

## GENERAL RESEARCH

## Solvent Screening for the Supercritical Hydrogenation of Polyunsaturated Hydrocarbons Using VLE Calculations

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Preliminary knowledge of VLE behavior of multiphasic reaction mixtures is required for the operation and design of chemical reactors that work with supercritical fluid as solvents. In this case, the operating parameters of a continuous fixed-bed catalytic reactor are to be optimized for the selective hydrogenation of 1,5,9-cyclododecatriene (CDT) to form the second intermediate cyclododecene (CDE). Commercial simulators (Aspen, HYSYS, PRO-II), as well as a user-written program based on high-pressure flash calculations, are tested in predictions of the phase envelope of the reaction mixture. Important binary interaction parameters (Peng–Robinson) are determined by fitting experimental and calculated data for the solubilities of CDT and CDE in supercritical CO<sub>2</sub>. Data are calculated with the user-written program, whereas experimental solubility points are obtained in quasi-binary-equilibrium runs at very low fluid flow rates. It is observed that the commercial simulators poorly predict the near-critical region. Thus, to choose an adequate supercritical solvent, the program is used to compare the solubilities of solutes (CDT and hydrogen) under relatively moderate temperature and pressure conditions. Among CO<sub>2</sub> and the lower alkanes tested (ethane to butane), propane is found to satisfy these criteria, although its flammability is inconvenient.

## Introduction

In recent years, the application of supercritical fluid technology to multiphase catalytic reactors has become a potential alternative to overcome major drawbacks of conventional processes. From an economical point of view, it is clear that, because of their increased costs, high-pressure equipment and facilities have to yield superior performance to make them competitive with existing processes.

For instance, widely used gaseous reactants such as hydrogen and oxygen are sparingly soluble in liquid media under subcritical conditions but can have high solubilities in supercritical fluids. Their physical properties at supercritical conditions (liquidlike density and gaslike viscosity) make them versatile solvents for both gases and liquids.<sup>1</sup> Also, it has been found that reactions occurring in a supercritical fluid phase greatly benefit from enhanced mass and heat transfer,<sup>2</sup> better product selectivities,<sup>3,4</sup> and potential in situ catalyst regeneration, thus improving catalyst lifetime.<sup>4,5</sup> In addition, a clean and complete separation of the solvent and the final products can be easily implemented at low cost at any point in the process following the reaction by an appropriate decrease of the system pressure.

Thus, the performance of a process based on a solid-catalyzed reaction in a supercritical solvent mainly

depends on providing a homogeneous (supercritical) fluid phase with an adequate composition at the given operating conditions. In the past, the fluids most frequently used as supercritical solvents were either CO<sub>2</sub> (usually in extraction processes) or water (in destruction processes), but investigations into new substitutes for CO<sub>2</sub>, especially lower alkanes (ethane to hexane), are underway.<sup>3,4,6</sup>

The aim of this study was to set up a simple method based on VLE calculations to test potential solvents prior to running any supercritical reaction experiments. Also, any supercritical kinetic study is of little value if the phase behavior of the mixture is not known.<sup>7</sup> The model reaction considered here is the consecutive hydrogenation of 1,5,9-cyclododecatriene (CDT) to form the desired second intermediate cyclododecene (CDE). This type of reaction is subject to strong selectivity and exothermicity constraints and is of great importance in fields such as the food, pharmaceutical, fine chemicals, and petrochemical industries.<sup>8</sup>

Phase equilibrium calculations were carried out with standard process simulators (Aspen, HYSYS, PRO-II) and a user-written program. In addition, quasi-binary-equilibrium runs were performed to measure the solubilities of CDT and CDE in dense CO<sub>2</sub>.

