J. Phys. Chem. A 2007, 111, 12007−12010

Enhancing Reaction Rate of Transesterification of Glycerol Monostearate and Methanol by CO_2

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Received: August 3, 2007; In Final Form: September 20, 2007

The effect of CO_2 as a green additive on the reaction rate of transesterification of glycerol monostearate with methanol was studied at 333.15 and 343.15 K up to 10.5 MPa. It was demonstrated that addition of CO_2 in the reaction system could increase the reaction rate significantly. The phase behavior of the CO_2+methanol+glycerol monostearate ternary system was also determined at 333.15 and 343.15 K. It is shown that addition of CO_2 can enhance the miscibility of the reactant. The main reasons for the reaction rate enhancement are that CO_2 can enhance the miscibility of the reactants, reduce the viscosity of the reaction mixture, and increase the diffusion coefficients of the reactants.

Introduction

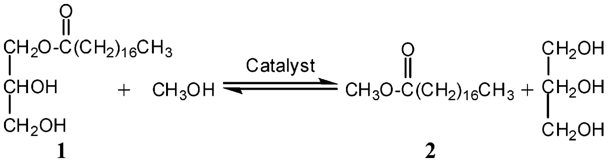
Supercritical fluids (SCFs) have been used in many fields, such as extraction and separation,[1] chemical reactions,[2] material science,[3] and microelectronics.[4] In recent years, supercritical fluid science and technology have received much attention. It is well known that many SCF technologies are environmentally more acceptable.

Chemical reactions in SCFs or under supercritical condition have many advantages.[2] For example, reaction rates, yields, and selectivity can be adjusted by varying temperature and pressure; environmentally benign SCFs (e.g., CO_2, H_2O) can be used to replace toxic solvents; mass transfer can be improved for heterogeneous reactions; and simultaneous reaction and separation can be accomplished more easily for some reactions. Supercritical (SC) CO_2 is the most attractive among SCFs because it is readily available, inexpensive, nontoxic, nonflammable, environmentally benign, and it has mild critical temperature (31.1 °C) and critical pressure (7.38 MPa).[5] Many chemical reactions have been conducted in SC CO_2, such as hydrogenation,[6] hydroformylation,[7] oxidation,[8] esterification,[9] dehydration of alcohols,[10] Friedel−Crafts alkylation,[11] etherealization,[12] Diels−Alder reaction,[13] transesterification,[14] and reaction of polymers.[15] SC CO_2 can also be used as a reactant in some reactions.[16]

It is well known that the solubility of SC or compressed CO_2 in many organic solvents is very high. As a result, the volume of the solvents increases greatly,[17] and the physical properties of the solvents, such as viscosity, diffusion coefficient, density, surface tension, and polarity, can be adjusted continuously by pressure. Some chemical reactions have been carried out in expanded liquids,[18] including polymerizations,[19] and the reaction rate and equilibrium conversion change with expansion rate of the liquids.

It is also interesting to study how SC or compressed CO_2 as a clean additive affects the properties of chemical reactions without any solvent. In this work, we studied the effect of CO_2 on reaction rate of transesterification of glycerol monostearate (**1**) and methanol to form methyl stearate (**2**) (Scheme 1). The results showed that the reaction time required for completion of the reaction could be reduced significantly in the presence of CO_2 at suitable conditions. The mechanism for the reaction rate enhancement is discussed on the basis of the effect of CO_2 on the miscibility and diffusivity of the reactants. We believe that CO_2 can be used as green additive to enhance the reaction rate of some other chemical reactions by tuning the phase behavior and other physicochemical properties of the reaction mixtures. In addition, biodiesel, which is produced by transesterification of triglycerides with small molecular alcohols, has received much attention as a renewable and cleaner fuel.[20] Our work indicates that CO_2 may be used to enhance the efficiency for producing biodiesel because the reaction studied in this work is the last step in the reaction to produce biodiesel.

SCHEME 1: Transesterification of Glycerol Monostearate (1) with Methanol To Produce Methyl Stearate (2)



1 **2**

Experimental Section

Materials. CO_2 with a purity of 99.99% was supplied by Beijing Analytical Instrument Factory. Glycerol monostearate was provided by Beijing Chemical Reagent Co. with a purity of better than 99.0%, and it was purified by recrystallization in ethanol three times prior to use. Methanol (A.R. grade), *N*,*N*-dimethylformamide (DMF, GC grade), and concentrated sulfuric acid were produced by Beijing Chemical Reagent Factory.

