Kinetic Modeling of the Glycerolysis Reaction for Soybean Oils in Supercritical Carbon Dioxide Media

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ABSTRACT: Production of MAG by glycerolysis is important for food, pharmaceutical, and cosmetic industries. Conducting glycerolysis in supercritical carbon dioxide (SC-CO_2) media has advantages over conventional alkali-catalyzed glycerolysis. However, kinetic data are lacking for such conversions in the presence of SC-CO_2. The objectives of this study were to estimate the rate constants and elucidate the mechanism for the glycerolysis of soybean oil in SC-CO_2 using previously reported data. The data were taken from experiments using soybean oil, glycerol (glycerol/oil molar ratios of 15–25) and water (3–8% w/w) in SC-CO_2 at 20.7–62.1 MPa and 250°C for a 4 h period. Rate constants for the parallel glycerolysis and hydrolysis reactions were estimated for each processing parameter (glycerol/oil, water content, pressure) by minimizing the summed squared error between the values calculated from the experimental data and those obtained from the kinetic model. The results suggested that water and pressure had an effect on rate constants but the glycerol/oil ratio did not. Findings provide the kinetic modeling data necessary for the optimization of supercritical processes involving glycerolysis reactions for the production of MAG from vegetable oils.

Paper no. J11098 in *JAOCS 82*, 613–617 (August 2005).

KEY WORDS: Diacylglycerol (DAG), free fatty acid (FFA), glycerol, glycerolysis of vegetable oil, hydrolysis, kinetics, monoacylglycerol (MAG), reaction rate, soybean oil, supercritical carbon dioxide.

MAG have many applications as emulsifiers, encapsulating agents (1), moisture barriers (2), lubricants (3), and anti-staling agents (1). They are found in foods, nutraceuticals (4), controlled-release medicinal tablets (5), and anti-inflammation dental pastes, as well as in hair and skin products (1). MAG are preferred for these applications because they are nonionic and stable in both acid and base media (1).

The conventional manufacture of MAG is energy-intensive; requires the addition and removal of catalysts such as NaOH, KOH, $Ca(OH)_2$, CaO, and SrO (6); and can lead to dark colors and burnt flavors in the final product (1,5). As an alternative to the conventional method to produce MAG, glycerolysis can be conducted in the presence of a supercritical fluid, which has been demonstrated to provide positive benefits (5,7).

Kochhar and Bhatnagar (8) initially reported that a heated aqueous solution of carbon dioxide (CO_2) enhanced the rate of MAG production during glycerolysis, but CO_2 is not used as an adjunct in conventional glycerolysis because it reacts with the alkali catalyst. However, supercritical carbon dioxide (SC-CO_2) offers many advantages as a solvent/catalyst because it is safe, inexpensive, abundant, and easily removed by depressurizing the reaction vessel. In addition, the use of CO_2 eliminates the need for catalyst neutralization. Furthermore, synthesis in a pressurized CO_2 environment prevents reversal of the glycerolysis reaction, which is a major concern in conventional glycerolysis (6).

In 1996, Temelli *et al.* (7) demonstrated that glycerolysis of soybean oil could be accomplished in the presence of SC-CO_2 and water. They found that the optimal reaction temperature was 250°C and reported a significant ($P < 0.05$) decrease in MAG formation with pressure above 20 MPa. As expected, they found that the reversal of glycerolysis was negligible and, in some cases, MAG concentration even increased toward the end of the reaction period studied. Similarly, Jackson and King (5) used an immobilized lipase in the presence of flowing SC-CO_2 to facilitate glycerolysis and reported that the reaction was dependent on the water content of the reagents. They found that when the water level was increased from 0.7 to 4.2%, MAG production decreased from 84 to 67% (5). Such a trend facilitates control over the composition of the final product. The authors of this study (5) also suggested that the reaction took place in a heterogeneous multiphase mixture.

