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LETTER TO THE EDITOR

Homogeneous Tubular-Flow Process for Monoolein Preparation

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Abstract Esterification of fatty acids with glycerol is characterized by negligible solubility of the two liquid phases. The reactions to mono-, di- and triglycerides taking place in the fatty acid phase, are limited by chemical equilibrium. The scope of this study is to investigate in a tubular reactor the conversion of a homogeneous mixture of oleic acid and glycerol in *tert*-butanol. The liquid composition in this study was 1 mol of oleic acid, 6 mol of glycerol and 14 mol of *tert*-butanol. Experiments were conducted in a tubular reactor at 35 atm over a temperature range of 200–240 °C and residence times of 0.7–17.6 h to determine the kinetics and the chemical equilibrium. The selectivity to monoolein was >95 mol %. A reversible second order reaction fits the data well.

Keywords Homogeneous tubular-flow process · Monoolein production in *tert*-butanol

Abbreviations

BSTFA	*N*,*O*-Bis(trimethylsilyl) trifluoroacetamide
DG	Diglycerides
DO	Diolein
GC	Gas chromatograph
HPLC	High-pressure liquid chromatography
ID	Internal diameter
MG	Monoglycerides
MO	Monoolein
TG	Triglycerides
TO	Triolein
ZIF	Zeolitic imidazolate framework

Introduction

The conversion of low-cost and abundant renewable raw materials into valuable chemical products is a significant scientific and technological challenge with a major environmental and economic impact. Extensive research has been carried out to develop green technologies for the utilization of glycerol, a by-product of the biodiesel industry [1, 2]. An important application is the conversion of glycerol to valuable monoglycerides (MG) that provide a wide range of applications such as emulsifiers in food, pharmaceutical and cosmetic, detergents and lubricants [3]. The methods of preparation and production of mono- and diglycerides (DG) by esterification, transesterification and other reactions and their applications were reviewed recently [4]. Industrially, MG are produced by glycolysis of fats, oils and fatty acids in presence of inorganic bases (NaOH or $Ca(OH)_2$) at 220–260 °C. The product contains 45–55 % MG, 38–45 % DG and 8–12 % triglycerides (TG) (Fig. 1) [3]. Many catalytic, homogeneous and heterogeneous, as well as enzymatic methods have been studied. Processes with strong acid catalysts such as H_2SO_4 and H_3PO_4 operated at 240–250 °C [5] yield 40–55 % MG. Operation at such high temperatures, especially for food applications, may also degrade the taste, aroma and color. The methods employed for purification of MG, e.g., distillation, are very complex, expensive and energy consuming while reusing the catalyst is not feasible.

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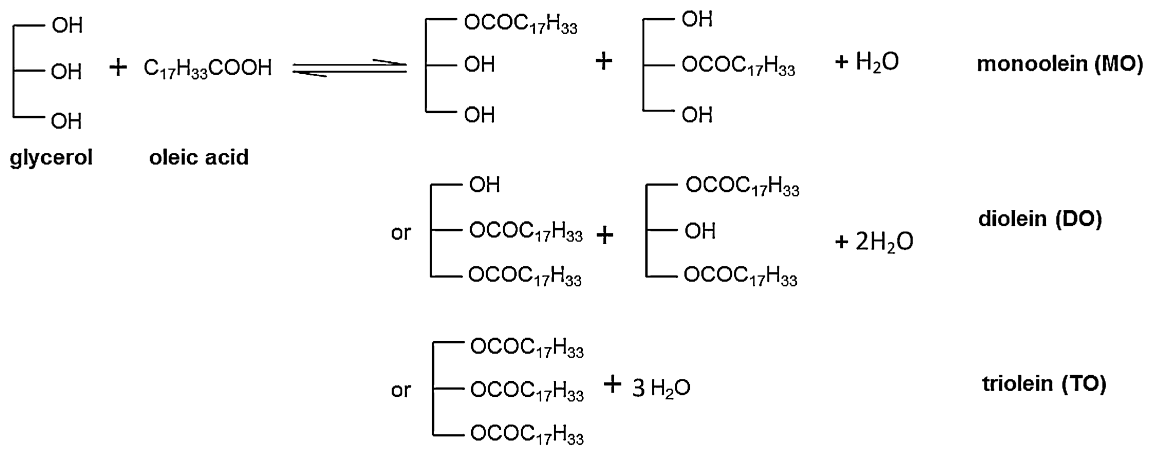

Fig. 1 Esterification reaction of glycerol with oleic acid

Stable and active heterogeneous catalysts such as zeolites, sulfonated mesoporous silica, ion-exchange resins, enzymes and metal–organic frameworks [6, 7] were employed in preparation of MG by esterification of fatty acids with glycerol at lower temperatures. Corma *et al.* [8] reported the transesterification of triolein with glycerol on solid basic catalysts sepiolite-Cs, MCM-41-Cs, MgO and hydrotalcites. MgO yielded 97 % triolein conversion and 75 % monoolein selectivity after 5 h at 240 °C.

