karlsruhe, Germany) was used for silylation. Hexadecane (>98%, Fluka) was used as an internal standard. For calibration, the chemicals used were: glycerol (>99%, Sigma), methyl oleate (99%, Aldrich, Steinheim, Germany), methanol (>99.9%, Roth),  $\alpha$ -monoolein (>99%, Fluka), diolein (99%, Sigma), and triolein (>99%, Fluka). The analysis was done using a Hewlett-Packard (Böblingen, Germany) 5890 series II GC with a capillary column and flame ionization detector. The GC column was DB5-HT (J&W Scientific, Folsom, CA, USA) with a

length of 30 m, an inner diameter of 0.32 mm and a film thickness of 0.1  $\mu\text{m}$ . Nitrogen gas was used as carrier.

### Experimental Set-up and Procedure

To carry out the reactions, a double-walled glass reactor (LF-100, Lenz Laborglas, Wertheim, Germany) was used. The reactant volume taken to be 300 ml. The reactor was equipped with four baffles and the liquid inside the reactor was stirred by a standard turbine impeller with six flat blades. The reactor was heated by thermostatically controlled oil bath ( $\pm 0.1$  °C). The reactants were fed into the reactor in the desired molar ratio and at ambient temperature. The reactor content was then stirred and heated to 135 °C, which took less than half an hour. In experiments with forced methanol removal, nitrogen gas was bubbled through the liquid (at 5 l per min) by a distributor at the reactor bottom. This distributor was essentially a silicone tube (inner diameter 3 mm) bent into a circle with holes around the periphery (2 mm  $\times$  4). The catalyst, sodium methoxide (1 wt% of total reactant), was added after the desired temperature had been reached. The time of catalyst addition was taken to be the start of the reaction. After adding the catalyst, the reactor temperature was kept constant at  $135 \pm 1.0$  °C. The stirrer was placed in the upper phase and the dispersion obtained was of glycerol in methyl ester (G/FAME) type. The stirrer was set at 550 rpm. In all of the experiments, except those with ester in glycerol (FAME/G) dispersion, the initial glycerol:ester molar ratio was taken to be 2:1. In some experimental runs, a phase inversion was observed during catalyst addition. Initially, to maintain the consistency of the experimental conditions, only the experiments with G/FAME dispersion were considered. Later, to confirm the effect of emulsion type, experiments were also carried out with FAME/G dispersion. In these experiments, the stirrer was placed in the lower phase and a glycerol:ester ratio of 3:1 was used. The dispersion type was judged on the basis of viscosity difference and the difference in settling time. FAME/G dispersion is more viscous and needs more time to separate into two phases than G/FAME dispersion. The dispersion type was also confirmed by visually observing the settling behavior after stopping the stirrer [12]. In all of our experiments, some of the methanol produced left the reactor continuously, so in a strict sense the experiments were semi-batch. But we will continue to use the term “batch reactor” here to refer to the liquid phase in the reactor.

## Sampling Procedure

Sampling can be difficult in a reacting two-phase system, and different procedures can lead to different results. This topic is often skipped over or only briefly described by authors. It was observed that incomplete information on the sampling and analysis procedure could lead to ambiguities when interpreting the results. Therefore, the sampling and analysis procedure is provided here in a little more detail. During initial experiments performed in our laboratory, it was found that the glycerol concentration in the ester phase increased during the reaction [13]. It was important to quantify this parameter for kinetic modeling. Besides measuring the ester conversion, another aim of the sampling procedure was to measure the glycerol concentration under the actual reaction conditions. Some investigators wash the samples with water before analysis in order to remove the alcohols. This procedure could not be followed in this study, as another aim was to measure the glycerol and methanol concentrations in the actual reaction sample.

