

CONTINUOUS ESTERIFICATION IN SUPERCRITICAL CARBON DIOXIDE

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Heterogeneous esterification of 2-ethyl-1-hexanol and 2-ethyl hexanoic acid using AMBERLYST 15 as solid acid-catalyst in supercritical carbon dioxide (SC-CO₂) has been studied. Effect of pressure (150, 200, and 250 bar), temperature (75, 110, and 140 °C), flow rate of liquid CO₂ (0.4, 0.6, and 0.8 mL.min⁻¹), type of sample collection, and mole ratio of alcohol to acid (2:1, 1:1, and 1:2) on ester yield have been studied. With increasing temperature from 75 to 110 °C the yield is increased, but at 140 °C the yield is significantly decreased. The flow rate of SC-CO₂ and the mole ratio of the alcohol to the acid have no significant effect on the esterification yield.

Introduction

Supercritical carbon dioxide (SC-CO₂) is an attractive and suitable solvent for chemical reaction because of low T_c and P_c, non-toxicity, high diffusivity, pressure tunability, and ease of separation from products. Heterogeneous catalytic chemical reactions, in SC-CO₂, generally are performed using either a continuous flow reactor or a batch reactor [1]. There are many reactions that are carried out in continuous flow reactors such as dehydration [2], esterification [3], hydrogenation [4]. There are also many examples for batch processes such as polymerization [5] and esterification [6].

Esterification reactions are equilibrium reactions that may be displaced to increase product yield by choosing excess amount of reacting materials, or removing products from reaction vessel but it may take many hours (>10h) to complete. Esterification reaction in SC-CO₂ offers some advantages over conventional processes such as: higher reaction rates, continuous removal of product(s), selective production of esters and free from solvent residue and final work-up processes.

In this work, 2-ethyl-hexyl-2-ethyl hexanoate, 2E2E, was continuously synthesized from the esterification of 2-ethyl-1-hexanol and 2-ethyl hexanoic acid in the presence of AMBERLYST 15 as a solid-acid catalyst. The products were continuously extracted from catalyst bed by SC-CO₂.

Experimental Section

(i) **Materials.** Carbon dioxide with purity of 99.5 mass% was purchased from ZamZam Co. Ltd. (Isfahan, Iran). 2-Ethyl-1-hexanol, 1-hexanol and n-hexane were purchased (with purity > 99%) from Merck Chemical Co. 2-Ethyl hexanoic acid was purchased from Tat Chemical Co. (purity > 99%) Isfahan, Iran. 2E2E and 2-ethyl hexyl ether (2EHE) were synthesized with purity of > 99% verified by GC.

(ii) **Apparatus and procedure.** The esterification reaction was carried out using a continuous flow apparatus. In each experiment desired amount of 2-ethyl-1-hexanol and 2-ethyl hexanoic acid were placed in a 10 mL equilibrium cell and filled with glass beads in order to decrease dead volume and increase contact surface of solutes with SC-CO₂. The exit end of the equilibrium cell was connected to bottom (in order to prevent the channeling effect) of catalyst bed (volume = 15 mL). The equilibrium cell and catalyst bed were placed in

an air oven and temperature was maintained within $\pm 1^\circ\text{C}$ using a thermocouple controller device (Alton Ray Co., model TC14, Tehran, Iran).

All experiments were performed at equilibrium and saturation conditions [7]. The liquid carbon dioxide was pressurized, by a JASCO model PU-980 reciprocating pump through a preheating coil in the oven, that enable CO_2 to reach oven temperature before entering the equilibrium cell. At the beginning of each experiment, the system was maintained at the desired temperature and pressure for at least 30 min. The saturated SC-CO_2 passes through the catalytic bed, where chemical reactions take place and SC-CO_2 along with products and unreacted substrates was depressurized through a back-pressure regulator (JASCO, BP 1580-81). After the trap, the flow rate of expanded CO_2 gas was measured with wet gas meter (model W-NK-18, Shinagawa, Japan). In all experiments Amberlyst 15 was used as catalyst. It was dried to constant weight before use in an air oven at 90°C .

(iii) Analytical Methods. In this work a modified trap as shown in Figure 1 was designed and used. The main parts of collection are a cooling coil and a condenser. The coolant liquid (ethylene glycol) was circulated (LAUDA E104) in a coil. The coil and the collection vial (a two neck 5 mL flask) were submerged into a 250 mL beaker that was filled with ethylene glycol, and the coolant was circulated around the condenser. The temperature of collection vial was -8 to -10°C and the condenser temperature was set at -12°C .