Glycerol and oleic acid are essentially immiscible liquids. A detailed study of this system [9] found that the glycerol solubility in the phase composed of oleic acid, monoolein (MO), diolein (DO) and triolein (TO) at 170 °C was 4–5 wt%, essentially independent of composition. The oleic acid solubility in glycerol was negligible. Therefore, the reaction takes place only in the oleic acid phase. Furthermore, it is expected that, given the great excess of oleic acid, the formed MO reacts further to DO and TO thus reducing selectivity with increasing oleic acid conversion. Although the esterification is reversible, the conversion of oleic acid measured in the batch reactor at 140–160 °C [9] reached >90 %, since the water produced in the reaction was transferred to the glycerol phase. The selectivity to the three products changed little with oleic acid conversion, being very close to its equilibrium values. Enhancing solubility is expected to improve selectivity. A recent patent application [10] proposes to use water as co-solvent at high temperatures (250 °C). The patent claims that a high yield of MG of up to 90 % was measured. Recently, we reported 100 % selective synthesis of MO at 57 % oleic acid conversion over hierarchical ZIF-8 catalyst at 150 °C after 24 h in the presence of *t*-butanol [6, 7].

In spite of the many studies published on this important topic, little progress has been made in improving the performance, especially the selectivity to MG. The esterification reaction of oleic acid with glycerol is an acid catalyzed reaction. The oleic acid substrate itself is a catalyst. The esterification reaction of carboxylic acid with glycerol has also been reported previously by Jacobs and co-workers [11]. The ionization constant of the fatty acid chain is very much dependent on the reaction temperature. Given the fact that the reaction is autocatalytic with respect to oleic acid, using a solvent that dissolves both reactants forming a homogeneous solution is a viable and promising route. Thus the composition can be adjusted so as increase the selectivity to MG and the conversion of the fatty acid. The practical merits and drawbacks that would determine its commercial application are expected to be done separately. Most studies published in the literature were performed in batch reactors. Tubular flow reactors are a preferred configuration that are run at steady-state and could produce a high selectivity to MG at a relatively high conversion of oleic acid. The scope of this study is to explore for the first time the possibility of performing a homogeneous continuous, tubular-type process.

Experimental

The esterification was carried out in a bench-scale high-pressure tubular reactor (Fig. 2), 0.65 cm ID and 132 cm total length, made of stainless-steel. The reactor was placed in a high temperature oven to ensure isothermal operation. The liquid was pumped from the feed tank upflow to the reactor by a HPLC pump. The residence time in the reactor was set by adjusting the liquid flow rate. The pressure in the reactor was kept at 35 atm by a backpressure regulator to avoid vaporization over the temperature range 200–240 °C. Most experiments were conducted in the empty reactor. In some runs, 30 % of the reactor was packed with 70–120 µm SiC inert particles.