Samples were taken at different times from the reacting mixture. About 2 ml of liquid was withdrawn from the reaction mixture by a preheated glass syringe after rinsing the syringe four times with the contents of the reactor. The liquid in the syringe was allowed to separate into two layers for less than a minute (the ester phase was still somewhat turbid). GC analysis of samples from the lower layer (glycerol) showed only small amounts of ester and product glycerides (<1 mol%). Therefore, only the upper layer was studied in more detail in order to investigate the kinetics. Initially three series of samples were taken. Series 1: the 2 ml sample was maintained at 135 °C in an oven until the upper phase was transparent, which took about 20–30 min, and the upper phase was then analyzed. Series 2: one drop (about 10 mg) of the ester phase was added to a small vial, cooled in ice bath and analyzed. Series 3: the upper and lower layers were allowed to separate for 2 min, the upper layer was collected in a vial and immediately cooled in an ice bath, and then it was analyzed after 1–3 h. Before analysis, the samples (Series 3) were centrifuged at 4,000 rpm for 10 min to obtain a clear transparent phase. Samples that had not undergone centrifugation often showed a relatively high (up to 20%) glycerol concentration.

To prepare the samples, 20 µl of each sample was added to 1 ml of a solution containing 0.38 wt% hexadecane, 1.00 wt% acetic acid and the rest 1,4-dioxane. Hexadecane served as an internal standard for the GC

analysis, and the acid was added to neutralize the catalyst. The samples were silylated with BSTFA, and thereafter they were injected into the GC column. The inlet temperature of the GC column was kept constant at 40 °C. The total time required to analyze one sample was 61.5 min. The temperature program was ramped in four steps: first, the initial column temperature was kept constant at 38 °C for 15 min; second, the temperature was raised at 1 °C/min to 46 °C; third, the temperature was raised to 370 °C at a rate of 16 °C/min and held at 370 °C for 10 min; and finally, the column was cooled to 40 °C at a rate of 40 °C/min. The chromatogram thus obtained was analyzed to check the composition of the sample.

## Data Analysis

The mass of component  $i$  in the injected sample is proportional to the area of the GC peak:

$$w_i \propto f_i A_i \quad (1)$$

where  $f_i$  is the response factor of component  $i$  for the GC method, as obtained by calibration.

The mole fraction of a component  $i$  in the injected sample was calculated as:

$$x_i = \frac{w_i/M_i}{\sum_{\text{all components}} (w_i/M_i)} \quad (2)$$

and the concentration (mol/kg) as:

$$C_i = \frac{x_i \times 1000}{\sum_{\text{all components}} (x_i M_i)} \quad (3)$$

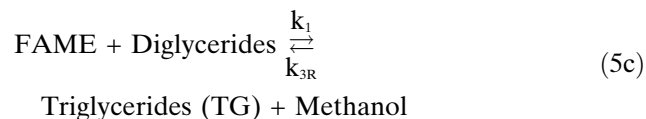
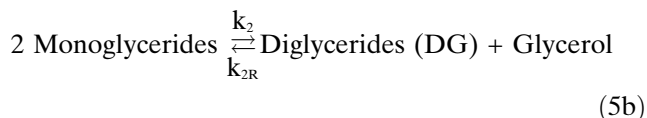
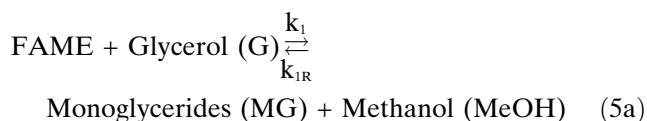
where  $M_i$  is the molecular weight of component  $i$ .

To determine the conversion, the ester phase was analyzed on a methanol- and glycerol-free basis. Since there was a considerable increase in the glycerol concentration in the ester phase, calculating the conversion based on the concentration of methyl ester in the ester phase would lead to false (overestimated) values. The ester molar conversion based on the methyl ester,  $X$ , at time  $t$  was calculated as:

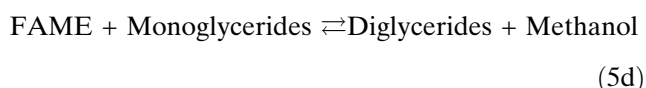
$$X = 1 - \frac{x'_{\text{FAME}_t}}{(x'_{\text{FAME}_t} + x'_{\text{MG}_t} + 2x'_{\text{DG}_t} + 3x'_{\text{TG}_t})} \quad (4)$$

where  $x'$  are the mole fractions calculated on a glycerol- and methanol-free basis.

