Critical Temperatures and Pressures of Several Binary and Ternary Mixtures Concerning the Alkylation of 2-Methylpropane with 1-Butene in the Presence of Methane or Carbon Dioxide

Junfen Li,[†,‡] Zhangfeng Qin,[†] Guofu Wang,[†] Mei Dong,[†] and Jianguo Wang*[,†]

State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, P.O. Box 165, Taiyuan, Shanxi 030001, People's Republic of China, and Graduate School of the Chinese Academy of Sciences, Beijing 100039, People's Republic of China

The critical temperatures and pressures of four binary mixtures (2-methylpropane + 1-butene, 2,2,4-trimethylpentane + 2-methylpropane, 2-methylpropane + methane, and 2-methylpropane + carbon dioxide) and four ternary mixtures (2-methylpropane + 1-butene + methane, 2-methylpropane + 2,2,4-trimethylpentane + methane, 2-methylpropane + 1-butene + carbon dioxide, and 2-methylpropane + 2,2,4-trimethylpentane + carbon dioxide) were measured using a high-pressure view cell. On the basis of that, the dependences of the critical properties of the reacting mixture in the alkylation of 2-methylpropane with 1-butene in the presence of a solvent methane or carbon dioxide upon the initial ratio of 2-methylpropane/1-butene, amounts of methane or carbon dioxide added, and reaction extent were estimated.

Introduction

Alkylation of 2-methylpropane with butene is an important process for the production of trimethylpentane which is an ideal component of gasoline because of its high research octane numbers (RON) and low volatility. The present commercial routes for the alkylation rely on using H_2SO_4 and HF as catalysts, which may cause serious corrosion and pollution problems. Therefore, considerable efforts have been made to develop heterogeneously catalytic processes using solid acid catalysts.[1−5] However, the solid acid catalysts often suffer from fast deactivation in the alkylation, which hinders the new process from rapid industrial application.

Performing reactions under supercritical conditions rather than in the gas or liquid phase could be an interesting option for improving equilibrium conversion, enhancing reaction rate, increasing throughput, prolonging catalyst lifetime, and making the process more environmentally benign.[6−8] Supercritical fluids (SCFs) with liquidlike densities and enhanced extraction ability are effective for the removal of coke precursors and thereby extension of catalyst activity. Moreover, a supercritical reaction is often very sensitive to the reaction conditions; operation in the regions near the critical point of the reacting system is most desirable to make the most of the unique characteristics of SCFs.[8] By carrying out the alkylation of 2-methylpropane with butene over solid acid catalysts under supercritical 2-methylpropane,[9−11] the catalyst lifetime can be prolonged. However, a temperature higher than 410 K is necessary to achieve supercritical conditions, which may lead to undesirable side reactions such as oligomerization and cracking. To cater to the best reaction conditions for alkylation, addition of suitable solvents is necessary to tune the critical properties of the reacting mixture and to alter the reaction behavior;[12−14] chemically inert substances such as alkanes, carbon dioxide, and water are often used as the supercritical solvent.

Methane and carbon dioxide with low critical temperature are considered as proper solvents to tune the critical properties of the reacting mixture in the alkylation of 2-methylpropane with butene. Using carbon dioxide as a solvent, butene conversion can be maintained at a steady level and C_8 alkylates production can be enhanced properly under the altered supercritical conditions.[15−17] To determine the proper operating parameters for the reaction under supercritical conditions and make the most of the unique characteristics of SCFs, it is essential to be cognizant of the critical properties of the reacting mixture.

In this work, the critical temperatures and pressures of four binary mixtures (2-methylpropane + 1-butene, 2,2,4-trimethylpentane + 2-methylpropane, 2-methylpropane + methane, and 2-methylpropane + carbon dioxide) and four ternary mixtures (2-methylpropane + 1-butene + methane, 2-methylpropane + 2,2,4-trimethylpentane + methane, 2-methylpropane + 1-butene + carbon dioxide, and 2-methylpropane + 2,2,4-trimethylpentane + carbon dioxide) were measured using a high-pressure view cell. On the basis of these results, the critical properties of the reacting mixture in the alkylation of 2-methylpropane with 1-butene in the presence of a solvent methane or carbon dioxide were estimated. The determination of operating conditions for the alkylation of 2-methylpropane with 1-butene under supercritical conditions using methane or carbon dioxide as solvent was thereby clarified.