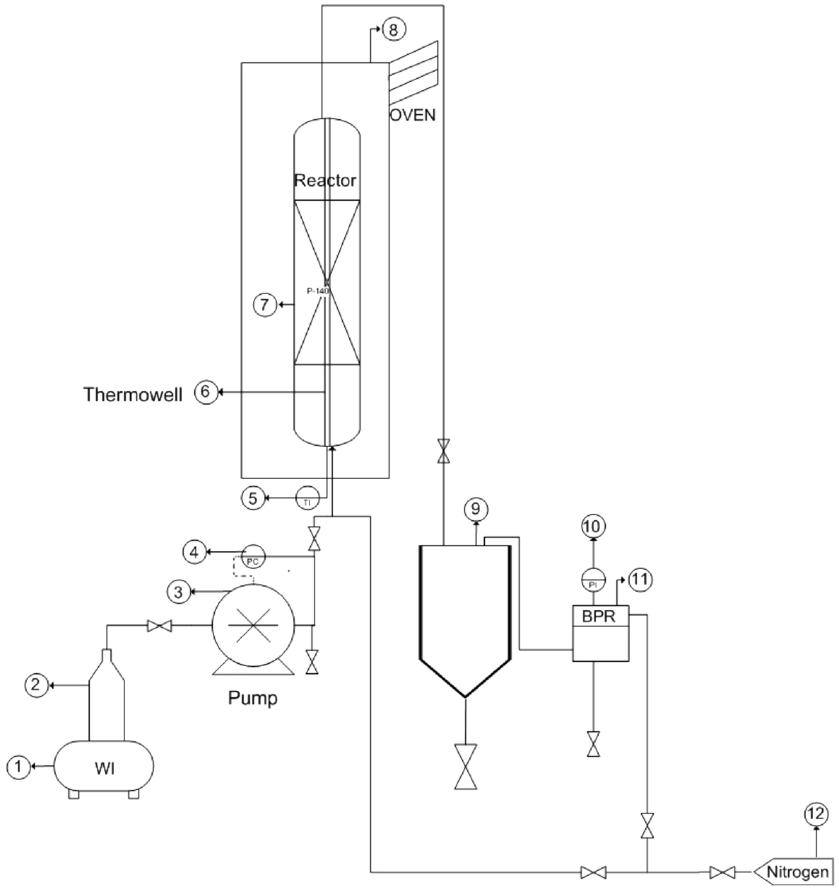

Fig. 2 Experimental setup: (1) balance, (2) feed tank, (3) high pressure pump, (4) pressure controller, (5) thermocouple, (6) thermowell, (7) tubular reactor, (8) oven, (9) product tank, (10) pressure gauge, (11) back pressure regulator, (12) nitrogen cylinder

All experiments were carried with a mixture composed of oleic acid (Sigma-Aldrich, Belgium), glycerol (Bio-Lab Ltd, Israel) and *tert*-butanol (Alfa Aesar, UK) at a molar ratio of 1:6:14. The concentration of oleic acid was determined by organic acid–base titration (0.01 M KOH in ethanol, Merck, Belgium). Glycerol mono-, di- and triolein were analyzed by a well-established GC method [12] using BSTFA (Sigma-Aldrich, Belgium). 0.03 g of product were mixed with 0.03 g of tetradecane (internal standard). 0.7 g of BSTFA and 0.7 g of pyridine were added. After 20 min in oven at 80 °C the solution was injected immediately into the warm (50 °C) HP6890 GC equipped with injector and a flame ionization detector and 10 m × 0.32 mm ID fused-silica capillary column coated with a 0.1 µm film of DB-5. The GC was programmed to heat from 60 to 190 to 420 °C, at a ramp rate of 50 °C/min to 190 °C and a second ramp rate of 6 °C/min to 420 °C.

Results and Discussion

Experiments were carried out at 200, 220 and 240 °C. The residence time in the reactor was varied over a wide range by changing the liquid flow rate. The performance at a particular residence time was measured after running the reactor for at least two times that residence time to ensure that a steady-state was reached. Indeed, measurements carried out at several times on stream indicated that steady-state was reached. No apparent effect of packing the reactor with inert SiC was recorded, as shown in Fig. 3.

The measured selectivity of MO was >0.95. The other product was DO Neither TO nor butyl ester was detected. There is no esterification reaction between oleic acid with *tert*-butanol as the alcohol part is sterically hindered around the ester bond. This was expected since the molar ratio of glycerol to oleic acid in the solution was 6. This is by far higher than the value in the heterogeneous system that contains only glycerol and oleic acid where the very low glycerol solubility limits this ratio to $\ll 1$. Therefore, esterification of oleic acid with glycerol is very selective to MO, in contrast with other systems published in the literature. Therefore the analysis of the data will account only for the esterification to MO.

The equilibrium constants of the reaction at 220 and 240 °C, calculated from the data measured at long residence times, are listed in Table 1. The two values indicate that the reaction over this temperature range is very mildly endothermic. The equilibrium constant at 200 °C, calculated by extrapolation of the two values, is 0.57.

