

Continuous Synthesis of Oleyl Oleate in Supercritical Carbon Dioxide using Solid *p*-Toluenesulfonic Acid as Catalyst

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ABSTRACT: Supercritical carbon dioxide (SC-CO₂) was used as solvent to synthesize oleyl oleate as an analog of Jojoba oil from oleic acid and oleyl alcohol with high conversion (100%) of the acid into ester in a short time of 100 min. Utilizing a low cost solid catalyst, *p*-toluenesulfonic acid monohydrate (PTSA), the esterification reaction was performed, without any prior preparation step, in a flow mode, at a pressure of 147 bar and a temperature of 60°C. This method seems industrially suitable for the production of oleyl oleate. The solubility of a mixture of oleyl alcohol and oleic acid in SC-CO₂ were also measured to calculate the alcohol to acid ratio and the esterification yield.

KEY WORDS: Supercritical carbon dioxide, Oleyl oleate, Esterification reaction, Jojoba oil, *p*-Toluenesulfonic acid

INTRODUCTION

Supercritical carbon dioxide (SC-CO₂), due to its unique thermodynamic and transport properties, has been used in a variety of applications [1-8]. Under the SC-CO₂ the reaction rates can be enhanced because of the high diffusivity of the reactants in the SC-CO₂ medium, the lack of surface tension, and the relatively low viscosity of the mixture [2]. Furthermore, the solubility of the components can be tuned

by changing the temperature and pressure (i.e., density) of the solvent used [1].

The continuous increase in the number of industrial applications of high molecular weight esters as lubricants in high-speed machinery, and for pharmaceutical uses, cosmetics, food additives, etc., has increased the importance of the synthesis of analogs of natural esters [9]. Oleyl oleate is a high molecular

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weight ester analogue of the Jojoba oil [10].

Sanchez et al. synthesized oleyl oleate from oleic acid and oleyl alcohol using zeolite as a catalyst in a batch stirred tank reactor (BSTR) within 8 h of reaction time [11]. The maximum yield of the ester was achieved at a temperature of 180°C, pressure of 16 mmHg, and maximum initial catalyst concentration of 0.6%. Higher conversions were obtained with zeolites of smaller crystal size (greater specific surface area).

Brennecke et al. showed that in the uncatalyzed esterification of phthalic anhydride with methanol in SC-CO₂, the reaction rate is enhanced 30 times when operating in the compressible region due to increased local concentration of methanol around the phthalic anhydride [12]. Moreover, the kinetic of the homogeneous liquid phase synthesis of oleyl oleate in a BSTR using cobalt chloride as catalyst has been studied [9]. At a temperature of 164°C, the catalyst concentration of 0.85% and alcohol to acid molar ratio of 1.7, 100% conversion was achieved after 8.3 h.

There are two reports on the synthesis of oleyl oleate in SC-CO₂ using *Mucor-Miehei* immobilized lipase as catalyst in a continuous fixed-bed reactor and a batch-stirred tank reactor [13]. Higher reaction rate at SC-CO₂ condition compared to solvent-free system was obtained. The highest conversion, 50% in the continuous system, was achieved at 60°C and 80 bar, which was strongly dependent on the water content of the enzymatic bed [14]. At higher pressure the water was removed from the catalytic bed, and the conversion was reduced. Higher conversion of 90% at 50°C and 80 bar was obtained in a BSTR. In this method the probable limitations may be the use of an expensive catalyst with many preparation steps [15], low conversion in a continuous mode, and reduced conversion after removal of water.

In the present work, the model esterification reaction is catalyzed by solid *p*-toluenesulfonic acid monohydrate (PTSA) as a low cost catalyst with no preparation step under SC-CO₂ conditions. PTSA (m.p.= 104°C) have been used in many applications under normal conditions to catalyze esterification reactions [16]. However, it has not yet been used in the solid state under SC-CO₂. The main objective was then to develop a continuous process for the syn-

thesis of oleyl oleate with a high yield and a short reaction time that would be industrially applicable.