**Kinetic modeling:** The reaction steps were modeled as:



In the literature [6], the production of diglycerides is suggested to occur according to:



The monoglyceride selectivity profiles calculated using Eq. 5b, which in effect is a disproportionation reaction, were closer to the experimental data than those calculated using Eq. 5d [13]. Also, since it was possible to describe the experimental data using Eq. 5b instead of Eq. 5d, there was no need to include 5d, although it cannot be excluded completely. Equation 5b was used in the present kinetic model. Equations 5a–5c lead to the following differential equations for a batch reaction:

$$\frac{dC_{\text{FAME}}}{dt} = -k_{1f}C_G C_{\text{FAME}} + k_{1R}C_{\text{MG}}C_{\text{MeOH}} - k_{3f}C_{\text{DG}}C_{\text{FAME}} + k_{3R}C_{\text{TG}}C_{\text{MeOH}} \quad (6)$$

$$\frac{dC_{\text{MG}}}{dt} = k_{1f}C_G C_{\text{FAME}} - k_{1R}C_{\text{MG}}C_{\text{MeOH}} - 2k_{2f}C_{\text{MG}}^2 + 2k_{2R}C_{\text{DG}}C_G \quad (7)$$

$$\frac{dC_{\text{DG}}}{dt} = k_{2f}C_{\text{MG}}^2 - k_{2R}C_{\text{DG}}C_G - k_{3f}C_{\text{DG}}C_{\text{FAME}} + k_{3R}C_{\text{TG}}C_{\text{MeOH}} \quad (8)$$

$$\frac{dC_{\text{TG}}}{dt} = k_{3f}C_{\text{DG}}C_{\text{FAME}} - k_{3R}C_{\text{TG}}C_{\text{MeOH}} \quad (9)$$

In the above equations, all concentration terms are based on the ester phase. The methanol concentration in the ester phase was found from experiment to be nearly constant and the glycerol concentration was found to increase as the reaction proceeds. Mathematically:

$$C_{\text{MeOH}} = \text{Constant} \quad (10)$$

And the glycerol concentration was described by:

$$C_G = A \cdot X + B \quad (11)$$

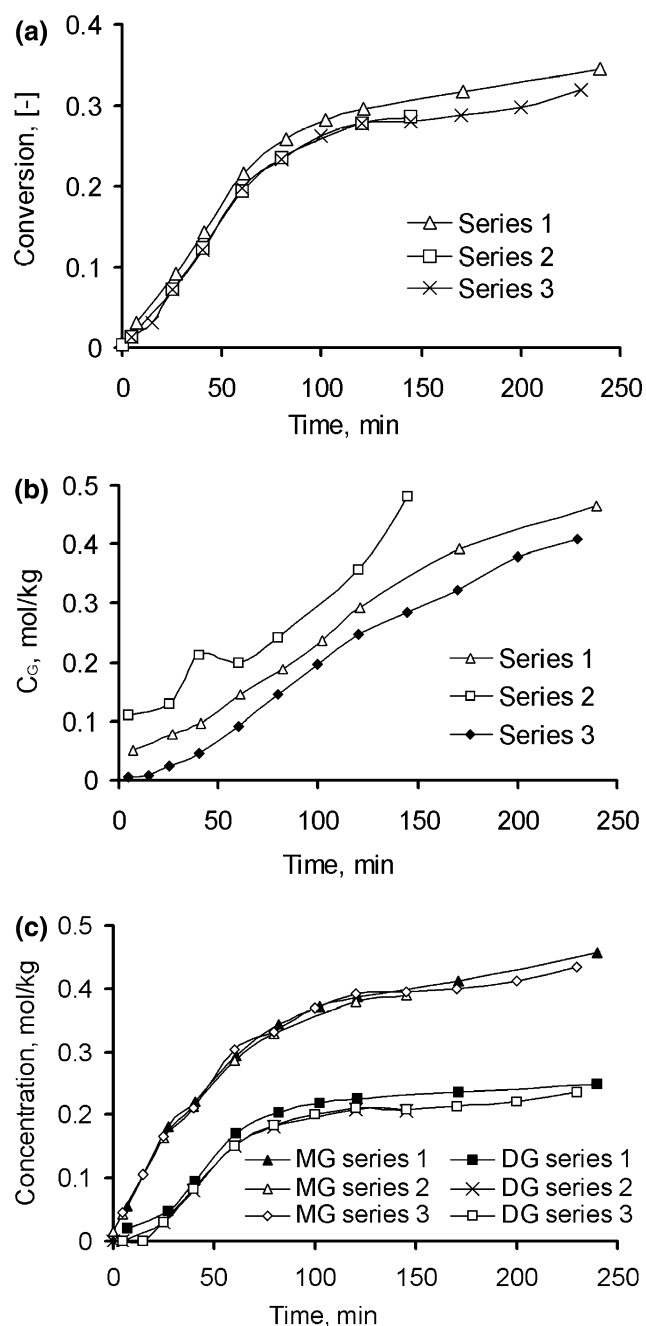
where  $X$  is the molar ester conversion.  $B$  (mol/kg) represents the solubility of glycerol in methyl ester at reaction temperature and  $A$  approximately represents the slope of the  $C_{\text{gly}}$  versus  $X$  plot. The glycerol concentration did not vary strictly linearly with conversion, and Eq. 11 gave only an approximate description, but the simulation results obtained based on this simple relation were acceptable. We also attempted to model this three-phase system [vapor (methanol-rich)–liquid (glycerol-rich)–liquid (ester-rich)] theoretically using the activity coefficient models available. But our attempts failed, as the activity coefficient models tested by us were unable to predict the high glycerol concentration in the oil phase containing ester and monoglyceride [14]. The models UNIFAC [15] and UNIFAC-Dortmund [16] could only qualitatively predict the increase in the glycerol concentration in the ester phase with increasing monoglyceride concentration. In the present study, all simulations and parameter fits were performed using ASPEN custom modeler (ACM) version 11.1. Simulations where the glycerol solubility was modeled using an activity coefficient model (UNIFAC and UNIFAC-Dortmund) showed very low conversions and were therefore not considered further.