Experimental Section

2-Methylpropane (mole fraction $x > 99.9$ %) and 1-butene ($x > 99.95$ %) were purchased from Tianjin Summit Specialty Gases Co., Ltd. 2,2,4-Trimethylpentane ($x > 99.0$ %) was supplied by Tianjin Dagang Xingshi Chemical Plant. Methane ($x > 99.9$ %) and carbon dioxide ($x > 99.95$ %) were obtained from the Beijing Analytical Instrument Corporation. All these

* To whom correspondence should be addressed. E-mail: iccjgw@sxicc.ac.cn. Phone: +86-351-4046092. Fax: +86-351-4041153.
[†] Institute of Coal Chemistry, Chinese Academy of Sciences.
[‡] Graduate School of the Chinese Academy of Sciences.

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Table 1. Critical Properties of the Pure Substances

	T_c/K		P_c/MPa		ρ_c/g·cm^{-3}	
substance	this work	ref	this work	ref	this work	ref
carbon dioxide	304.8	304.1[19]	7.38	7.38[19]	0.473	0.469[19]
2-methylpropane	409.9	407.8[20]	3.62	3.64[20]	0.220	0.224[20]
1-butene	421.2	419.5[21]	4.00	4.02[21]	0.233	0.233[21]
2,2,4-trimethylpentane	544.1	543.8[20]	2.57	2.57[20]	0.251	0.244[20]

Table 2. Critical Temperatures and Pressures of the Binary Mixtures of 2-Methylpropane + 1-Butene, 2,2,4-Trimethylpentane + 2-Methylpropane, 2-Methylpropane + Methane, and 2-Methylpropane + Carbon Dioxide

x_2	T_c/K	P_c/MPa	x_2	T_c/K	P_c/MPa
2-Methylpropane (1) + 1-Butene (2)					
0	409.9	3.62	0.600	416.0	3.85
0.158	411.3	3.67	0.831	418.5	3.93
0.259	412.2	3.71	1	421.2	4.00
0.417	413.9	3.77			
2,2,4-Trimethylpentane (1) + 2-Methylpropane (2)					
0	544.1	2.57	0.899	435.8	4.01
0.302	523.0	3.21	0.956	421.2	3.81
0.621	489.2	3.96	1	409.9	3.62
0.795	458.1	4.21			
2-Methylpropane (1) + Methane (2)					
0	409.9	3.62	0.623	328.5	10.78
0.186	396.2	5.32	0.670	313.1	11.37
0.419	372.8	7.77	0.695	304.7	11.54
0.470	365.8	8.38	0.711	299.2	11.63
0.542	350.9	9.47	1 (ref 19)	190.4	4.60
0.616	330.3	10.69			
2-Methylpropane (1) + Carbon Dioxide (2)					
0	409.9	3.62	0.591	358.6	7.11
0.285	388.6	5.50	0.747	335.1	7.53
0.386	380.2	6.13	0.802	326.4	7.55
0.508	369.3	6.76	1	304.8	7.38

reagents were directly used without further treatment. The purity of all the chemicals was checked before measurement by gas chromatography and proven to be better than the criterion of each reagent.

The critical properties were measured with the same view cell and procedure as described previously.[18] The cell is equipped with two thermocouples, a pressure sensor, and three extension tubes and is put in a temperature-controlled air bath during the measurement. One thermocouple is placed outside the cell and used to control the air bath temperature, and another is embedded inside the cell to measure the interior temperature of the cell. The extension tubes (each of 0.10 cm^3) can slightly extend the volume of the cell when necessary. Before each measurement, the view cell was first evacuated with a vacuum pump. A known mass of 2,2,4-trimethylpentane was then charged into the pre-evacuated cell, and 2-methylpropane, 1-butene, methane, or carbon dioxide were pressurized into the cell through a sampling tube. 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.

The critical temperature and pressure readings were made by the occurrence of strong red-glow critical opalescence and the 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 critical density was the mass in the cell divided by the cell volume. It was also noted that a small deviation from the equal volumes of the two phases had limited effects on the critical temperature and pressure readings but gave a critical density of less accuracy; therefore, the critical densities of binary and ternary mixtures were not reported, which is of less concern in this work. 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.