EXPERIMENTAL

Materials

Carbon dioxide with purity of 99.95% was purchased from Iwatani Sangyo Co. Ltd. (Sendai, Japan). Sigma Chemicals Co. (St. Louis, USA) supplied the oleic acid with purity of 99% (GC). Wako Pure Chemicals Industries (Tokyo, Japan) provided Oleyl alcohol with purity of 99% (GC), ethyl acetate, and *n*-hexane with purity of 96% (GC). Oleyl oleate, PTSA, and behenic acid with purities of 98% (GC), 98%, and 95% (GC), respectively, were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). All chemicals were used without further purification.

Methods

A detailed schematic diagram of the continuous flow apparatus for solubility measurements and performing reactions under SC-CO₂ is shown in Fig. 1. The solubility of a mixture of oleic acid and oleyl alcohol in SC-CO₂ was also measured. The liquid CO₂ was transferred from a cylinder equipped with an inserted dip-tube through a cleanup trap to the cooling coil and the conventional HPLC pump (JASCO Co., Tokyo, Japan). A 50 mL high-pressure reactor, as an equilibrium cell, was filled with glass beads (o.d.= 0.5 mm) to lower its dead volume and to increase the contact surface. Oleic acid and oleyl alcohol was poured in it before it was placed in the oven to measure their solubility or to carry out the reaction under SC-CO₂. Standard ss HPLC columns (5- mm I.D.×150- and 250-mm length) obtained from JASCO Co. (Tokyo, Japan) and a home made one (9.5- mm I.D.×250-mm length) were used as the catalyst container. The standard 2-μm-ss frit and glass wool were used at the end to prevent physical entrapment of non-dissolved liquid sample into the SC-CO₂. A back-pressure regulator model 880-81 from JASCO Co. (Kyoto, Japan) was used to maintain the pressure within ±0.5 bar. Three 6-port Rheodyne 7000 switching valves were also used in the apparatus. The first valve was used for bypassing the equilibrium cell and the catalyst container. The second was used for by-

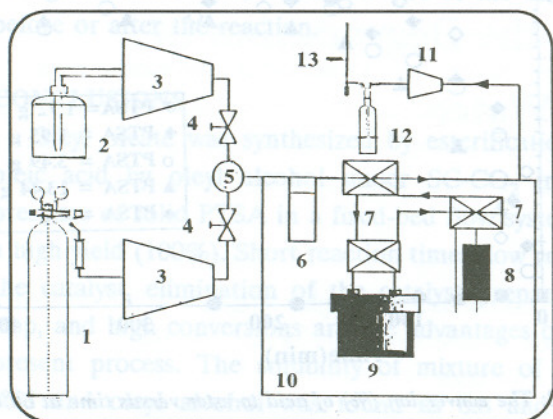


Fig. 1: Apparatus for the solubility measurements and performing reactions under supercritical carbon dioxide condition. 1: carbon dioxide cylinder with a dip-tube; 2: washing solvent; 3: pumps; 4: on-off valve; 5: ss tee; 6: preheating coil; 7: six port valve; 8: catalyst container; 9: equilibrium cell; 10: air bath; 11: back pressure regulator; 12: trap; 13: Flow meter

passing the equilibrium cell at the end of each experiment to clean the connection lines and the catalyst container. The third one was used for bypassing the catalyst container at the time of the solubility measurements.

Oleic acid and oleyl alcohol in a ~1:1 molar ratio (1.5 g of each) was added to the equilibrium cell and the temperature was raised to the desired value within 30 min. Thereafter the equilibrium cell was pressurized by CO₂ within 2 min to reach the set pressure and the relative amounts of solutes in the outflowing SC-CO₂ were measured without passing over a catalyst. The effluent samples were collected (each 10 min at the beginning and each 30 min after 30 min from the 1st sample collection) and analyzed by GC-FID as explained below. The solubility was defined as the μ moles of reactants extracted per liter of expanded gas.