The six kinetic constants in Eqs. 5a–5c were obtained by fitting Eqs. 6–11 simultaneously to the experimental data. The data was taken from experiments carried out with and without methanol stripping. The values of the rate constants are given in Table 1.

**Table 1** Parameters used in the kinetic model

Parameter	Value
$k_{1f}$	0.074 kg.mol <sup>-1</sup> min <sup>-1</sup>
$k_{1b}$	0.645 kg.mol <sup>-1</sup> min <sup>-1</sup>
$k_{2f}$	0.348 kg.mol <sup>-1</sup> min <sup>-1</sup>
$k_{2b}$	0.717 kg.mol <sup>-1</sup> min <sup>-1</sup>
$k_{3f}$	0.004 kg.mol <sup>-1</sup> min <sup>-1</sup>
$k_{3b}$	0.227 kg.mol <sup>-1</sup> min <sup>-1</sup>
$A$	0.8 (without methanol stripping) 0.4–0.8 (with methanol stripping and under vacuum)
$B$	0.06 mol/kg
$C_{\text{MeOH}}$	0.20 mol/kg (without methanol stripping) 0.01 mol/kg (with methanol stripping) (<0.20 mol/kg under vacuum)

Reaction conditions:  $T = 135$  °C, catalyst = 1 wt%



**Fig. 1a–c** **a** FAME conversion determined by different sampling methods. **b** Glycerol concentration in the ester phase obtained by different sampling methods. **c** Mono- and diglyceride concentration profiles obtained by different sampling methods. *Series 1* Samples were taken from the ester phase of the reaction mixture and kept at reaction temperature until the finely dispersed glycerol had settled and a clear ester phase was obtained. *Series 2* Samples were taken directly from the ester phase at reaction temperature without allowing the phases to separate completely. *Series 3* Samples taken from the reaction mixture were cooled to room temperature and centrifuged to get a clear ester phase. All of the figures show concentrations in the ester phase.  $T = 135\text{ }^{\circ}\text{C}$ ,  $P = 1\text{ bar}$