The trapped mixture was transferred into a volumetric flask and after addition of 1 mL 1-hexanol, as an internal standard, the volume were made to 5 mL with n-hexane. The samples were analyzed with GC-TCD with a packed SE-30 column (Shimadzu Co. model GC-14A) using a temperature programming as follows: The injection port and the detector temperature of GC were set at 240°C and 250°C respectively. The column temperature was programmed as zero min. at 50°C , 0 min at 90°C , and 10 min at 240°C with the temperature ramp of $6^\circ\text{C}\cdot\text{min}^{-1}$ and $40^\circ\text{C}\cdot\text{min}^{-1}$, respectively.

2E2E and 2EHE were determined by external calibration and alkene was determined based on mass balance of initial mole of 2-ethyl-1-hexanol. The yield of 2E2E was calculated based on number of reacted moles of 2-ethyl hexanoic acid. The yields of 2EHE and alkene were calculated based on initial mole of 2-ethyl-1-hexanol.

Results and Discussions

In our previous works [8] it was shown that the solubility of 2-ethyl-1-hexanol and 2-ethyl hexanoic acid in SC-CO_2 , for a 1:1 molar ratio of alcohol to acid in the equilibrium cell, were similar. This co-solubility may be due to the existence of intermolecular hydrogen bonding between molecules of 2-ethyl-1-hexanol and 2-ethyl hexanoic acid. Moreover similar solubility was maintained versus time [7].

In this work the concept of co-solubility was used to perform chemical reaction in SC-CO_2 . The SC-CO_2 dissolves 2-ethyl-1-hexanol and 2-ethyl hexanoic acid and then passes through the heterogeneous catalyst where dehydration, etherification and esterification reactions may take place.

The effect of the temperature on product yield is shown in Table 1. Raising the temperature from 75 to 110°C increases the conversion and the product yields. With further increase in temperature from 110 to 140°C a significant reduction in conversion of alcohol and acid to ester takes place. That might be due to catalyst deactivation [2] or desulfonation.

The effect of pressure on the esterification was also studied in the pressure range of 150 to 250 bar (Table 2). At higher pressures the solubility of 2-ethyl-1-hexanol and 2-ethyl hexanoic acid and the residence time over the catalyst are increased [2]. The yield of esterification reaction is approximately constant and independent of pressure. This behavior

may be due to the fact that in the pressures beyond 180 bars solubility of 2-ethyl-1-hexanol and 2-ethyl hexanoic acid remains constant and raising the pressure has no effect on their solubility [9]. Therefore in the esterification reaction increase in pressure do not have any effect on the solubility of the acid and the alcohol.

The effects of variation of the molar ratio (r) of 2-ethyl-1-hexanol to 2-ethyl hexanoic acid from 1:2 to 2:1 are shown in Table 3. With increasing the molar ratio, the yield of 2E2E and 2EHE are changed slightly. This shows that the esterification reaction is controlled by 2-ethyl hexanoic acid protonation. Increasing the amount of 2-ethyl-1-hexanol promotes the alcohol protonation and increases the yield of 2EHE and alkene formation.

The effect of liquid CO₂ flow rate on esterification reaction was also studied. There are no significant changes in the substrates conversion and product yields. This is because of low and similar solubilities of the alcohol and the acid at 150 bar and 110 °C [9].

The reusability of Amberlyst 15 was also studied and the results are shown in Table 4. After each run the catalyst was washed with methanol, dried in an oven at 90 °C up to constant weight. The results show that the yield of 2E2E formation decreases in later run.

To investigate the effect of sample trapping method, a purge test was performed and the results are shown in Table 5. The purge test was performed with (1) n-hexane solvent, (2) glass beads, (3) glass beads and n-hexane with modified sample trapping (Figure 1). The results show that by solvent collection the loss due to aerosol formation significantly are reduced. The aerosol formation is very significant in glass beads sample trapping method and the loss in the trapped sample is about 40% for the alcohol and 30% for the acid and the ester. But in modified methods the loss of the test materials is very small (5% for alcohol and 4% for acid and ester). The efficiency of the reactant(s) and product(s) trapping are listed in Table 5. The modified system can trap acid, alcohol, and ester with the same trapping efficiencies. There are many factors that reduce ester yield in continuous flow system such as removal of unreacted acid from catalytic bed due to high solubility of 2-ethyl hexanoic acid in SC-CO₂ [10] and dehydration of alcohol in the presence of strong solid-acid catalyst that converts the alcohol to alkene and promotes ether formation (as side reactions). We are working to improve these drawbacks and modify the system.