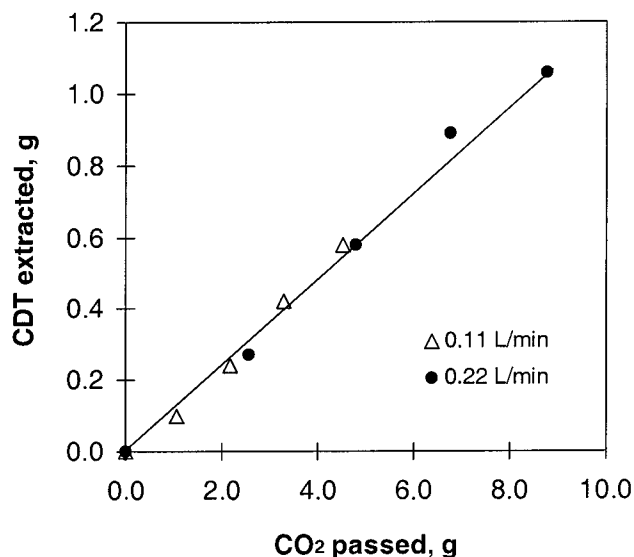
## Experimental Methods

A detailed description of the experimental setup has been given elsewhere.<sup>9</sup> To measure the solubilities of the reactant (CDT) and the second intermediate (CDE)

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**Figure 1.** Extracted mass of CDT versus amount of CO<sub>2</sub> passed at low flow,  $P = 250$  bar,  $T = 380$  K.

in supercritical CO<sub>2</sub>, quasi-static-equilibrium runs at very low CO<sub>2</sub> flow rates were carried out at pressures, temperatures, and flow rates of 200–250 bar, 380–423 K, and 0.1–0.3 L/min, respectively. This method has already provided good results in the cases of the binary and ternary systems toluene–CO<sub>2</sub>, benzene–CO<sub>2</sub>, and ethylbenzene–CO<sub>2</sub><sup>9</sup> and  $\alpha$ -naphthol–CO<sub>2</sub>,  $\beta$ -naphthol–CO<sub>2</sub>, and  $\beta$ -naphthol–CO<sub>2</sub>–toluene.<sup>10,11</sup> For the runs, porous steel cylinders ( $h = 0.8$  cm,  $d = 0.8$  cm) were impregnated overnight with either CDT or CDE and were then placed into a preheated steel extractor cell ( $h = 5$  cm,  $d = 2.1$  cm). The temperature was monitored by J-type thermocouples. Simultaneously, CO<sub>2</sub> was fed into the extractor to raise the system pressure using a two-head HPLC plunger pump. Before it entered the pump, the liquid CO<sub>2</sub> stored at room temperature was cooled to approximately  $-5$  °C to avoid cavitation at the pump inlet. Once the pressure and temperature in the extractor cell reached the desired set values, two downstream valves were opened to achieve the required low flow rates of supercritical CO<sub>2</sub>. The second of the valves had to be heated to 100 °C to avoid clogging by dry ice as a result of the Joule–Thompson effect. The flow was monitored with a flow meter and a flow totalizer. After expansion of the mixture to atmospheric pressure, the flow was passed through a dry ice cold trap to condense the extracted hydrocarbon. The ends of the U-tubes of the cold trap were filled with glass wool plugs to prevent carry-over of the solute. In each experiment, the valves were closed 3–4 times every 10 min to change the tubes and to note their weight as well as the total amount of CO<sub>2</sub> passed through the extractor. The CO<sub>2</sub> flow rate had to be kept very low (0.1–0.3 L/min at 1 bar and 20 °C) to ensure that the fluid leaving the cell was saturated with solute. A typical quasi-static-equilibrium run is presented in Figure 1 for the CDT–CO<sub>2</sub> system. As can be seen in Figure 1, the solubility of CDT in CO<sub>2</sub> at different flow rates is constant, confirming that the fluid exiting the cell is always saturated.