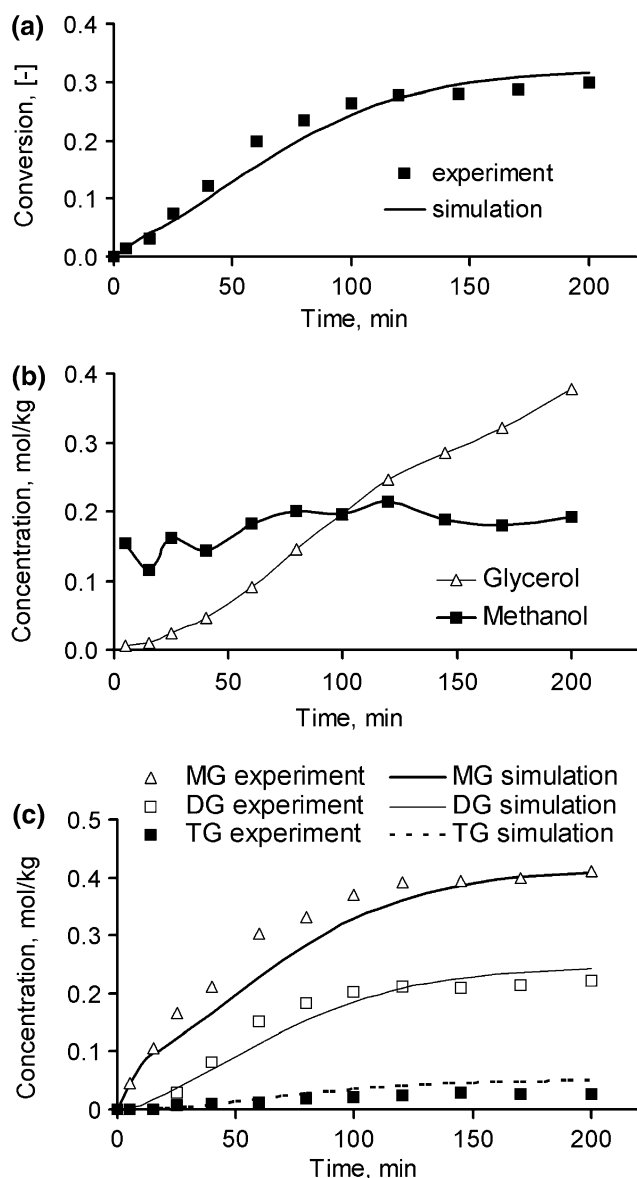
## Results and Discussion

### Effect of Sampling on Measured Conversion and Glycerol Concentration

Figure 1a shows the batch reaction run conversions obtained by different sampling methods. Conversions obtained from series 2 (samples taken directly from the ester phase at reaction temperature without letting the phases separate completely) and series 3 (samples cooled to room temperature and centrifuged) were the same. The conversions obtained from series 1 (samples taken from the ester phase at reaction temperature after allowing the dispersed glycerol to separate) were slightly higher in comparison to series 2 and 3. Figure 1b shows the glycerol concentrations in the ester phase obtained by different sampling methods. As expected, series 2 shows the highest concentrations, since the samples were turbid. The finely dispersed glycerol leads to overestimated concentration values in the ester phase. The concentrations shown by series 3 are lower than actually found in the reactor, as the samples were cooled and prepared at room temperature. Series 1 lies in the middle and represents the actual situation better. Unexpectedly, the samples taken at  $135\text{ }^{\circ}\text{C}$  (series 1) and at room temperature (series 3) gave similar glycerol concentrations. We observed that the data shown by series 3 were consistent, more reproducible than all of the others, and the samples were easier to prepare. Therefore, this procedure was used to collect data that were used later in the kinetic modeling. Figure 1c shows the mono- and diglyceride concentrations in the samples obtained by different sampling methods. No major effect of sampling method was seen in the product distribution.