Apparatuses. The schematic diagram of the apparatus used to determine the phase behavior is shown in Figure 1, which was similar to that used previously.[14] It consisted mainly of a CO_2 cylinder, a high-pressure pump (DB-80), a magnetic stirrer,

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10.1021/jp0762222 CCC: $37.00

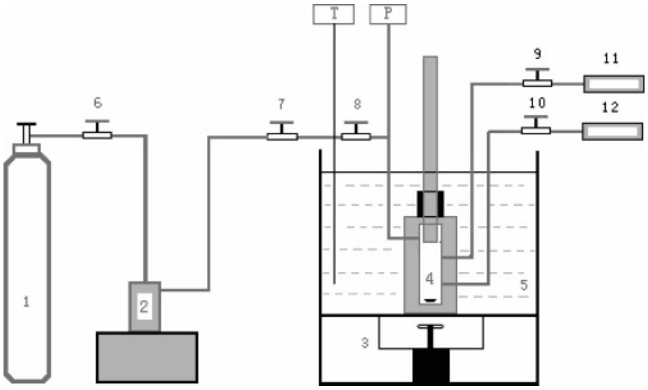

Figure 1. The schematic diagram of the apparatus used to determine phase behavior: (1) CO_2 cylinder; (2) high-pressure pump; (3) magnetic stirrer; (4) view cell; (5) constant temperature water bath; (6−10) valves; (11,12) sample bombs; (T) temperature controller; (P) pressure gauge.

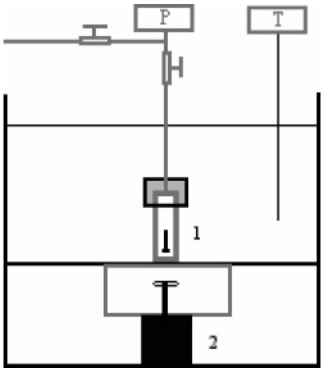

Figure 2. The schematic diagram of the apparatus used for the reaction: (1) reactor; (2) magnetic stirrer; (P) pressure gauge; (T) temperature controller.

a constant temperature water bath, a high-pressure volume-variable view cell, two sample bombs of 15 mL, a temperature controller, and a pressure gauge. The high-pressure view cell was composed of a stainless steel body, a stainless steel piston, and two borosilicate glass windows. The two windows were installed on opposite sides of the cell over the whole height so that phase behavior could be observed clearly. The volume of the view cell could be changed in the range from 20 to 50 mL by moving the piston. The view cell was immersed in the constant temperature water bath controlled by a Haake-D3 temperature controller, and the temperature was measured by an accurate mercury thermometer with the accuracy of better than 0.05 K. The pressure gauge was composed of a pressure transducer (FOXBORO/ICT model 93) and an indicator, and its accuracy was 0.025 MPa in the pressure range of 0−20 MPa.

The apparatus used to study the transesterification of glycerol monostearate with methanol is illustrated in Figure 2. It was composed of a stainless steel reactor of 15 mL, a constant temperature water bath, a magnetic stirrer, a pressure gauge, and a temperature controller.

Procedures To Determine the Phase Behavior. The phase behavior of the CO_2+methanol+glycerol monostearate system was studied in the absence of catalyst to avoid composition change originated from reaction, and the compositions of the methanol-rich phase (middle phase) and the glycerol monostearate-rich phase were determined. The procedures were similar to that used previously.[14] It is known from the phase rule that at fixed temperature and pressure, compositions of all phases are fixed if there exist three phases. On the basis of this principle, we controlled the experimental condition in such a way that there were three phases in the system. In a typical experiment to determine the composition of the glycerol monostearate-rich phase, suitable amounts of methanol and glycerol monostearate were charged into the view cell, and the air in the cell was replaced by CO_2. The view cell was placed into the constant temperature water bath. Next, CO_2 was charged into the system slowly using the high-pressure pump, and the mixture was stirred. After equilibrium was reached, some sample of the bottom phase was collected by opening the valve of the sample bomb slowly. At the same time, the volume of the view cell was adjusted to keep the pressure unchanged during the sampling process. The valve was closed after the desired amount of sample was collected. The sample bomb was removed for composition analysis. To analyze the composition of the sample, the mass of the sample bomb was determined by an electronic balance (Mettler MP1200) with a resolution of 0.001 g. The mass of the sample was known by the mass difference of the sample bomb before and after sampling. Next, the sample bomb was cooled in ice and CO_2 was released slowly through a cooled trap with DMF as the absorbent. The amount of methanol in the cooled trap was known by gas chromatography (Agilent 4890D, Agilent Technologies Inc.) analysis. The mass of the methanol and glycerol monostearate in the sample bomb was determined gravimetrically. The mass of CO_2 was known from the total mass of the sample and the mass of methanol and glycerol monostearate. The mass of methanol and glycerol monostearate was known after vaporization of methanol. Using the similar procedures, the composition of the methanol-rich phase was determined independently.