Few nonenzymatic studies involving reactions of vegetable oils and fatty esters have gone beyond basic experimental results with respect to consideration of reaction kinetics (3,9–12), and only one of these studies (11) noted the fact that ester hydrolysis reactions were taking place in parallel with transesterification.

The literature lacks information on the kinetics of the glycerolysis reaction in the presence of SC-CO_2 media. Such information is essential for better understanding the reaction mechanism as well as for the design of reaction equipment and processes. Therefore, the objective of this study was to model

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the kinetics of the glycerolysis of soybean oil in SC-CO_2 media, taking into account that hydrolysis reactions can also occur in parallel with glycerolysis, using previously reported data (7).

EXPERIMENTAL PROCEDURES

Experimental parameters. The materials and experimental protocols used to study the glycerolysis of soybean oil and other vegetable oils with glycerol in the presence of SC-CO_2 were described by Temelli *et al.* (7). Reactions were conducted at 250°C and pressures of 20.7, 41.4, and 62.1 MPa; glycerol/oil molar ratios of 15, 20, and 25; and water concentrations varying from 3 to 8% (w/w). Samples were collected every 0.5 h for 4 h, and the composition of the lipid phase (MAG, DAG, TAG, and FFA, expressed as moles per 100 g of sample) was determined. The change in the glycerol content over time was not taken into account by Temelli *et al.* (7) but was calculated in this study based on the initial glycerol/oil ratio and the amount of products formed. To account for the moisture in the glycerol reagent used, the actual water concentration was calculated by adding 4 g of water per 100 g of glycerol to the concentrations reported by Temelli *et al.* (7).

Kinetic modeling. Modeling was carried out to estimate rate constants for all possible reactions. This approach requires a thorough understanding of the sequential reaction steps taking place. The overall glycerolysis reaction is given by Equation 1.

$$\mathrm{TAG} + 2\ \mathrm{Gly} \rightleftarrows 3\ \mathrm{MAG} \qquad [1]$$

The overall reaction occurs in two consecutive steps (3,6). In the first step (Eq. 2), the transfer of a FA from TAG to glycerol (Gly) gives MAG and DAG. In the second step (Eq. 3), MAG is formed by the transfer of a FA from DAG to glycerol.

$$\mathrm{TAG} + \mathrm{Gly} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{MAG} + \mathrm{DAG} \qquad [2]$$

$$\mathrm{DAG} + \mathrm{Gly} \underset{k_4}{\overset{k_3}{\rightleftarrows}} 2\ \mathrm{MAG} \qquad [3]$$

Assuming that Equations 2 and 3 are reversible, k_{1-4} represent the rate constants for each step. In Equations 2 and 3, it is assumed that the available acyl groups are randomly distributed among the TAG, DAG, and MAG moieties and that water is not participating in these reactions (3). Thus, by using excess glycerol, a higher yield of total MAG can be obtained (6). Higher conversions can also be achieved by continuously removing MAG from the product mixture as they are being formed, thereby preventing the breakdown of MAG due to Equation 4.

$$\mathrm{TAG} + \mathrm{MAG} \underset{k_6}{\overset{k_5}{\rightleftarrows}} 2\ \mathrm{DAG} \qquad [4]$$

The above glycerolysis scheme does not account for the presence of FFA in the product mixture. Since water is present in the reaction system (7), ester hydrolysis must be taken into account as a competitive reaction. Hydrolysis can also occur in a stepwise manner. In the first step, a TAG becomes DAG by releasing a FFA after ester hydrolysis (Eq. 5). In the second step, DAG is hydrolyzed, giving MAG and a FFA (Eq. 6). MAG can then be further hydrolyzed into glycerol and FFA or, if glycerol is in excess, glycerol can react with FFA to produce even more MAG (Eq. 7).

$$\mathrm{TAG} + \mathrm{H_2O} \underset{k_8}{\overset{k_7}{\rightleftarrows}} \mathrm{DAG} + \mathrm{FFA} \qquad [5]$$

$$\mathrm{DAG} + \mathrm{H_2O} \underset{k_{10}}{\overset{k_9}{\rightleftarrows}} \mathrm{MAG} + \mathrm{FFA} \qquad [6]$$

$$\mathrm{MAG} + \mathrm{H_2O} \underset{k_{12}}{\overset{k_{11}}{\rightleftarrows}} \mathrm{Gly} + \mathrm{FFA} \qquad [7]$$