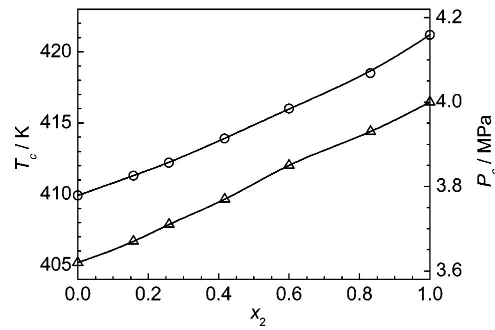

Figure 1. Critical temperature and pressure of the binary mixture of 2-methylpropane (1) + 1-butene (2): ○, critical temperatures; △, critical pressures.

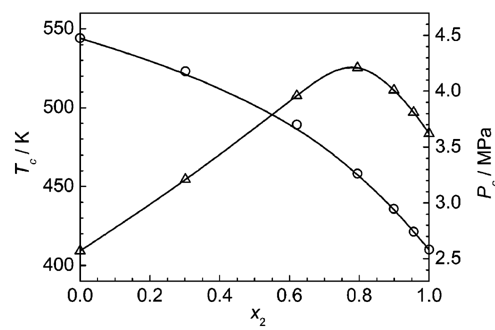

Figure 2. Critical temperature and pressure of the binary mixture of 2,2,4-trimethylpentane (1) + 2-methylpropane (2): ○, critical temperatures; △, critical pressures.

Results and Discussion

Pure Substances. A comparison of the critical properties of 2-methylpropane, 1-butene, 2,2,4-trimethylpentane, and carbon dioxide measured in this work with those in refs 19 to 21 is shown in Table 1. The agreement should be satisfactory; the difference may be ascribed to certain impurities in the reagents and deviations in charging the cell.

Binary Mixtures. The critical properties of the binary mixtures of 2-methylpropane + 1-butene, 2,2,4-trimethylpentane + 2-methylpropane, 2-methylpropane + methane, and 2-methylpropane + carbon dioxide are listed in Table 2.

As shown in Figure 1, both the critical temperature and pressure of the binary mixture of 2-methylpropane (1) + 1-butene (2) increase monotonically with the content of 1-butene (x_2) between those of two pure components, which may indicate that the mixture of 2-methylpropane + 1-butene is close to an ideal solution. For the binary mixture of 2,2,4-trimethylpentane (1) + 2-methylpropane (2) (Figure 2), the critical temperature decreases monotonically with an increase in the content of 2-methylpropane (x_2), whereas the critical pressure passes through a maximum at $x_2 = 0.790$.

For the alkylation of 2-methylpropane with 1-butene, isooctane (2,2,4-trimethylpentane as the representative) is the objective product, and its selectivity can reach up to 80 %.[2,3] During the reaction, certain byproducts from cracking, multialkylation, and oligomerization are also detected. 2-Methylpropane is generally in excess compared with 1-butene to alleviate the

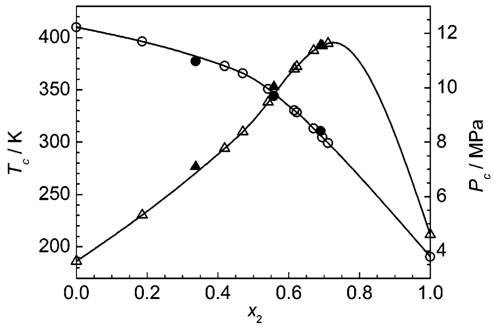

Figure 3. Critical temperature and pressure of the binary mixture of 2-methylpropane (1) + methane (2): ○, critical temperatures in this work; △, critical pressures in this work; ●, critical temperatures by Olds et al.;[22] ▲, critical pressures by Olds et al.[20]

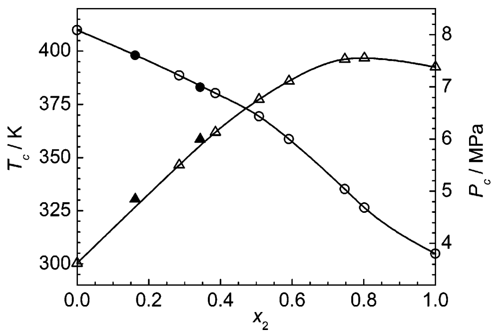

Figure 4. Critical temperature and pressure of the binary mixture of 2-methylpropane (1) + carbon dioxide (2): ○, critical temperatures in this work; △, critical pressures in this work; ●, critical temperatures by Leu et al.;[23] ▲, critical pressures by Leu et al.[23]

oligomerization of 1-butene. Thus, the binary mixture of 2-methylpropane + 1-butene represents the initial reacting mixture, whereas the binary mixture of 2,2,4-trimethylpentane + 2-methylpropane represents the final reacting mixture with a complete conversion of 1-butene, if only the following reaction is considered

$$CH(CH_3)_3 + CH_2CHCH_2CH_3 \rightarrow (CH_3)_3CCH_2CH(CH_3)_2$$

The critical temperature and pressure of the reacting mixture thus depend on the initial ratio of 2-methylpropane/1-butene as well as the reaction extent (conversion of 1-butene).