To reach equilibrium is crucial for studying phase behavior. Our experiments showed that the system could reach equilibrium in 1 h for the system studied in this work, which was known by the fact that the composition of the phases was independent of the equilibration time after 1 h.

Procedures To Conduct the Reaction. In a typical experiment, 0.01 mol of glycerol monostearate (3.586 g), 0.045 mol of methanol (1.442 g), and 0.03 g of concentrated sulfuric acid (catalyst) were loaded into the reactor. Next, the reactor was placed in the constant temperature water bath. CO_2 was charged into the reactor to desired pressure, and the system was stirred. After a suitable reaction time, the reactor was cooled rapidly in ice and CO_2 was released slowly from the reactor. The amount of the product methyl stearate in the reactor was analyzed by gas chromatography (Agilent 4890D, Agilent Technologies Inc.) using DMF as internal standard.

Results and Discussion

Reaction. The transesterification of glycerol monostearate with methanol to produce methyl stearate was carried out at 333.15 and 343.15 K and at different CO_2 pressures. In the reaction system, the original molar ratio of methanol to glycerol monostearate was 4.5, and the weight ratio of concentrated sulfuric acid to methanol was 0.02. Figures 3 and 4 show the dependence of conversion on reaction time at different pressures, including the results without CO_2. It can be observed that the reaction rate of the reaction in the presence of CO_2 is much faster than that without CO_2 and the rate increases significantly with increasing pressure of CO_2. In other words, CO_2 can enhance the reaction rate significantly. For example, at 343.15 K and 10.5 MPa, glycerol monostearate can approach complete conversion within 5 h, while about 35 h is required to reach similar conversion in the absence of CO_2. Figure 5 demonstrates the dependence of temperature on the conversion at 10.5 MPa and in the absence of CO_2. As expected, the conversion increases with increasing temperature. At other pressures, the effect of temperature on the conversion is similar.

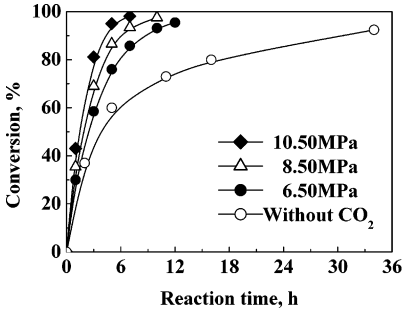

Figure 3. Dependence of conversion of glycerol monostearate on reaction time at 333.15 K and different pressures.

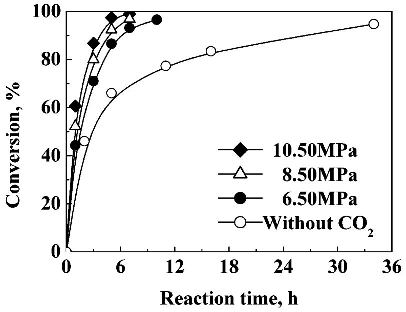

Figure 4. Dependence of conversion of glycerol monostearate on reaction time at 343.15 K and different pressures.

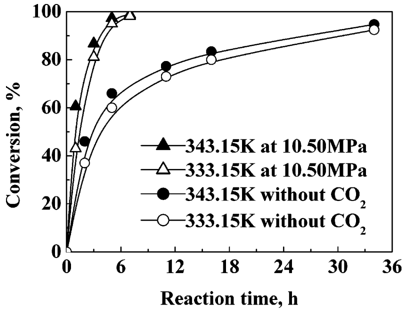

Figure 5. Comparison of conversion of glycerol monostearate at 333.15 and 343.15 K at some typical conditions.

We also studied the effect of stirring speed on the reaction rate in the range of 150−600 rpm at 10.5 MPa and without CO_2 at the two temperatures. The results showed that the reaction rate was independent of stirring speed.

Discussion. There are several possible reasons for the reaction rate enhancement by CO_2. For example, addition of CO_2 into the reaction mixtures affects the viscosity and diffusion coefficient of the reactants. CO_2 may influence the phase behavior of the reaction system. All of these influence the reaction rate. In this work, we studied the phase behavior of the glycerol monostearate+methanol+CO_2 ternary system at 333.15 and 343.15 K, respectively.

Figure 6 demonstrates the effect of pressure on the mole fraction of methanol in the glycerol monostearate-rich phase and methanol-rich phase on CO_2-free basis. At a fixed temperature, there are three phases between the two curves, CO_2-rich phase, methanol-rich phase (middle phase), and glycerol monostearate-rich phase (bottom phase). There are two phases in the system outside the three-phase region, vapor phase and liquid phase. It is interesting that addition of CO_2 can increase the concentration of glycerol monostearate in the methanol-rich phase and that of methanol in the glycerol monostearate-rich phase. In other words, CO_2 can enhance the miscibility of the methanol and glycerol monostearate.