As in glycerolysis, each step of Equations 5–7 is reversible, and their respective rate constants are k_{7-12}. By taking into account all of the reaction steps described in Equations 2–7, the rate of change in concentration for each of the reaction components can then be described by the following differential rate equations (Eqs. 8–13), where Gly is glycerol:

$$\begin{aligned}\frac{d(\mathrm{MAG})}{dt} = {} & k_1(\mathrm{Gly})(\mathrm{TAG}) - k_2(\mathrm{DAG})(\mathrm{MAG}) + 2k_3(\mathrm{Gly})(\mathrm{DAG}) - 2k_4(\mathrm{MAG})^2 - \\ & k_5(\mathrm{TAG})(\mathrm{MAG}) + k_6(\mathrm{DAG})^2 + k_9(\mathrm{DAG})(\mathrm{H_2O}) - k_{10}(\mathrm{MAG})(\mathrm{FFA}) - \\ & k_{11}(\mathrm{H_2O})(\mathrm{MAG}) + k_{12}(\mathrm{Gly})(\mathrm{FFA})\end{aligned} \qquad [8]$$

$$\begin{aligned}\frac{d(\mathrm{DAG})}{dt} = {} & k_1(\mathrm{Gly})(\mathrm{TAG}) - k_2(\mathrm{DAG})(\mathrm{MAG}) - k_3(\mathrm{Gly})(\mathrm{DAG}) + k_4(\mathrm{MAG})^2 + \\ & 2k_5(\mathrm{TAG})(\mathrm{MAG}) - 2k_6(\mathrm{DAG})^2 + k_7(\mathrm{TAG})(\mathrm{H_2O}) - k_8(\mathrm{DAG})(\mathrm{FFA}) - \\ & k_9(\mathrm{DAG})(\mathrm{H_2O}) + k_{10}(\mathrm{MAG})(\mathrm{FFA})\end{aligned} \qquad [9]$$

$$\begin{aligned}\frac{d(\mathrm{TAG})}{dt} = {} & -k_1(\mathrm{Gly})(\mathrm{TAG}) + k_2(\mathrm{DAG})(\mathrm{MAG}) - k_5(\mathrm{TAG})(\mathrm{MAG}) + k_6(\mathrm{DAG})^2 - \\ & k_7(\mathrm{TAG})(\mathrm{H_2O}) + k_8(\mathrm{DAG})(\mathrm{FFA})\end{aligned} \qquad [10]$$

$$\begin{aligned}\frac{d(\mathrm{FFA})}{dt} = {} & k_7(\mathrm{TAG})(\mathrm{H_2O}) - k_8(\mathrm{DAG})(\mathrm{FFA}) + k_9(\mathrm{DAG})(\mathrm{H_2O}) - k_{10}(\mathrm{MAG})(\mathrm{FFA}) + \\ & k_{11}(\mathrm{H_2O})(\mathrm{MAG}) - k_{12}(\mathrm{Gly})(\mathrm{FFA})\end{aligned} \qquad [11]$$

$$\begin{aligned}\frac{d(\mathrm{H_2O})}{dt} = {} & -k_7(\mathrm{TAG})(\mathrm{H_2O}) + k_8(\mathrm{DAG})(\mathrm{FFA}) - k_9(\mathrm{DAG})(\mathrm{H_2O}) + k_{10}(\mathrm{MAG})(\mathrm{FFA}) - \\ & k_{11}(\mathrm{H_2O})(\mathrm{MAG}) + k_{12}(\mathrm{Gly})(\mathrm{FFA})\end{aligned} \qquad [12]$$

$$\begin{aligned}\frac{d(\mathrm{Gly})}{dt} = {} & -k_1(\mathrm{Gly})(\mathrm{TAG}) + k_2(\mathrm{DAG})(\mathrm{MAG}) - k_3(\mathrm{Gly})(\mathrm{DAG}) + k_4(\mathrm{MAG})^2 + \\ & k_{11}(\mathrm{MAG})(\mathrm{H_2O}) - k_{12}(\mathrm{Gly})(\mathrm{FFA})\end{aligned} \qquad [13]$$