The critical temperatures and pressures of the binary mixtures of 2-methylpropane (1) + methane (2) are shown in Figure 3. The data of the mixture with $x_2 > 0.711$ were not obtained, and those of pure methane were cited from ref 19 because their critical temperatures are below room temperature and not in the measuring range of the apparatus. The present data agree well with those of Olds et al.[22] that are also plotted in the figure. The critical temperatures and pressures of the binary mixtures of 2-methylpropane (1) + carbon dioxide (2) are shown in Figure 4, which agree well with those of Leu et al.[23] The critical temperature of the binary mixture decreases substantially with an increase in the content of methane or carbon dioxide, which indicates that the addition of either methane or carbon dioxide is an effective way to reduce the critical temperature of the mixtures and to tune the critical properties of the reacting mixture. This is helpful in searching for the proper operation region for carrying out the reaction under supercritical conditions that can also meet the requests of alkylation catalysts.

The critical point loci of these four binary mixtures in the pressure vs temperature projection are also shown in Figure 5. For the binary mixtures of 2-methylpropane + 1-butene, 2,2,4-trimethylpentane + 2-methylpropane, and 2-methylpropane +

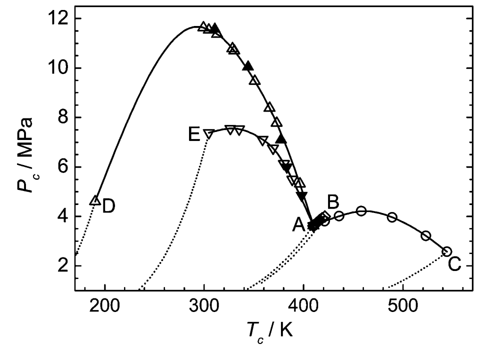

Figure 5. Projection of critical pressure vs critical temperature for the binary mixtures: ◇, 2-methylpropane (A) + 1-butene (B); ○, 2,2,4-trimethylpentane (C) + 2-methylpropane (A); △, 2-methylpropane (A) + methane (D); ▽, 2-methylpropane (A) + carbon dioxide (E); hollow symbols, critical points in this work; ▲, critical points by Olds et al.;[22] ▼, critical points by Leu et al.;[23] dotted lines, vapor pressure of each pure component below the critical temperature.[19]

Table 3. Critical Temperatures and Pressures of the Ternary Mixture of 2-Methylpropane + 1-Butene + Methane, 2-Methylpropane + 2,2,4-Trimethylpentane + Methane, 2-Methylpropane + 1-Butene + Carbon Dioxide, and 2-Methylpropane + 2,2,4-Trimethylpentane + Carbon Dioxide