### Batch Reactor without Methanol Stripping

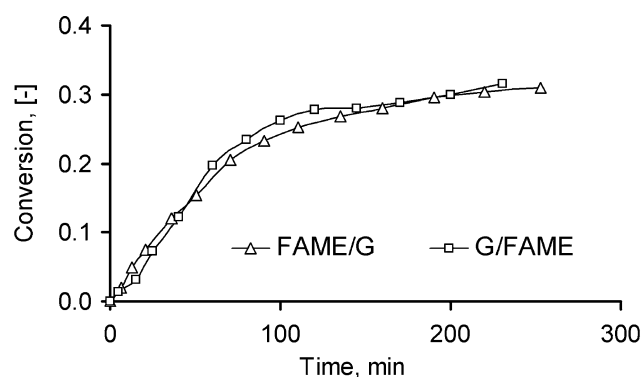
Figure 2a shows the ester conversion with time for a reaction run without inert gas flow. The reaction is quite slow and approaches a low equilibrium conversion at atmospheric pressure. The methanol and glycerol concentrations in the samples taken at room temperature are shown in Fig. 2b. Since methanol is very volatile and produced continuously, the amount present in the liquid phase at reaction temperature is determined by the operating pressure and to a lesser extent by the composition of the liquid. At constant pressure, the concentration of methanol in the ester phase was found to be nearly constant. Figure 2c shows



**Fig. 2a–c** a Variation in FAME conversion (experimental and simulation) in a batch reactor without methanol stripping. **b** Variation in glycerol and methanol concentration in the ester phase with reaction time, as determined by GC. **c** Experimental and simulated concentration–time profiles for product glycerides without methanol stripping.  $T = 135\text{ }^{\circ}\text{C}$ ,  $P = 1\text{ bar}$

the concentration profiles of the glycerides produced. Figure 2a and c also show that there was good agreement between the simulations and the experimental results. To study the effect of the type of emulsion, the reaction was also carried out with FAME/G dispersion. No significant difference was found between the reaction rates obtained in G/FAME and FAME/G dispersions, as can be seen in Fig. 3.

A higher interfacial area is generated in FAME/G than in G/FAME dispersion under the same operating

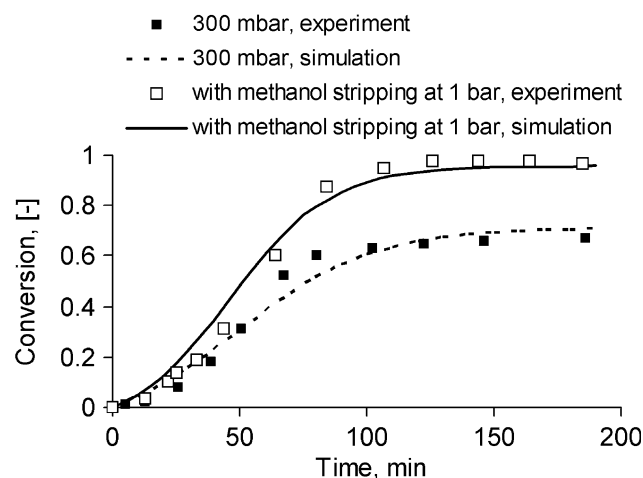


**Fig. 3** Comparison of FAME conversions obtained for different types of dispersions. FAME/G ester phase dispersed in glycerol. G/FAME glycerol dispersed in ester phase.  $T = 135\text{ }^{\circ}\text{C}$ ,  $P = 1\text{ bar}$

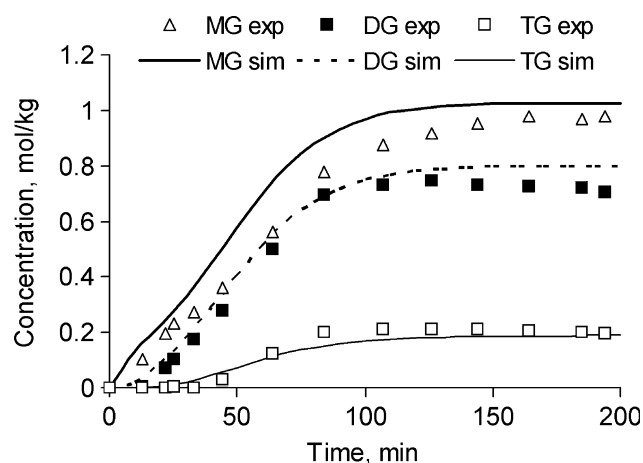
conditions [17]. Hence, the reaction rate would be higher if mass transfer were the controlling factor. Also, our previous studies performed at different stirring rates did not show any significant change in the reaction rate [13]. Therefore, it was concluded that mass transfer effects were not relevant in this reaction system under well-stirred conditions.