In a second set of experiments the outflowing mixture was passed over a catalytic bed to perform the reaction. The reaction mixture was collected continuously in a 10 mL volumetric flask containing 5 mL of *n*-hexane as 1st trap and the expanded CO₂ gas was passed through a 2nd trap half-filled with *n*-hexane. The content of the 2nd trap was regularly analyzed after each experiment to ensure that all the material exiting from the backpressure regulator had

been collected in the collection flask. The percent conversion (%C) of oleic acid was calculated as the moles of oleyl oleate produced (the moles of oleic acid reacted) times 100 to the total moles of oleic acid dissolved in the SC-CO₂. A wet-gas meter (Shinagawa, Tokyo, Japan) measured the expanded-gas volume (within the discharge period). The flow rate was kept constant at about 250 mL/min. An air-bath thermostated oven was used to control the temperature of the equilibrium cell and the catalytic bed to within $\pm 0.5^\circ\text{C}$. The temperature of the equilibrium cell was monitored with a thermocouple controller.

Analytical method

The separation and identification of reactants and products were carried out using an on-column injection gas chromatograph (Hewlett-Packard, 5890) equipped with a flame ionization detector (FID) and mass spectrometry (a 5973 Hewlett-Packard GC-MS). The measurement was repeated four times and the average was adopted. The calculated standard error in the analysis was less than 5%. A fixed amount of behenic acid was added to the samples and standard solutions as an internal standard. To avoid the oxidation of reactants [17] in diffused daylight, all the standard and analyte samples should be prepared in amber color volumetric flasks and kept in a dark place before analysis.

RESULTS AND DISCUSSION

Solubility Measurements

Solubility of oleic acid in SC-CO₂ at 40°C and 129.45 bar was 0.45% wt, in agreement with that is reported in the literature [18]. The extraction of a mixture of oleic acid and oleyl alcohol by SC-CO₂ was investigated to determine the amount of the reactants that is fed onto the catalytic bed at the time of performing the esterification reaction. As shown in Fig. 2, the amount of oleyl alcohol and oleic acid extracted has reached a steady state ratio of ~2.5:1 beyond 50 min. Hence, the alcohol/acid molar ratio in SC-CO₂ was 2.5 at a pressure of 147 bar and a temperature of 60°C. To ensure the saturation of the SC-CO₂ coming out of the equilibrium cell, its flow rate was kept low (1 mL/min) [19]. Therefore, these

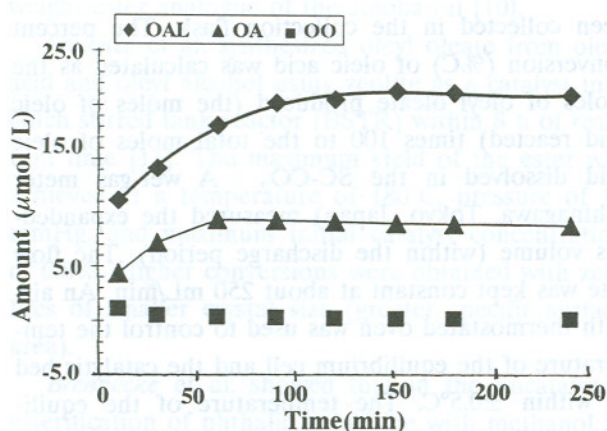


Fig. 2: Amount of reactants extracted per unit volume of the expanded gas versus time at 60°C and 147 bar. OAL: Oleyl Alcohol, OA: Oleic Acid, OO: Oleyl Oleate

values may also be considered as solubility of the mixture of the reactants in SC-CO₂.

The solubility of PTSA in pure SC-CO₂ at pressure of 147 bar was also investigated. It was negligibly small because the weight difference of the catalytic bed during the solubility measurement was so low (i.e. 1.13 μmol/L). Its solubility may be further reduced when the SC-CO₂ is saturated with the reactants before entering the catalytic bed.

The weight of the collected solutes was compared with that left in the equilibrium cell to evaluate trapping efficiency of the collection in the volumetric flasks. Small amounts of the reactants (less than 2%) could not be collected. However, using a second liquid trap the escaped reactants were collected.