### Prediction of Multicomponent VLE

Knowledge of the phase behavior of multicomponent mixtures can be obtained by means of either experi-

ments or thermodynamic VLE calculations. The second procedure is often more convenient, as experimental determination usually requires both expensive high-pressure equipment and carefully performed experiments. Among the existing thermodynamic models, classical cubic equations of state (EOSs) [Peng–Robinson (PR), Soave–Redlich–Kwong (SRK), etc.] are commonly used. Commercial simulators, which find increasing application in chemical process design, include these EOSs in thermodynamic function blocks and allow very user-friendly VLE calculations. Their performance in VLE predictions was tested and compared to a programmed algorithm for high-pressure flash calculations proposed by Reid et al.<sup>12</sup>

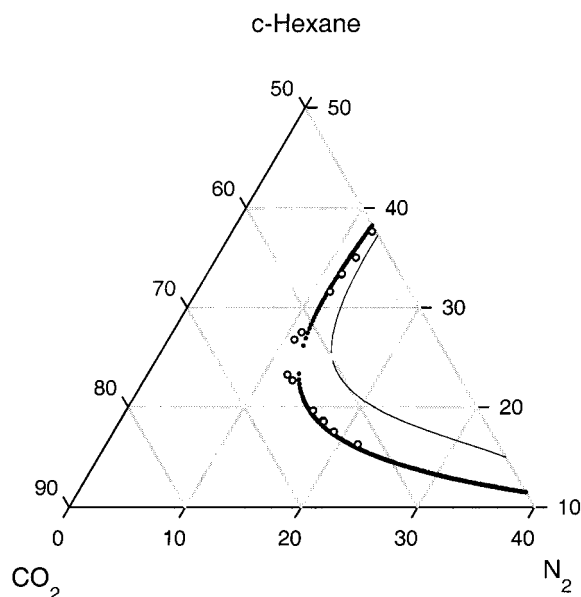
The programmed algorithm is based on the well-known PR EOS that is stated to perform as well as other more complicated EOSs when appropriate binary interaction coefficients are available.<sup>13</sup> To calculate the attractive and repulsive parameters for the system studied, the classical vdW mixing rules with only one adjustable binary interaction parameter were used, whereas in the case of polar and highly asymmetric systems, the use of two model parameters is strongly recommended.<sup>14,15</sup> The pure-component attractive and repulsive parameters, as well as the temperature dependence function of the attractive one, were determined by the usual equations, with the exception of hydrogen, for which the Boston–Mathias equation<sup>16</sup> was used.

The algorithm proposed by Reid et al.<sup>12</sup> does not account for specific programming features that can arise during program execution. It might be useful to mention that, for convergence of the algorithm, especially close to the critical point, primary attention should be paid to both defining adequate initial guess values and finding the proper routes that correspond to the respective phases.

In addition to an adequate solving strategy, accurate VLE calculations mainly depend on the precise knowledge of critical component properties (critical temperature and pressure, acentric factor) and binary interaction parameters. The reaction system investigated can contain up to six species, namely, H<sub>2</sub>, CO<sub>2</sub>, and four cyclic hydrocarbons [CDT, CDD (cyclododecadiene), CDE, and CDA (cyclododecane)]. However, the behaviors of the cyclic hydrocarbons (HCs) are assumed to be similar, and the system is assumed to reduce to a ternary one (HC–CO<sub>2</sub>–H<sub>2</sub>). Except for the H<sub>2</sub> and CO<sub>2</sub> species, no specific data are available in the literature. This implies the estimation of the critical properties of the cyclic hydrocarbons by group contribution methods.<sup>12</sup> In the case of the binary interaction parameters (HC–CO<sub>2</sub> and HC–H<sub>2</sub>), a first assumption is to use the values for the most similar system found in the literature. Obviously, the direct application of these values has to be tested, at least, through a simple sensibility study, as outlined later. This will help to determine whether the precision of the results is acceptable or not. If not, experimental parameter determination is indispensable in improving the quality of VLE calculations.