x_1	x_2	x_3	T_c/K	P_c/MPa	x_1	x_2	x_3	T_c/K	P_c/MPa
2-Methylpropane (1) + 1-Butene (2) + Methane (3)									
0.580	0.093	0.327	376.8	6.58	0.439	0.028	0.533	349.7	9.13
0.500	0.079	0.421	365.0	7.55	0.401	0.025	0.574	338.5	9.81
0.411	0.065	0.524	347.5	8.84	0.639	0.023	0.338	380.3	6.82
0.374	0.060	0.566	336.1	9.49	0.547	0.020	0.433	369.3	7.88
0.629	0.040	0.331	379.7	6.69	0.444	0.016	0.540	349.0	9.34
0.537	0.034	0.429	367.6	7.75	0.406	0.015	0.579	338.7	10.01
2-Methylpropane (1) + 2,2,4-Trimethylpentane (2) + Methane (3)									
0.535	0.103	0.362	417.3	7.71	0.423	0.029	0.548	363.5	9.93
0.458	0.086	0.456	405.2	8.78	0.385	0.026	0.589	351.9	10.71
0.369	0.070	0.561	383.2	10.51	0.629	0.024	0.347	387.8	7.08
0.334	0.063	0.603	371.3	11.41	0.538	0.020	0.442	376.1	8.14
0.612	0.042	0.346	395.4	7.23	0.435	0.016	0.549	356.0	9.75
0.520	0.036	0.444	383.7	8.32	0.396	0.015	0.589	344.3	10.46
2-Methylpropane (1) + 1-Butene (2) + Carbon Dioxide (3)									
0.483	0.071	0.446	376.6	6.49	0.351	0.036	0.613	355.8	7.22
0.387	0.057	0.556	364.4	7.01	0.280	0.028	0.692	343.6	7.47
0.346	0.051	0.603	357.6	7.20	0.514	0.019	0.467	373.4	6.59
0.273	0.040	0.687	345.1	7.47	0.405	0.015	0.580	360.5	7.07
0.496	0.050	0.454	375.4	6.54	0.359	0.013	0.628	353.8	7.25
0.396	0.041	0.563	362.8	7.03	0.286	0.011	0.703	341.5	7.48
2-Methylpropane (1) + 2,2,4-Trimethylpentane (2) + Carbon Dioxide (3)									
0.445	0.077	0.478	405.3	7.43	0.327	0.037	0.636	364.8	8.17
0.351	0.061	0.588	385.3	8.20	0.257	0.029	0.714	347.5	8.39
0.311	0.054	0.635	373.1	8.51	0.502	0.019	0.479	378.0	6.86
0.244	0.042	0.714	354.8	8.81	0.397	0.015	0.588	364.4	7.39
0.469	0.052	0.479	391.8	7.16	0.352	0.014	0.634	356.1	7.56
0.369	0.043	0.588	377.3	7.94	0.275	0.011	0.714	342.3	7.67

carbon dioxide, the critical points of pure components are connected by continuous critical lines, and these loci belong to the type I fluid-phase behavior according to the classification of van Konynenburg and Scott;[24] the locus of the binary mixture of 2-methylpropane + methane could be the same type, though the critical data adjacent to methane were absent. The critical temperatures and pressures of all these pure components and binary mixtures cover a very wide range, which further suggests that the critical properties of the reacting mixture in alkylation can be tuned through adjusting the content of solvent and the 2-methylpropane/1-butene ratio.

Ternary Mixtures. The critical temperatures and pressures of ternary mixtures of 2-methylpropane (1) + 1-butene (2) + methane (3), 2-methylpropane (1) + 2,2,4-trimethylpentane (2) + methane (3), 2-methylpropane (1) + 1-butene (2) + carbon

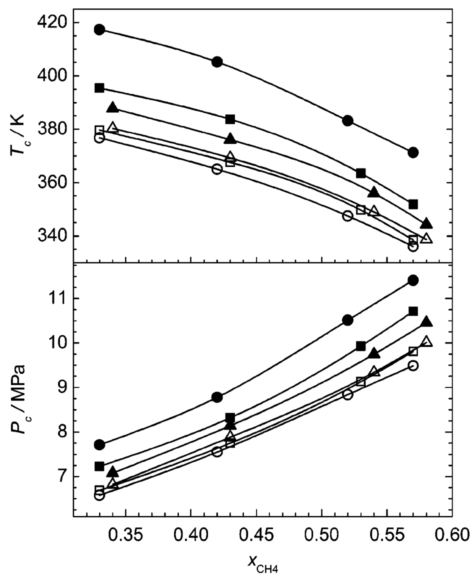

Figure 6. Alkylation of 2-methylpropane with 1-butene in the presence of solvent methane: the dependence of critical temperature (upper) and pressure (lower) of the reacting mixture on the solvent content. Hollow symbols, 1-butene conversion is 0; solid symbols, 1-butene conversion is 100 %; circle symbols, initial 2-methylpropane/1-butene ratio is 6; square symbols, initial 2-methylpropane/1-butene ratio is 16; and triangle symbols, initial 2-methylpropane/1-butene ratio is 28.