The initial water concentration was calculated by using Equation 14,

$$\%\ \text{water (w/w)} = \frac{(\text{Gly/Oil})(n_{\text{TG}_0})(92.09\ \text{g/mol})(\%\ \text{H}_2\text{O}_{\text{added}} + 0.04)}{\text{Wt}_{\text{total}}} \quad [14]$$

where % water (w/w) is the initial amount of water as a percentage of the total weight of the reactants (oil, glycerol, and water) added to the system, Gly/Oil is the glycerol/oil molar ratio, n_{TG_0} is the initial number of moles of TAG, 92.09 g/mol is the M.W. of glycerol, % $\text{H}_2\text{O}_{\text{added}}$ is the percentage of water (as wt% of glycerol) added to the reaction system as reported by Temelli *et al.* (7), 0.04 is the percentage of water (w/w) in the glycerol reagent used by Temelli *et al.* (7), and Wt_{total} is the total weight of the reactants. Since the actual concentration of water was known at time zero, it was also possible to estimate the change in water concentration over time. This was achieved by subtracting the experimental FFA concentration from the calculated water concentration obtained in Equation 14, since formation of every mole of FFA requires the use of one mole of water (Eqs. 5–7).

Determination of rate constants. To calculate k_{1-12} in Equations 8–13, the change in concentrations over time for each chemical species (TAG, DAG, MAG, FFA, water, and glycerol) had to be known. Unfortunately, no experimental data were available to establish the change in concentration over time for glycerol. Therefore, in the first set of calculations, glycerol was assumed to be in excess and the rate of change in glycerol concentration was omitted to determine a set of *k*-values, called k'_{1-12}. Then, in the second set of calculations, Equation 13 and k'_{1-12} were used to determine the rate of change in glycerol concentration, which was then used to determine k_{1-12}.

To facilitate calculations, the experimentally determined (7) change in concentrations over time for TAG, DAG, MAG, and FFA as well as the calculated change in concentration over time for water was converted into mathematical expressions. This was achieved using a curve-fitting computer program (13). With this program, TAG data were described by a Harris Model [$y = 1/(a + b \cdot t^c)$] (R^2 range 0.94–0.99), DAG by a Logistic Model [$y = a/(1 + b \cdot e^{-c \cdot t})$] ($R^2$ range 0.89–0.99), FFA by an MMF Model [$y = (a \cdot b + c \cdot t^d)/(b + t^d)$] ($R^2$ range 0.90–0.99), MAG by two segments of linear fit [$y = a + b \cdot t$] (R^2 range 0.93–0.99), and H_2O by linear fit (R^2 range 0.69–0.93), where *a*, *b*, *c*, *d* were fixed constants determined by the program and *t* was the time. By using these mathematical expressions, the molar concentration (C_{exp}) for each component (TAG, DAG, MAG, FFA, and H_2O) was obtained for every 12 min time interval over the 4-h reaction period.

To calculate k'_{1-12}, the C_{exp} values were introduced into Equations 8–12 along with variable k'_{1-12} values and the estimated rate of change (r'_{calc}) in the concentration of TAG, DAG, MAG, FFA, and H_2O was obtained. The following expression was then used to obtain the estimated concentration (C'_{calc}) for each component:

$$C'_{\text{calc}} = C|_{t+\Delta t} = C|_{t} + r'_{\text{calc}} \cdot \Delta t \quad [15]$$

where $C|_{t+\Delta t}$ is the concentration at time $t + \Delta t$, $C|_{t}$ is the previously obtained concentration at time *t*, and Δt is the time interval. The summed squared error (SSE) between C_{exp} and C'_{calc} was then obtained using the expression $\Sigma(C_{\text{exp}} - C'_{\text{calc}})^2$. Using the Generalized Reduced Gradient (GRG2) nonlinear optimization code (14) and the constraint that k' had to be positive and less than or equal to 1, the sum of SSE for all components between 0 and 4 h was minimized to obtain k'_{1-12}.