Esterification reaction under SC-CO₂

When the reactants dissolved in SC-CO₂ was passed through the catalytic bed, the esterification reaction started and oleyl oleate was effectively synthesized as shown in Fig. 3. The flow apparatus was adopted to make sure that the reaction is performed only in the supercritical phase or at the surface of the solid PTSA. Negligible conversion was observed in the absence of the catalyst under SC-CO₂. In the presence of 1.7-2 g of the catalyst the reaction proceeded very rapidly and 100% conversion was achieved in a short time of 100 min at 60°C and 147 bar. It is after this time span that all oleic acid extracted and transported reacts over the solid catalyst to form a

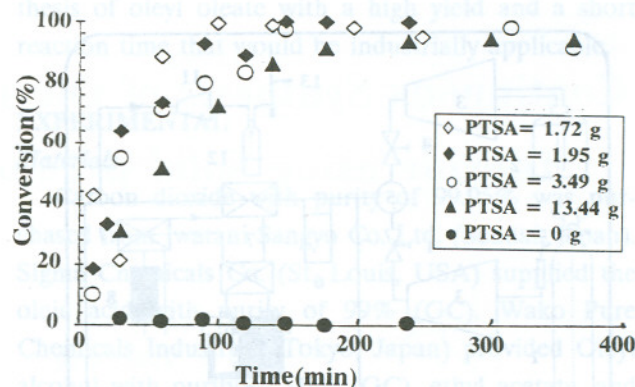


Fig. 3: The conversion (%) of acid to ester versus time at 60°C and 147 bar in the presence of different amounts of the catalyst

steady state concentration of the effluent product. This means that under the chosen conditions, all of the oleic acid undergoes the esterification reaction in a single pass, i.e. in a very fast and efficient reaction. These results show that PTSA has a high catalytic efficiency even in the solid state under SC-CO₂. Higher amounts of PTSA was used in the catalyst container, led to lower conversions. This could possibly be due to adsorption of the product on the catalyst surface. Therefore, the optimum amount of catalyst is reported as 1.7-2 g of catalyst.

The catalysts are usually impregnated onto substrates. However, in this work the PTSA powder can be directly used in a packed bed as a catalyst due to high diffusivity of the SC-CO₂, leading to the substantial simplification in the catalyst preparation step. Moreover, by using a solid catalyst below its melting point (i.e. 104°C) in a separate catalyst container, the separation process of the catalyst from product can be eliminated. From industrial and economic point of view, the method developed is attractive in giving a valuable product in a high yield.

In order to drive the reaction forward, the produced water during esterification must be removed from the catalytic bed. In a continuous system, SC-CO₂ can dissolve the water and remove it from the catalytic bed [14,18]. This promotes the reaction forward and leads to high conversions. Moreover, the possible solubility of PTSA is reduced. Visual observation of the catalyst before and after reaction revealed no change in the physical state of the catalyst. No

change was also observed in the pH of the effluent before or after the reaction.

CONCLUSIONS

Oleyl oleate was synthesized by esterification of oleic acid by oleyl alcohol under SC-CO₂ in the presence of solid PTSA in a fixed-bed flow system in a high yield (100%). Short reaction times, low cost of the catalyst, elimination of the catalyst preparation step, and high conversions are the advantages of the present process. The solubility of mixture of oleic acid and oleyl alcohol was found as 8.8 and 21.8 μmol/L respectively which leads to an alcohol/acid molar ratio of 2.5 in SC-CO₂.

ACKNOWLEDGEMENT

I, H.S.G., would like to thank JICA for supporting my stay in Japan and for providing the financial support for this work and to TNIRI for providing the research facilities. Also many thanks to all members of the chemical reaction science section of TNIRI especially Mr. K. Hatakeda, Mr. N. Saito, and Dr. M. LeClercq for their kind cooperations.

Received, 6th, February 2000 ; Accepted, 17th, April 2000

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