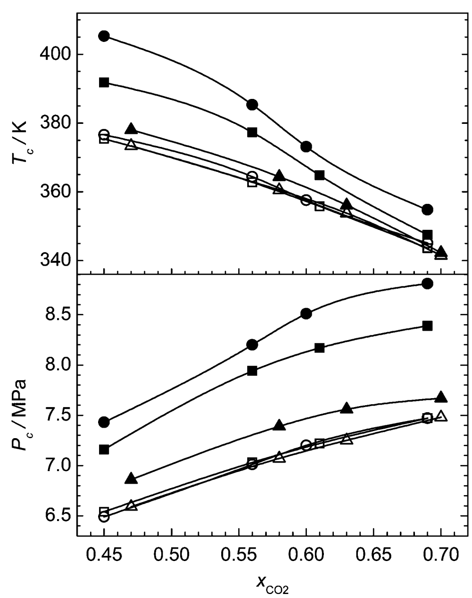

Figure 7. Alkylation of 2-methylpropane with 1-butene in the presence of solvent carbon dioxide: the dependence of critical temperature (upper) and pressure (lower) of the reacting mixture on the solvent content. Hollow symbols, 1-butene conversion is 0; solid symbols, 1-butene conversion is 100 %; circle symbols, initial 2-methylpropane/1-butene ratio is 7; square symbols, initial 2-methylpropane/1-butene ratio is 10; and triangle symbols, initial 2-methylpropane/1-butene ratio is 27.

dioxide (3), and 2-methylpropane (1) + 2,2,4-trimethylpentane (2) + carbon dioxide (3) are shown in Table 3.

The critical temperatures and pressures of these ternary mixtures with different 2-methylpropane/1-butene ratios and solvent contents are deduced from Table 3, to clarify the influences of the initial 2-methylpropane/1-butene ratio and solvent addition on the critical properties of the reacting mixture in the alkylation of 2-methylpropane with 1-butene in the presence of a solvent methane or carbon dioxide. As shown in Figures 6 and 7, the mixture of 2-methylpropane + 1-butene + methane (or carbon dioxide) represents a nominal reacting mixture at the beginning of the reaction (1-butene conversion being 0), whereas the mixture of 2-methylpropane + 2,2,4-trimethylpentane + methane (or carbon dioxide) is the final reacting mixture (1-butene conversion being 100 %).

It can be seen that either methane or carbon dioxide is an effective solvent to reduce the critical temperature of the reacting mixture in the alkylation of 2-methylpropane with 1-butene; the critical temperature decreases with an increase in the solvent content. However, the critical pressure of the reacting mixture increases substantially with the solvent content. The critical pressure of the reacting mixture with carbon dioxide as a solvent is much lower than that with methane as a solvent. This makes it possible that the supercritical reaction may be realized at a relatively lower pressure.

Both the critical temperature and pressure shift to higher values as the 1-butene conversion increases from (0 to 100) %. Moreover, the critical properties of the reacting mixture change considerably with the reaction extent at a lower initial 2-methylpropane/1-butene ratio, which is unfavorable for regulating the reaction under supercritical conditions near the critical point of the reacting system along the whole reaction course. On the other side, a high initial 2-methylpropane/1-butene ratio may be able to keep the critical properties relatively stable during the whole reaction course. This will help to regulate the reaction conditions in the vicinity of the critical point of the reacting mixture in the course of the reaction, which is often desirable to make the most of the unique characteristics of the supercritical fluid.

Conclusions

The critical temperatures and pressures of four binary mixtures (2-methylpropane + 1-butene, 2,2,4-trimethylpentane + 2-methylpropane, 2-methylpropane + methane, and 2-methylpropane + carbon dioxide) and four ternary mixtures (2-methylpropane + 1-butene + methane, 2-methylpropane + 2,2,4-trimethylpentane + methane, 2-methylpropane + 1-butene + carbon dioxide, and 2-methylpropane + 2,2,4-trimethylpentane + carbon dioxide) were measured.

On the basis of these results, the dependences of the critical properties of the reacting mixture in the alkylation of 2-methylpropane with 1-butene in the presence of a solvent methane or carbon dioxide upon the initial ratio of 2-methylpropane/1-butene, amounts of methane or carbon dioxide added, and reaction extent were estimated. The results indicate that the addition of a solvent is an effective way to tune the critical properties of the reacting mixture; the critical temperature decreases and the critical pressure increases with an increase of the solvent extent. Both the critical temperature and critical pressure shift to higher values as the 1-butene conversion increases from (0 to 100) %. A flat critical temperature and pressure along the reaction course can be obtained at a high initial 2-methylpropane/1-butene ratio, which is favorable for regulating the reaction under proper supercritical conditions.

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