Conclusion

The continuous esterification reaction was performed in SC-CO₂. The benefits of the continuous esterification in SC-CO₂ are easy separation of product(s) from solvent and unreacted materials, smaller reactors, and milder condition were experienced. Our results show that due to high solubility of 2-ethyl hexanoic acid in SC-CO₂ it is removed from the bed and the yield can not be improved from the catalytic bed. The dehydration of 2-ethyl-1-hexanol and its etherification to 2EHE are the main side products that reduce the ester yield. The modified trap has significantly lowered the aerosol formation and increased the trapping efficiency to prevent the sample loss

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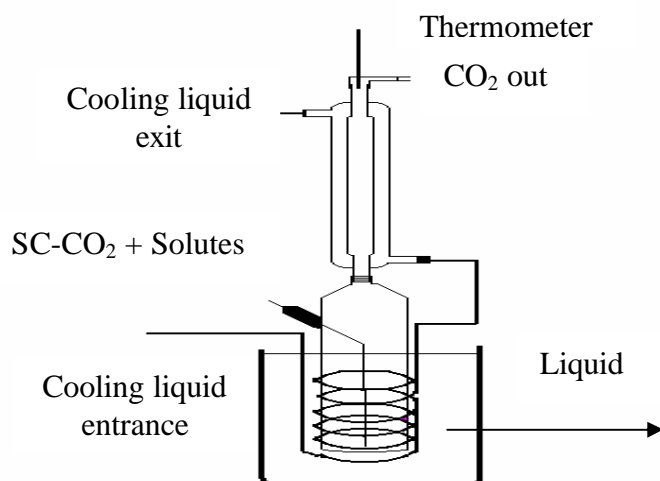


Figure 1. Modified trap

Table 1. Continuous Synthesis of 2E2E from 2-Ethyl-1-hexanol + 2-Ethylhexanoic Acid in SC-CO₂ at different temperatures^a

T (°C)	Yield (%)		
	2E2E	2EHE	Alkene
75	15.20	ND ^b	65.00
110	27.38	1.57	70.52
140	0.24	0.91	98.85

^a Other reaction conditions: Amberlyst 15 as catalyst; 15 mL reactor; flow rate of CO₂ = 0.4 mL/min; pressure of 150 bar; alcohol to acid ratio of 1.0. ^b Not detectable.

Table 2. Continuous Formation of 2E2E from 2-Ethyl-1-hexanol + 2-Ethylhexanoic Acid in SC-CO₂ at different pressures^a

P (bar)	Yield (%)		
	2E2E	2EHE	Alkene
150	22.51	2.08	75.00
200	21.00	2.00	77.00
250	27.38	2.92	69.70

^a Other reaction conditions: Amberlyst 15 as catalyst; 15 mL reactor; flow rate of CO₂ = 0.4 mL/min; Temperature of 75 °C; alcohol to acid mole ratio of 1.0.

Table 3. Continuous Formation of 2E2E from 2-Ethyl-1-hexanol + 2-Ethylhexanoic Acid in SC-CO₂ at different Alcohol to Acid Ratios^a

r	Yield (%)		
	2E2E	2EHE	Alkene
1.0	22.51	2.08	75.00
2.0	31.90	11.55	68.50
0.5	24.63	3.37	71.37

^a Other reaction conditions: Amberlyst 15 as catalyst; 15 mL reactor; flow rate of CO₂ = 0.4 mL/min; at 150 bar and 110 °C; alcohol to acid mole ratio of 1.0.

Table 4. Continuous Formation of 2E2E from 2-Ethyl-1-hexanol + 2-Ethylhexanoic Acid in SC-CO₂^a

Catalyst	Yield (%)		
	2E2E	2EHE	Alkene
Fresh	22.51	2.08	75.00
Recovered	17.97	4.56	77.47

^a Other reaction conditions: Amberlyst 15 as catalyst; 15 mL reactor; CO₂ flow rate of 0.4 mL/min; at 150 bar and 110 °C; the alcohol to the acid ratio of 1.0

Table 5. The Result of Purge Test

Purge	Recovery (%)		
	2-Ethyl-1-hexanol	2-Ethyl hexanoic acid	2E2E
1 ^a	89.38	94.51	93.56
2 ^b	66.48	72.10	71.37
3 ^c	94.61	96.80	95.69

^a Trapped using n-hexane; ^b Trapped on the glass beads; ^c Trapped on the glass beads and n-hexane with the modified method; CO₂ flow rate of 0.6 mL/min; at 150 bar and 110 °C; purge time of 6 h.

Table 6. Continuous Formation of 2E2E from 2-Ethyl-1-hexanol + 2-Ethylhexanoic Acid in SC-CO₂ Using Different Collection Methods^a.

Collection Method	Yield (%)		
	2E2E	2EHE	Alkene
1 ^b	22.27	3.14	74.10
2 ^c	24.41	4.29	71.29
3 ^d	22.30	3.96	70.83

^a Other reaction conditions: Amberlyst 15 as catalyst; 15 mL reactor; CO₂ flow rate of 0.6 mL/min; at 150 bar and 110 °C; the alcohol to the acid ratio of 1.0. ^b Trapped over glass beads.

^c Trapped in n-hexane solvent. ^d Trapped over glass beads, n-hexane and the modified system.