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Kinetic modeling of glycerolysis–hydrolysis of canola oil in supercritical carbon dioxide media using equilibrium data

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Abstract

Glycerolysis–hydrolysis reactions to produce monoacylglycerol (MAG) and diacylglycerol (DAG) used in the production of functional foods and nutraceuticals were conducted in supercritical carbon dioxide (SC-CO_2) media to elucidate the reaction kinetics, provide the reaction mechanism and assess the potential catalytic agent involved. Reactions were conducted in an electrically heated, magnetically stirred autoclave at 250 °C, 10–30 MPa, anhydrous glycerol/canola oil molar ratio of 34:1 and initial water content of 0 to 8% (w/w). Reactions were also conducted in supercritical nitrogen at 250 °C, 10 MPa, and 8% (w/w) initial water. Samples were collected as a function of time and the concentrations of MAG, DAG, free fatty acids (FFA) and triacylglycerol (TAG) were obtained using thin layer chromatography–flame ionization detection. The maximum rate of MAG formation at 20 MPa was significantly higher ($p \leq 0.05$) than that at 30 MPa, but similar ($p > 0.05$) to that at 10 MPa; a finding that has economical impact because a pressure of 10 MPa can be reached without the use of a high-pressure pump. Rates of MAG formation in SC-CO_2 and -N_2 media were similar ($p > 0.05$) thereby demonstrating that SC-CO_2 does not contribute to catalysis. The maximum rate of MAG production at 10 MPa was significantly higher ($p \leq 0.001$) for reaction with 4% (w/w) initial water compared with anhydrous reactions and was significantly lower ($p \leq 0.05$) compared to that of reaction with 8% (w/w) initial water. Although this study was unable to identify the catalytic reagent, it did show that water played an important role. Reactions were carried out up to 14 h and equilibrium was reached at 9 h. The average equilibrium composition (mol%) obtained at 9–10 h for the reactions conducted at 10–30 MPa with 4–8% (w/w) water was 66–71% MAG, 13–15% DAG, 13–17% FFA and 0–1% TAG. A MAG concentration of >65% is higher than that obtained in conventional glycerolysis where the concentration of MAG generally does not exceed 58%. Such findings not only demonstrate improved yields but also lead to a better understanding of the complex mechanisms of simultaneous glycerolysis–hydrolysis reactions and are critical for optimal process design targeting the MAG and DAG products.

Keywords: Canola oil; Glycerolysis; Hydrolysis; Kinetics; Monoglycerides; Supercritical media

1. Introduction

Recent developments in supercritical fluid technology have shown that these fluids have a promising future in green chemistry. In fact, in addition to being exceptional extraction solvents, supercritical fluids have also been shown to be useful as reaction media. One important industrial reaction that appears to be well suited for supercritical fluids is the glycerolysis reaction [1,2] since conventional glycerolysis requires strict and energy-intensive operating conditions. For instance, conventional glycerolysis requires high temperatures (220–260 °C) to increase the solubility of glycerol in the fat phase, the addition of nitrogen gas to prevent oxidation, and the presence of an inorganic catalyst [3]. The reactants must also be vigorously stirred throughout the reaction and, at the end of the reaction, the catalyst must be neutralized and reaction mixture must be rapidly cooled to prevent reversion [3]. Conducting glycerolysis in supercritical carbon dioxide (SC-CO_2) simplifies the conventional process because, as reported by Temelli et al. [1], it does not require the addition and removal of any catalyst. Furthermore, due to the high temperature required, it is possible to reach the desirable working pressure with minimal pressurization.

Monoacylglycerol (MAG) and diacylglycerol (DAG) are the most valuable products of glycerolysis. MAG's emulsifying

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properties have long been exploited by food, pharmaceutical and lubricant manufacturers. Recently, new products, such as nutraceuticals [4] and controlled-release medicinal tablets [2], also make use of food grade MAG. DAG, on the other hand, has recently attracted attention as a fat that could prevent obesity [5], while being beneficial to diabetics [6] and prevent atherosclerosis [7].