### Results and Discussion

**Commercial Simulators and Programmed Algorithm.** The VLE predictions of the simulators and the programmed algorithm were compared to literature data for the system cyclohexane–CO<sub>2</sub>–N<sub>2</sub>.<sup>17</sup> These ternary phase diagrams at high pressure were also

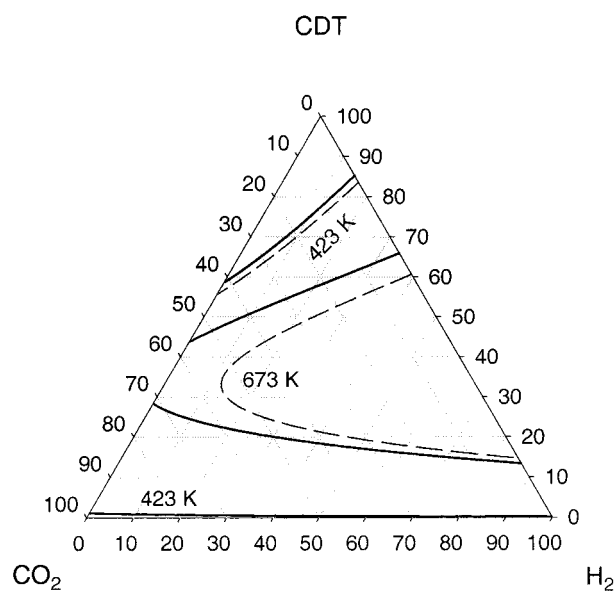


**Figure 2.** Comparison of VLE calculations between PRO-II (points), programmed algorithm (thick solid line), and Srinivas et al.<sup>17</sup> (thin solid line) for the system cyclohexane-CO<sub>2</sub>-N<sub>2</sub> at  $P = 205$  bar and  $T = 410$  K.

constructed using the one-parameter PR EOS. The values of the binary interaction coefficients were obtained from experiments, but the authors did not explicitly report these values.

Figure 2 shows as an example a plot of a ternary phase diagram obtained with PRO-II and the programmed algorithm, compared to the literature data. Similar results were found when HYSYS or Aspen was used instead, as well as at different conditions of temperature and pressure. Figure 2 reveals that the algorithm and the simulator give the same curves except in the vicinity of the critical point. Yet, they are not in perfect agreement with the results of Srinivas et al.<sup>17</sup> This can certainly be related to the use of slightly different values of the binary interaction coefficients, as we had to take values from a different literature source.<sup>18,19</sup> An interesting result is the inability that the simulators exhibit to perform consistent VLE calculations very close to the critical point. Figure 2 indicates that the dew and bubble lines predicted by the simulator have a tendency to diverge. This is probably due to an inadequate precision of computation near the critical point. A thorough check could not be done as access to the source program is impossible. Further calculations were carried out with the programmed algorithm, as it is reliable near the critical point. The algorithm used was proposed by Reid et al.<sup>12</sup> for high-pressure flash calculations. Nevertheless, one should keep in mind that commercial simulators are very useful tools for rapidly performing VLE calculations at pressures up to close to the critical one.

**Critical Properties and Binary Interaction Coefficients.** As noted before, accurate VLE calculations depend on precise values of both the critical properties of the pure substances and the binary interaction coefficients. The critical properties of CDT and CDE were determined using different group contribution methods,<sup>12</sup> whereas values of binary interaction coefficients were taken from available literature. Table 1 lists the critical properties of CDT calculated by the Ambrose and Joback methods. The largest deviations were found for this hydrocarbon. In the following, VLE calculations were carried out with these two sets of



**Figure 3.** CDT-CO<sub>2</sub>-H<sub>2</sub> phase diagrams at 423 and 623 K and 200 bar for critical properties calculated by different methods of group contribution: Joback (continuous lines), Ambrose (dashed lines).

**Table 1. Critical Properties of CDT Calculated by the Ambrose and Joback Methods<sup>12</sup>**

method	$T_c$ (K)	$P_c$ (bar)	$V_c$ (cm <sup>3</sup> /mol)	$\omega$
Joback	757	28.5	551.5	0.299
Ambrose	742	25.5	529.0	0.356

values and a fixed CDT-CO<sub>2</sub> binary interaction coefficient. Figure 3 shows the resulting ternary phase diagrams for the CDT-CO<sub>2</sub>-H<sub>2</sub> system at a given pressure of 200 bar and two different temperatures of 423 and 673 K. It can be observed that, at the lower temperature (more common for supercritical processes), the dew and bubble lines fall very close together. However, with an increase in temperature, the predicted phase envelopes are strongly affected by small variations in the critical properties. At 673 K, the critical properties listed in Table 1 lead to a significant difference in the predicted extents of the two-phase region, i.e., in one case, a critical point of the mixture exists, whereas in the other, it does not.