#### Batch Reactor with Methanol Stripping by Inert Gas

Batch reaction runs were also performed with the same reaction conditions but with nitrogen flowing through the liquid mixture. when this method was used, the reaction rate was accelerated and the ester conversion was shifted to nearly 100% (Fig. 4). In an earlier study, experiments were carried out under



**Fig. 4** FAME conversion with methanol removal by vacuum ( $P = 300\text{ mbar}$ ,  $T = 140\text{ }^{\circ}\text{C}$ ) and by stripping with an inert gas at  $1\text{ bar}$ ,  $T = 135\text{ }^{\circ}\text{C}$



**Fig 5** Experimental (denoted by *exp*) and simulated (denoted by *sim*) concentration profiles for product glycerides in the ester phase with methanol stripping at  $P = 1$  bar,  $T = 135$  °C

vacuum (300, 450 and 600 mbar) and at 1 bar with nitrogen purge in our laboratory [13]. It was found that methanol stripping by an inert gas was more effective at removing methanol than vacuum or inert gas purge, thus giving rise to higher equilibrium conversion (Fig. 4). Figure 5 shows product concentration profiles obtained with methanol stripping. A comparison of the simulated profiles with the experimentally obtained data is also shown in these figures. In the experiments with methanol stripping, the glycerol concentrations found in the ester phase were less than those obtained without methanol stripping for the corresponding conversion values. Therefore, a lower value of parameter  $A$  in Eq. 11 was used in this case (Table 1). In reactions with methanol stripping, the conversion profile was not always exactly reproducible, as the slow initial regime occurred for a longer period in some cases. The final conversion approached unity in each reaction run under the same reaction conditions. The glycerol concentration in the ester phase was found to be lower in reactions with a longer initially slow regime. Although it was found that the amount of monoglyceride controls the glycerol concentration in the ester phase, the factors that cause the small variations in the glycerol concentration are not known at present.

#### Where Does the Reaction Take Place?

Glycerolysis represents a complex reaction system that involves three phases, where the reaction can take place in one or both of the liquid phases, or at their interface. It is generally observed that at higher

stirring rates the reaction rate is independent of the stirring rate. Hence it can be concluded that interfacial area is not rate-controlling, ruling out the possibility of an interfacial reaction. The catalyst is found in both the liquid phases, although a greater fraction is present in the glycerol phase [13]. However, at the same time almost no ester is soluble in glycerol. So there is more chance that the reaction takes place in the ester phase. In the ester phase, the reaction could occur mainly in the film near the interface or in the bulk of the ester phase (following film theory [18]). Experiments at lower stirring speeds showed a reaction rate dependency on the stirring rate, indicating that the reaction rate is also mass transfer limited. At higher stirring rates it was found that one phase was finely dispersed into droplets. From drop size measurements in G/FAME dispersion, it was found that in the Sauter mean diameter during the glycerolysis reaction was 80–150  $\mu\text{m}$  [19, 20]. For a glycerol:ester molar ratio of 2:1, the dispersed phase fraction is 0.30. An estimation for the film thickness can be obtained using:

$$\delta_l = \frac{D_{AB}}{k_l}$$

The values of  $D_{AB}$  and  $k_l$  for the initial reaction conditions were estimated by Wilke–Chang and Calderbank and Moo–Young correlations [21], and were found to be  $D_{AB} = 5 \times 10^{-9} \text{ m}^2\text{s}^{-1}$  and  $k_l = 1 \times 10^{-4} \text{ ms}^{-1}$ , respectively. This gives an ester film thickness of 50  $\mu\text{m}$ . With this film thickness, the total film volume around the glycerol droplets is found to be more than the volume of the continuous phase. Hence the continuous phase where the reaction is taking place can be expected to be present as a thin film, not as a bulk phase. Therefore, under well-dispersed conditions, mass transfer limitation cannot be expected. The dispersed drops are bigger at the start of the reaction, i.e., 2–5 min after adding the catalyst, and an initial mass transfer regime will be present if the phases are not completely dispersed. Under well-dispersed conditions, the ester phase is almost saturated with glycerol all of the time. During the reaction, the glycerol concentration in the ester phase increases as the solubility of the glycerol in the ester phase increases with increasing conversion.

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