The rate of change for glycerol was then estimated by introducing the newly calculated k'_{1-12} and the original experimentally determined molar concentrations into Equation 13. The molar concentration for glycerol was then obtained using Equation 15 and described by a linear fit equation. From this linear fit, C_{exp} for glycerol was obtained ($R^2 > 0.80$) for every 12-min time interval over the 4-h reaction period.

To calculate k_{1-12}, the C_{exp} for TAG, DAG, MAG, FFA, and glycerol were introduced into Equations 8–13 along with variable k_{1-12} and the rate of change, r_{calc}, of each component was obtained. The following expression was then used to obtain the predicted concentration (C_{calc}) for each component:

$$C_{\text{calc}} = C|_{t+\Delta t} = C|_{t} + r_{\text{calc}} \cdot \Delta t \quad [16]$$

Using the GRG2 program (14) and the constraints described above, the SSE between C_{exp} and C_{calc} for all components over the 4-h period was minimized to obtain the actual k_{1-12}. In all cases, 98% of the variation in C_{calc} was accounted for in the model.

The rate constants, k'_{1-12} and k_{1-12}, were calculated for three sets of experimental parameters (7): water concentrations of 3–8% w/w (at 20.7 MPa and a Gly/Oil ratio of 25), Gly/Oil ratios of 15, 20, and 25 (at 41.4 MPa and 4% water), and pressures of 20.7, 41.1, and 62.1 MPa (at a Gly/Oil ratio of 15, and 6% water).

RESULTS AND DISCUSSION

Chemistry of the glycerolysis of soybean oil. The mechanism proposed for the glycerolysis reaction in the presence of SC-CO_2 media is described in Equations 2–4. This mechanism is based on the chemical equation for glycerolysis of oils as given by Sonntag (6). Although it accounts for the production of MAG and DAG, it does not explain the formation of FFA observed by Temelli *et al.* (7). Therefore, both the hydrolysis and the glycerolysis reactions were considered. The hydrolysis reactions are described in Equations 5–7. This additional parallel process might be further complicated by the different phases potentially present inside the reactor, namely, the lipid phase, aqueous phase (glycerol and water), and vapor phase. Unfortunately, it is not known whether the reactions described in the preceding equations were taking place in one or more phases since the reaction system was a closed high-pressure batch reactor and thus the system was assumed to be homogeneous under the tested conditions for the purpose of kinetic modeling carried out in this study.

Equations 2–7 are reversible reactions that are controlled by concentration effects and reaction equilibrium. These equations are also consecutive reactions where the product of one is the substrate for the subsequent step. For instance, Equation 1 consists of two steps: First, TAG reacts with glycerol to form MAG plus DAG, then this newly formed DAG reacts with a second glycerol molecule to form more MAG. If the rate constant of the first step of the reaction is larger than that of the second step, then the second step of the reaction controls the net rate at which MAG is produced. Equations 2–7 are further complicated by the fact that glycerolysis and hydrolysis occur simultaneously. This means that both reactions occur in parallel and that the DAG formed in Equation 2 can be used up in Equations 3–6. Such parallel reactions add another level of complexity to the system, which has not been reported previously. The challenge is then to obtain the kinetic parameters to describe the relationships between the different reaction steps.

