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Critical temperatures and pressures of reacting mixture in synthesis of dimethyl carbonate with methanol and carbon dioxide

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Abstract

Critical temperatures and pressures of nominal reacting mixture in synthesis of dimethyl carbonate (DMC) from methanol and carbon dioxide (quaternary mixture of carbon dioxide + methanol + water + DMC) were measured using a high-pressure view cell. The results suggested that the critical properties of the reacting mixture depended on the reaction extent as well as its initial composition (initial ratio of carbon dioxide to methanol). Such information is essential for determining the reaction conditions when one intends to carry out the synthesis of DMC with CO_2 and methanol under supercritical conditions.

Keywords: Critical properties; Reacting mixture; Supercritical fluid; Dimethyl carbonate; Synthesis; Methanol; Carbon dioxide

Dimethyl carbonate (DMC) can be used as fuel additives, carbonylating reagents, alkylating reagents and polar solvents. Moreover, DMC exhibits wide applications in synthesis of polycarbonate and polyurethane. Direct synthesis of DMC from carbon dioxide and methanol is one of the most promising routes, because carbon dioxide is utilized as a carbon source and poisonous or corrosive reagents such as phosgene are avoided in this direct route [1,2]. Several articles have reported the synthesis of DMC with carbon dioxide and methanol, and found that high yield and reaction rate were obtained at near supercritical conditions [2–4]. The supercritical reaction conditions were often presumed with the critical point of the initial reacting mixture or one pure substance in the reactants like carbon dioxide; this is however improper, because the critical properties of the reacting mixture depend on the initial composition and the reaction extent [5–7]. A careful determination of phase state and critical properties of the reacting mixture may be favorable to optimize the operating conditions and improve the synthesis efficiency. Although the critical properties of some related mixtures have been reported [8,9], a systematical study of the critical properties of the reacting mixture in the direct synthesis of DMC with carbon dioxide and methanol along the reaction course is still imperative.

In this work, the critical temperatures and pressures of the nominal reacting mixture in synthesis of DMC from methanol and carbon dioxide (quaternary mixture of carbon dioxide + methanol + water + DMC) were measured using a high-pressure view cell. The dependences of the critical properties of the reacting mixture upon the initial ratio of carbon dioxide to methanol and the reaction extent were estimated.

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1. Experimental

The critical properties were measured with the same view cell and procedure as described previously [7]. Briefly, the view cell was first evacuated with a vacuum pump before each measurement. Based on the composition of the nominal reacting mixture, liquid mixture (methanol + water + dimethyl carbonate) was charged with a syringe and carbon dioxide were pressurized into the cell through a high pressure sampling tube; the exact amounts of each component can be determined by the weight change of the syringe or sampling tube before and after charging. The amount of the mixture in the cell was controlled to make the density of the mixture close to or slightly higher than the critical density. The eligibility of the mixture amount was identified through the observation of the appearance of the red-glow critical opalescence as well as nearly equal volumes of the two phases when phase separation occurred at the critical point; this can be achieved through controlling the amounts of liquid mixture and gaseous carbon dioxide charged into the cell. The critical temperature and pressure readings were made by occurrence of strong red-glow critical opalescence and reappearance of a meniscus on slow cooling (less than 0.3 K min^{-1}) through the critical point. The readings were repeatable at least for three cycles, which indicated that the change in the mixture composition due to any reaction during the period of measurement is negligible. The uncertainties of the critical temperature, critical pressure, and mole fraction were estimated to be within ±0.3 K, ±0.03 MPa, and ±0.003, respectively.

2. Results and discussion

For the direct synthesis of DMC from carbon dioxide and methanol, as shown in following equation:

$$CO_2 + 2CH_3OH \rightarrow CH_3OCOOCH_3 + H_2O \quad (1)$$

The consumption of carbon dioxide and methanol during the reaction will produce dimethyl carbonate and water; the nominal reacting mixture is a quaternary mixture of carbon dioxide (1) + methanol (2) + water (3) + DMC (4) and its composition may be determined according to the reaction extent (methanol conversion) and the initial mole ratio of carbon dioxide to methanol (x_1/x_2). The critical properties of the nominal reacting mixture with the initial x_1/x_2 value being 1–4 are listed in Table 1. Based on that, the dependences of the critical properties of the reacting mixture upon its initial composition (x_1/x_2) and methanol conversion are illustrated in Fig. 1.

Table 1
Critical properties of the quaternary mixture carbon dioxide (1) + methanol (2) + water (3) + dimethyl carbonate (4)

x_1	x_2	x_3	x_4	T_C (K)	P_C (MPa)	x_1	x_2	x_3	x_4	T_C (K)	P_C (MPa)
Initial molar fraction $x_1/x_2 = 1$											
0.500	0.500	0.000	0.000	444.2	15.55	0.412	0.235	0.177	0.176	485.0	14.42
0.474	0.421	0.053	0.053	455.2	15.30	0.394	0.182	0.212	0.212	498.0	14.12
0.444	0.333	0.111	0.111	469.7	15.01	0.355	0.065	0.290	0.290	512.7	12.94
Initial molar fraction $x_1/x_2 = 1.5$											
0.600	0.400	0.000	0.000	419.0	16.54	0.545	0.182	0.136	0.136	454.3	16.41
0.583	0.333	0.042	0.042	428.6	16.49	0.524	0.095	0.191	0.191	466.8	16.27
0.565	0.261	0.087	0.087	441.7	16.60	0.500	0.000	0.250	0.250	482.9	16.25
Initial molar fraction $x_1/x_2 = 2$											
0.667	0.333	0.000	0.000	402.8	16.62	0.623	0.113	0.132	0.132	436.4	17.34
0.649	0.246	0.053	0.053	417.2	16.96	0.615	0.077	0.154	0.154	452.5	17.59
0.636	0.182	0.091	0.091	425.8	17.09	0.600	0.000	0.200	0.200	460.8	17.72
Initial molar fraction $x_1/x_2 = 3$											
0.750	0.250	0.000	0.000	386.4	16.08	0.733	0.133	0.067	0.067	411.7	17.26
0.744	0.205	0.026	0.026	393.5	16.56	0.722	0.056	0.111	0.111	430.2	18.90
0.737	0.158	0.053	0.053	402.9	16.98	0.718	0.028	0.127	0.127	441.2	19.68
Initial molar fraction $x_1/x_2 = 4$											
0.800	0.200	0.000	0.000	377.7	15.43	0.787	0.085	0.064	0.064	402.8	17.79
0.796	0.163	0.020	0.020	387.7	16.27	0.783	0.043	0.087	0.087	413.1	18.59
0.792	0.125	0.042	0.042	394.7	16.90	0.778	0.000	0.111	0.111	429.2	20.62