Even though MAG is the most abundant product of the glycerolysis reaction, its concentration generally does not exceed 58% of the reaction products [8]. To increase this yield, a more thorough understanding of the reaction kinetics is required. However, the literature lacks the required kinetic studies for the conventional process as well as for the process in SC-CO_2 media. Furthermore, glycerolysis reactions alone might not account for the production of MAG and DAG. Indeed, water is often inadvertently added to the reactants, due to the hydrophilic nature of glycerol. When this occurs, hydrolysis takes place in parallel to glycerolysis, resulting in the formation of free fatty acids (FFA). Temelli et al. [1] conducted glycerolysis–hydrolysis of soybean oil in SC-CO_2 and reported the formation of FFA in reactions where no water was intentionally added. The investigators [1] explained that 4% water present in glycerol might have been the reason for FFA formation. In addition, an increase in pressure was reported to cause a decrease in MAG production [1]. More recently, a kinetic investigation [9] showed that, to understand and optimize such a complex system, the rate constants of six reversible independent reactions had to be determined. However, in the absence of equilibrium data, only approximate rate constants could be established [9]. Based on these previous studies, it was hypothesized that some catalytic effect is occurring under the investigated conditions of 250 °C as glycerolysis could only occur at a reasonable rate if the reactants were heated to 287 °C [3]. However, the nature of the active catalysis occurring in SC-CO_2 media is not known. The objectives of this study were therefore to obtain reliable rate constants by using the reactant concentrations at equilibrium, gain a better understanding of the catalytic agent involved in the glycerolysis–hydrolysis reaction in supercritical media and assess the effect of SC-CO_2 under different conditions on reaction rate.

2. Materials and methods

2.1. Materials

The reactants were commercially refined, bleached and deodorized canola oil graciously donated by Canbra Foods Ltd. (Lethbridge, AB, Canada), anhydrous glycerol (Gly) from J.T. Baker (Phillipsburg, NJ), deionized distilled water (DDW), and 99.8% bone dry CO_2 and 99.95% compressed nitrogen (N_2) from Praxair Canada Inc. (Mississauga, ON, Canada). Thin layer chromatography–flame ionization detection (TLC–FID) system determinations were performed using analytical grade glacial acetic acid from BDH Inc. (Toronto, ON, Canada), and laboratory grade ethyl ether and HPLC grade hexane from Fisher Scientific (Fairlawn, NJ). TLC reference standard containing 25% (w/w) of each of oleic acid, monoolein, diolein and triolein was obtained from Nu-Chek Prep Inc. (Elysian, MN).

2.2. Reactions

The reaction was conducted in batch mode in a Nova Swiss (Nova-Werke AG, Effretikon, Switzerland) high pressure, electrically heated, magnetically stirred 200 mL autoclave setup as shown in Fig. 1. A total volume of 75 mL of reactants, consisting of canola oil, Gly and DDW were added to the autoclave: the Gly/oil molar ratio was 34:1 and DDW was 0, 4 or 8% (w/w of glycerol). When mixing reactants for the anhydrous reactions (0% water), the autoclave was flushed with a flow of dry nitrogen to prevent the accumulation of moisture from the air. Once the autoclave was sealed, the reaction mixture was purged with CO_2 or N_2 and constantly stirred (∼100 rpm). Tank pressure CO_2 or N_2 (∼6 MPa) was then added to the autoclave before increasing the temperature to 250 °C. Once the desired temperature was established, the autoclave was pressurized to 10, 20 or 30 MPa and the mixing rate was increased to 250 ± 30 rpm. Samples (1 mL) were collected by building vacuum in the sampling tube and then filling the sampling tube with reaction mixture taken 2 mm from the bottom of the autoclave. The sampling port on the system made sample collection during the reaction possible without significantly affecting the pressure inside the autoclave. The length of the sampling tube between the two on–off valves was designed to be slightly longer than the total length of tubing extending from the bottom of the autoclave to the first on–off valve. During sample collection, the first sampling – comprised of the stagnant material left in the tube since the last sampling – was discarded, the content of the sampling tube was sucked dry by vacuum and then a second sample was taken. Samples were collected every 30 min for 4 h reactions and every hour for 10 h reactions. For 14 h reactions, samples were collected every 2 h but after 10 h, a sample was collected every hour. These different sampling protocols were implemented in order to maximize kinetic data without affecting the equilibrium of the reactions.

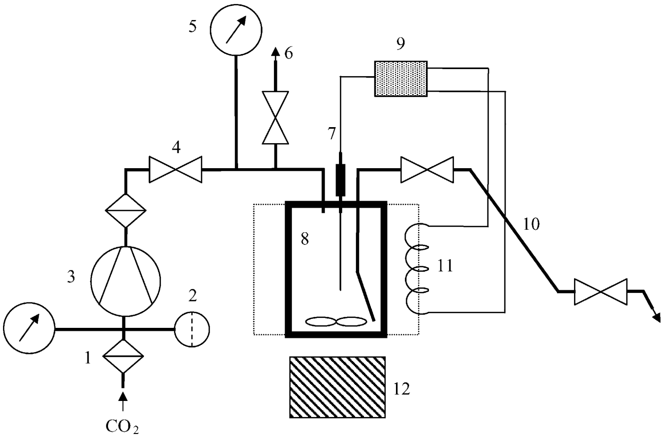

Fig. 1. Schematic of the experimental apparatus: (1) filter, (2) rupture disk, (3) compressor, (4) on–off valve, (5) pressure gauge, (6) vent, (7) thermocouple, (8) reactor, (9) temperature controller, (10) sampling tube, (11) electric heater, (12) magnetic stirrer.