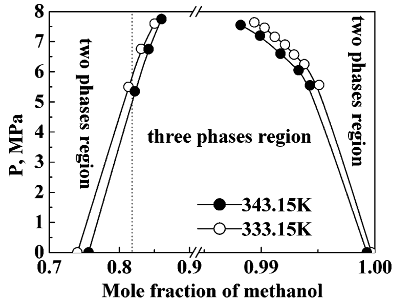

Figure 6. Effect of CO_2 pressure on the mole fraction of methanol in the glycerol monostearate-rich phase and methanol-rich phase (CO_2-free basis); the dotted line represents the mole fraction of methanol in the glycerol monostearat+methanol mixture charged into the reactor.

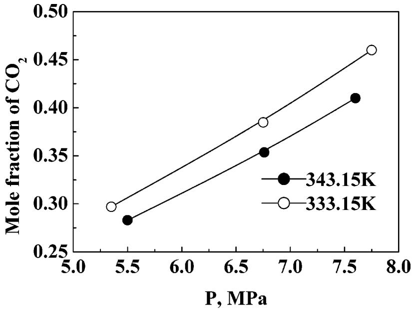

Figure 7. Effect of pressure on mole fraction of CO_2 in the glycerol monostearate-rich phase at 333.15 and 343.15 K.

The original mole fraction of methanol in the methanol+glycerol monostearate mixture charged into the reactor is marked in Figure 6 (the dotted line). The volume ratio of the reactant mixture and the reactor was the same as that in the phase behavior. The methanol and glycerol monostearate in the reactor is immiscible in the absence of CO_2, and the concentration of glycerol monostearate in methanol-rich phase is very low. The sulfuric acid distributed between the two phases. At 333.15 and 343.15 K, the concentration (mol/g) ratios of sulfuric acid in the methanol-rich and glycerol monostearate-rich phases were 3.80 and 3.64, respectively, which was determined by conventional titration method using phenolphthalein as the indicator. The large difference of the concentration of sulfuric acid in the two phases and the existence of the liquid/liquid interface were not favorable to the reaction. However, methanol and glycerol monostearate became miscible in the presence of CO_2 at suitable pressures, and the reaction took place in the liquid phase where sulfuric acid existed, which was favorable to the reaction. We believe that the effect of CO_2 on the phase behavior or miscibility of the reaction system is one of the main reasons for the significant enhancement of reaction rate.

Concentration of CO_2 in the reactants may also affect the reaction rate. Figures 7 and 8 show the mole fraction of CO_2 in the glycerol monostearate-rich phase and methanol-rich phase as a function of pressure at different temperatures determined in this work. As expected, the mole fraction of CO_2 in the two liquid phases increased with increasing pressure. It can be deduced that the solubility of CO_2 in the reaction mixture increased with increasing pressure. It has been demonstrated that dissolution of CO_2 in liquids can reduce the viscosity of liquids significantly.[21] Therefore, we can conclude that addition of CO_2 can reduce the viscosity of the reaction mixture and increase the diffusion coefficients of the reactants, which is also favorable to the reaction. The effect of CO_2 on the viscosity and diffusion was larger at higher pressures. Reduction of viscosity and increase of diffusivity of the reactants are the other reasons for the reaction rate enhancement by CO_2.

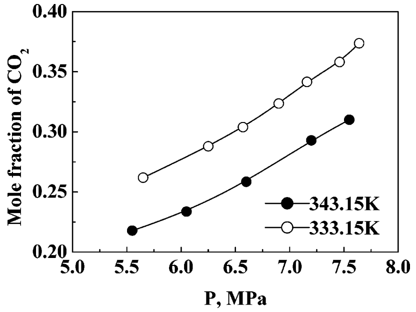

Figure 8. Effect of pressure on mole fraction of CO_2 in the methanol-rich phase at 333.15 and 343.15 K.

Conclusion

The effect of CO_2 on the reaction rate of transesterification of glycerol monostearate with methanol has been studied at 333.15 and 343.15 K and at different pressures. The reaction rate increases significantly with increasing pressure of CO_2. The main reasons for the reaction rate enhancement are that CO_2 can increase the miscibility of the reactants, reduce the viscosity of the reaction mixture, and increase the diffusion coefficients of the reactants. We believe that CO_2 can be used as green additive to enhance the reaction rate of some other chemical reactions, including production of biodiesel because the reaction studied in this work is the last step in the reaction to produce biodiesel.

Acknowledgment. This work was supported by the National Key Basic Research Project of China (2006CB202504) and the National Natural Science Foundation of China (20633080, 20473105).

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