With respect to the binary interaction coefficients, as expected, the one for the CDT-CO<sub>2</sub> system was found to significantly influence the extent of the supercritical zone phase of the system studied. Values of  $k_{\text{CDT-CO}_2}$  of 0.105, 0.15, and 0.2 were chosen for the sensibility test, the first being a reported value for cyclohexane-CO<sub>2</sub> system,<sup>18</sup> the others more conservative values. At conditions of 200 bar and 423 K, the liquid mole fraction of CO<sub>2</sub> in the CO<sub>2</sub>-CDT system varies from 0.58 ( $k = 0.105$ ) to 0.43 ( $k = 0.2$ ), but again, the deviations become important with increasing temperature.

**CDT and CDE Solubilities in Dense CO<sub>2</sub>.** The solubilities of hydrocarbons in supercritical CO<sub>2</sub> obtained by means of the quasi-static-equilibrium method are reported in Tables 2 (CDT-CO<sub>2</sub>) and 3 (CDE-CO<sub>2</sub>), along with the respective experimental conditions. From an economical consideration, both CDT and CDE have vapor mole fractions that are at the given temperature and pressure, ranging only from 1 to 2%. A second result worth stating is that the CDT-CO<sub>2</sub> system shows a clear reversed behavior with temperature, whereas in the case of CDE-CO<sub>2</sub>, this behavior is less obvious.



**Table 2. Experimental and Calculated Vapor Mole Fractions of CDT in CO<sub>2</sub>**

<i>T</i> (K)	<i>P</i> (bar)	<i>k<sub>ij</sub></i>	<i>y<sub>exp</sub></i>	<i>y<sub>cal</sub></i>	error (%)
380	200	0.160	0.0125	0.0117	6.40
380	250	0.160	0.0185	0.0192	-3.78
423	200	0.217	0.0109	0.0105	3.67
423	250	0.217	0.0138	0.0143	-3.62

**Table 3. Experimental and Calculated Vapor Mole Fractions of CDE in CO<sub>2</sub>**

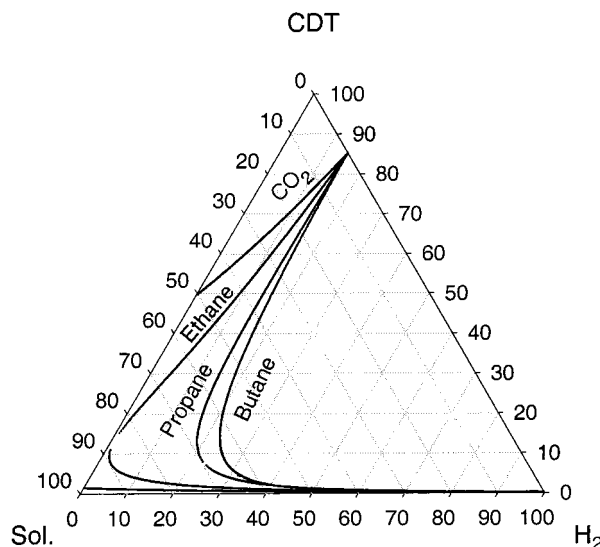
<i>T</i> (K)	<i>P</i> (bar)	<i>k<sub>ij</sub></i>	<i>y<sub>exp</sub></i>	<i>y<sub>cal</sub></i>	error (%)
380	200	0.175	0.0125	0.0115	+8.4
380	250	0.175	0.0170	0.0175	-2.94
423	200	0.195	0.0132	0.0125	+5.3
423	250	0.195	0.0172	0.0179	-4.07

The experimental data points of the CDT and CDE solubilities were used to adjust the binary interaction coefficients  $k_{\text{CO}_2\text{-CDT}}$  and  $k_{\text{CO}_2\text{-CDE}}$  for better calculations of the supercritical region of the ternary mixture. The critical parameters used for CDT and CDE were estimated by the correlation of Joback. Further, a simple trial-and-error procedure was applied to optimize the binary interaction coefficients so that the predicted vapor mole fraction of CDT or CDE in supercritical CO<sub>2</sub> matched the experimental value. Tables 2 and 3 also list the predicted mole fractions of CDT and CDE in CO<sub>2</sub>, respectively, as well as the relative error in each data point.