Kinetics: constraint and assumption. The aim of kinetics modeling is to find a reaction mechanism that is consistent with the experimental kinetic data. To achieve this, it was necessary to set the following constraint: k_{1-12} should have positive values between zero and one. Assumptions were made to obtain the change in glycerol concentration as a function of time. Because excess glycerol was used, where the initial concentration of glycerol was at least 15 times that of TAG (7), it was assumed that the molar concentration of glycerol did not change appreciably throughout the 4-h reaction. Consequently, the reactions involving glycerol were assumed to follow pseudo first-order kinetics. This meant that the glycerol concentration was not required to calculate the k'-values because the effect of glycerol was embedded into them. It was then assumed that these k'-values could be used to obtain the change in glycerol concentration as a function of time. This approach allowed the determination of actual k_{1-12} values in the second step. Later, determination of the glycerol content as a function of time through material balance and reaction stoichiometry confirmed these results.

Trends in calculated rate constants. The values for k_{1-12} are presented in Table 1 for different levels of water contents and Gly/Oil ratios and in Figure 1 for different levels of pressure. It was found that the reactions described by Equations 2–6 were not reversible. In addition, only the reverse reaction of Equation 7 occurred. This was particularly evident when glycerol was considered to be in excess. Indeed, in some cases the k_{12} values obtained by assuming excess glycerol were double those obtained using the estimate for glycerol concentration. This clearly demonstrates the importance of the excess glycerol on the reaction rate. Aside from k_{12} values, k_1 values demonstrated a similar trend, making it evident that only reaction steps involving glycerol were affected by the pseudo first-order kinetics assumption. Apart from this, high k_5 values were consistently obtained under all tested conditions. This is probably due to the large excess of TAG in the reactants and to the accumulation of MAG with time, which dramatically switches the equilibrium of the reaction toward the production of DAG.

Effect of water. During the initial stages of this study, in an effort to simplify the reaction kinetics, water was assumed to be in excess. However, this assumption did not hold and was eliminated from further consideration, especially at the lower water concentrations where k_4 values were found to be larger than k_3, a situation that would not be chemically feasible because of the high Gly concentration. Indeed, a reaction that would produce Gly would act against a large concentration gradient.

Figure 2 shows that, up to 3.5 h, more MAG was produced with an initial water content of 8% (w/w) compared with those at lower water levels. With the exception of the initial water concentration of 3% (w/w), comparable amounts of MAG were produced at other water levels during the 4-h study. These results therefore demonstrate the positive influence of water on MAG production.

The rate constants reported in Table 1 were expected to have similar values at different water levels because they were conducted at the same pressure (20.7 MPa), temperature (250°C), and Gly/Oil ratio of 25. However, this did not seem to be the case when lower water concentrations were used. In fact, at 3%

TABLE 1
Effect of Glycerol/Oil Ratio and Water Content on Rate Constants

	k-Values[a]			*k*-Values[b]				
	Initial Glycerol/Oil ratio			Initial water concentration (% w/w)				
Rate constant	15	20	25	3	4	6	7	8
k_1	0.04	0.03	0.02	0.04	0.04	0.04	0.04	0.05
k_2	0	0	0	0	0	0	0	0
k_3	0	0	0	0.06	0.02	0.03	0	0
k_4	0	0	0	0	0	0	0	0
k_5	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
k_6	0	0	0	0	0	0	0	0
k_7	0.07	0.06	0.04	0.06	0.07	0.07	0.07	0.07
k_8	0	0	0	0	0	0	0	0
k_9	0.09	0.02	0.07	0	0.41	0.28	0.36	0.39
k_{10}	0	0	0	0	0	0	0	0
k_{11}	0	0	0	0	0	0	0	0
k_{12}	0.09	0.07	0.08	0.09	0.30	0.13	0.13	0.13

[a] Initial water content = 4% (w/w), pressure = 41.4 MPa.
[b] Initial Glycerol/Oil ratio = 25, pressure = 20.7 MPa.