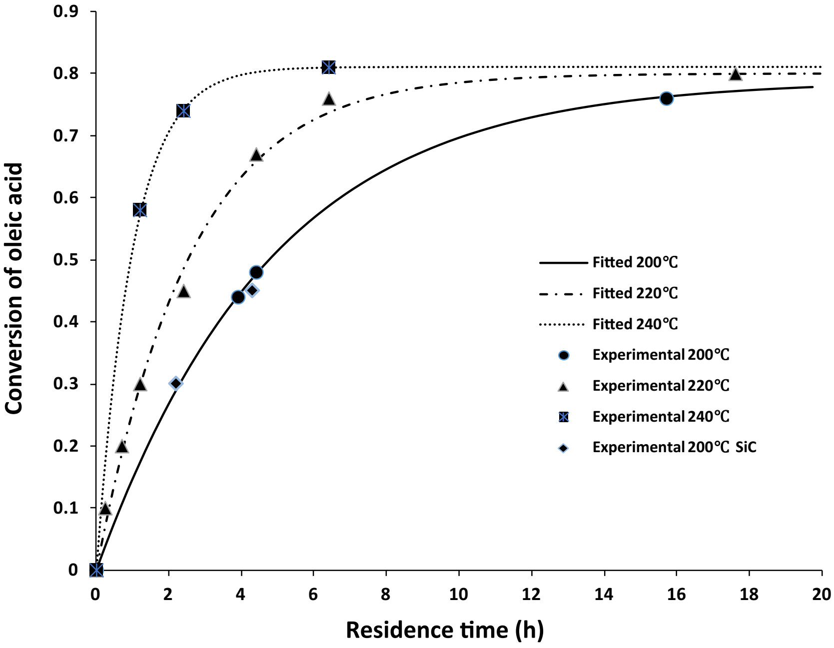

Fig. 3 Second-order reaction expression displays a very good fit of kinetic data

Table 1 Chemical equilibrium constants

Temperature (°C)	Residence time (h)	Oleic acid conversion	Equilibrium constant
220	17.6	0.8	0.62
240	6.4	0.81	0.67

The kinetic data are plotted in Fig. 3. Calculation of the Reynolds number from estimated density and viscosity of the *tert*-butanol yields values in the order of 10 meaning that the flow was laminar. Therefore the data were analyzed according the method developed for a laminar flow reactor given in expression (1) and assuming a second rate of reaction as shown in Eq. (3):

$$x = \int_{\frac{\theta}{2}}^{\infty} x(t)E(t)\mathrm{d}t \tag{1}$$

where $E(t)$ is defined as:

$$E(t) = \frac{\theta^2}{2 \cdot t^3} \tag{2}$$

$$\frac{\mathrm{d}x}{\mathrm{d}t} = kC_{10}\left((6-x)(1-x) - x^2/K\right)$$
$$x = 0 \text{ at } t = 0 \tag{3}$$

The rate constant k is defined as:

$$k = A\exp\left(-\frac{E_\mathrm{a}}{\mathrm{RT}}\right) \tag{4}$$

x is the oleic acid conversion, θ is the residence time, $E(t)$ is the residence time distribution, E_a is the activation energy, C_{10} is the oleic acid feed concentration and K is the chemical equilibrium constant. The solution [13] of Eq. (3) is:

$$x(t) = \frac{7 + \sqrt{K}\sqrt{24+25K} \cdot \tan h\left(0.5 \cdot \frac{-C_{10}k\sqrt{24+25Kt}}{\sqrt{K}} - D\sqrt{K}\sqrt{24+25K}\right)}{-2+2K} \tag{5}$$

$$D = \frac{2 \cdot \tan h^{-1}\left(\frac{-7\sqrt{K}}{\sqrt{24+25K}}\right)}{-\sqrt{K}\sqrt{24+25K}} \tag{6}$$

The rate constant was calculated by fitting the calculated value of x from expression (1) to the measured values at each temperature. The goodness of fit, defined as $\sum(x_{\text{exp–}}x_{\text{fitted}})^2$, varied from 2.5×10^{-3} at 220 °C to 6.5×10^{-5} at the other two temperatures. This is clearly illustrated by the curves in Fig. 3. The activation energy calculated from the plot in Fig. 4 is 81 kJ/mol, A is 5.3×10^7 L/mol/h and the coefficient of determination is $r^2 = 0.98$.

Conclusions

The esterification of oleic acid with glycerol (molar ratio of 1:6) dissolved in *tert*-butanol was carried out in a tubular reactor at 35 atm and 200–240 °C. The residence time in the reactor was varied over a wide range to determine selectivity to monoolein, diolein and triolein, the reaction kinetics and equilibrium constant. A high selectivity to monoolein of >95 mol% was measured. It was shown

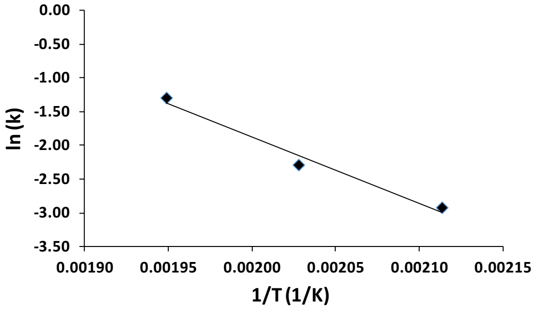

Fig. 4 Estimation of activation energy

that in this system only the esterification of oleic acid with glycerol is significant. This is because of the great excess of glycerol in the homogeneous solution. Furthermore, the rates of reaction were high at 240 °C so that a conversion of 74 % was achieved at a residence time of 2.4 h. The conversion is limited by chemical equilibrium to about 80 %. This conversion can be further increased by increasing the glycerol to oleic acid molar ratio. Fitting the data to a second order reaction yielded an excellent fit with activation energy of 81 kJ/mol.

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