As can be seen, the quality of prediction is reasonably good, with a relative error of 8% in the worst case. Binary interaction coefficient values were found to be moderately higher than those recommended in the literature, ranging from 0.16 to 0.217 and 0.175 to 0.195 for CDT-CO<sub>2</sub> and CDE-CO<sub>2</sub>, respectively. Within the (small) interval of pressure and temperature studied, the obtained values of the binary interaction coefficients follow the trends indicated in the literature, i.e., they depend on temperature, but not on pressure.

**Solvent Prescreening.** To obtain a homogeneous supercritical phase in the CDT-CO<sub>2</sub>-H<sub>2</sub> system, severe pressure (>200 bar) and temperature (>600 K) conditions that are beyond of any acceptable operating conditions of a hydrogenation reactor are required. Thus, an alternate solvent is needed. Beside CO<sub>2</sub>, lower alkanes such as ethane, propane, and butane are thought to be potential solvents because of their hydrophobic character, favorable critical properties, and expected higher solubilities. Still, an unavoidable drawback is flammability.

To test their VLE behaviors, ternary phase diagrams of solvent-CDT-H<sub>2</sub> systems were constructed. Binary interaction coefficients of the systems CO<sub>2</sub>-CDT and lower alkane-CDT were taken from this work and from literature data available for the systems lower alkane-benzene,<sup>18</sup> respectively. The plot obtained for 200 bar and 423 K is illustrated in Figure 4. Among the solvents studied, propane appears to be an appropriate solvent. Compared to CO<sub>2</sub> and ethane, it combines greatly enhanced reactant solubility (like butane) and an acceptable critical temperature ( $T_c = 96.8^\circ\text{C}$ ), which, in the case of butane, is a little too high ( $T_c = 152.02^\circ\text{C}$ ). Furthermore, butane is a mixture of isomers including unsaturated components in some Western countries. Also, the condition of being gaseous at ambient temperature and pressure permits an easy separation of solute and solvent. Finally, the fluid-phase composition close to the critical point is favorable. Figure 4 and

**Figure 4.** Ternary phase diagrams for the system CDT-H<sub>2</sub>-solvent at 423 K and 200 bar. In order of increasing solubility, the lines correspond to CO<sub>2</sub>, ethane, propane, and butane.

additional phase diagrams (at 373–423 K and 100–400 bar) indicate that, for 150–200 bar and 423 K, the fluid mole fraction of CDT close to the plait point reaches up to 10% and that of hydrogen is about 2 times higher. The fluid mole fraction of hydrogen is thus very close to the stoichiometric value required for the consecutive hydrogenation of CDT to stop at the desired second intermediate CDE. This should allow for easy tuning of the intermediate selectivity through appropriate control of the hydrogen concentration in the reactor feed.

## Conclusion

Ternary VLE calculations using the classical PR EOS were performed to assist in choosing a potential supercritical solvent under feasible operating conditions for the catalytic and consecutive hydrogenation of 1,5,9-cyclododecatriene (CDT). Commercially available simulators (Aspen, HYSYS, PRO-II) allow for easy determination of the phase envelopes but have the inconvenience of making poor predictions very close to the critical point of the mixture. Thus, a user-written program was developed to improve the VLE predictions in this important zone. The screening of possible supercritical solvents (CO<sub>2</sub> and lower alkanes) showed that propane is adequate to replace CO<sub>2</sub> because of the very low solubility of CDT in CO<sub>2</sub>. From the thus-constructed phase diagrams, it is also possible to set operating conditions for the hydrogenation reactor that should provide favorable fluid compositions that afford selectivity for the desired intermediate product.

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