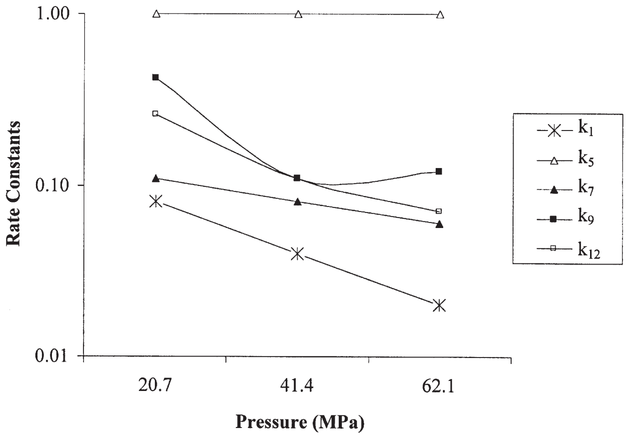

FIG. 1. Rate constants as a function of pressure where the initial water content was 6% (w/w) and the initial Glycerol/Oil ratio was 15.

(w/w) water the forward reaction of Equation 3 occurred whereas that of Equation 6 did not, thereby indicating a tendency toward glycerolysis at lower water concentrations. On the other hand, the opposite was true at higher water concentrations tested, demonstrating a tendency toward hydrolysis. Although such differences might be a reflection of changes in phase behavior, further investigation is necessary. Another important observation is the difference in k_{12} value obtained for the reaction at 4% initial water concentration compared with those at other water levels. Again, such a difference can only be attributed to changes in phase behavior.

Effect of Gly/Oil. As expected, only minor differences were seen between rate constants obtained at 15, 20, and 25 Gly/Oil ratios as presented in Table 1. Such differences are within experimental error.

Effect of pressure. Figure 1 provides rate constants obtained at three tested pressures and suggests a marked pressure effect. It appears that a pressure of 20.7 MPa favors TAG breakdown because k_1 and k_7 are higher than those obtained at 41.4 and 62.1 MPa. A pressure of 20.7 MPa also increases the reverse reaction of Equation 7. This may again be a reflection of a change in phase behavior due to pressure. In addition, it is also possible that the phase behavior might be changing over time as the reaction progresses and emulsifiers such as MAG and DAG are formed.

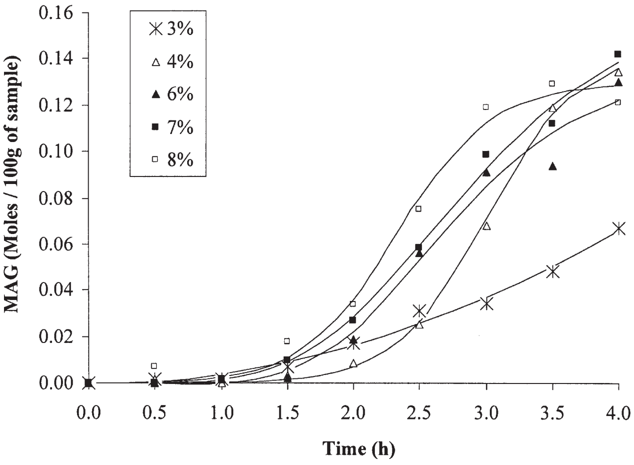

FIG. 2. MAG formation as a function of time where the initial Glycerol/Oil ratio was 25, pressure was 20.7 MPa, and different levels (3–8%, w/w) of initial water content were used. Experimental data were from Temelli *et al.* (7).

The Results in Figure 1 also provide a simple mechanistic description of the overall reaction and permit the identification of the rate-limiting reaction. First, TAG is broken down by three reactions (forward reaction of Equations 2, 4, 5) to form MAG, FFA, and a large amount of DAG. DAG is then hydrolyzed by the forward reaction of Equation 6 to form MAG and FFA. Finally, the FFA is used in the reverse reaction of Equation 7 to form more MAG. Out of all these reactions, the ones responsible for the initial breakdown of TAG are the slowest and therefore rate-limiting. Consequently, parameters affecting the rate of those reactions, such as phase behavior, must be optimized to enhance the efficiency of this process further.

ACKNOWLEDGMENT

The authors express their gratitude to the Natural Sciences and Engineering Research Council of Canada for their financial support.

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[Received March 29, 2005; accepted June 10, 2005]