Fluid-Phase Behavior of the Guaiacol + CO₂ System at High Pressures

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Abstract. The binary phase behavior of supercritical CO₂ with guaiacol, a model lignin monomer that is a liquid at near-ambient conditions, has been determined. A variable-volume, high-pressure view cell was used to observe both liquid–liquid cloud points as well as bubble points along the liquid–liquid–vapor (LLV) three-phase line for this system. CO₂ + guaiacol was found to exhibit Type III phase behavior according to the classification system of Scott and Van Konynenburg, indicating that even at high pressures the mutual solubility of the two components is relatively low. However, the system does exhibit a pressure minimum in the liquid–liquid critical curve at 15 °C and pressures just under 500 bar. The upper critical end point U for the CO₂-rich liquid phase extends to temperatures and pressures 2.1 °C and 2.2 bar above the critical point of CO₂.

Keywords: *guaiacol, carbon dioxide, lignin, phase behavior, liquid–liquid, supercritical fluid*

1. Introduction

Lignin is one of the most common organic compounds on earth, comprising about 30% of all organic carbon and about 30% of wood on a dry basis. Only cellulose is more abundant. Interest in lignin is at an all-time high, as evidenced by the five-fold increase in Web of ScienceTM citations over the past decade. It is unique among abundant, renewable biopolymers in having an aromatic backbone. Proposed and existing uses for lignin that take advantage of that molecular structure include carbon fibers and activated carbon [1,2], polyurethane foams [3], composites [4], and phenol–formaldehyde resins [5].

Generally speaking, the monomer units of lignin are derived from phenylpropane, with the two dominant lignin monomers being given in **Figs. 1a** and **b**. Of interest to us in this work were fundamental phase-behavior measurements for a model lignin monomer with dense, supercritical carbon dioxide (CO₂). Guaiacol (see **Fig. 1c**) was selected for measurement, as it contains both the methoxyl and hydroxyl groups present in most lignin monomers. Furthermore, guaiacol has a relatively low melting point (28 °C). Measurements were desired for a model system where fluid-phase (and not solid–fluid) equilibria would play a key role, as our research program on lignin recovery [7,8] is directed towards systems where a liquid-lignin phase (vs. a solid phase) exists. Additionally, CO₂ plays an important role in processes for recovering lignin from Kraft black liquor [9], so it was an obvious choice as the supercritical fluid solvent for the guaiacol.

In spite of the high degree of interest in lignin today, phase-behavior measurements of lignin or lignin model compounds with supercritical fluids are practically nonexistent. McHugh and co-workers [10] measured the high-pressure phase behavior of vanillin, a lignin monomer, with CO₂. Because vanillin has a melting point of 81.5 °C, the focus of their measurements

wason the solid–liquid–gas phase equilibriathat exist for this system. To our knowledge, no otherphase-behavior measurements of lignin model compounds with supercritical fluids have been made.

2. Materials

Guaiacol (98% minimum purity, CAS 90-05-1, mpt = 28 °C, bpt = 204-206 °C) was obtained from Sigma-Aldrich and used as received. Coleman Grade CO₂ (99.99% purity) was obtained from National Welders/Airgas and used as received.

3. Phase Behavior Measurements

A schematic of the experimental apparatus used to measure phase behavior for the system guaiacol–carbon dioxide is shown in **Fig.2**. The phase behavior is observed within a variable-volume view cell (1.59 cm i.d. x 24.29 cm long), which is rated for 690 bar and 200 °C. The cell design was supplied by McHugh [11], and the cell was constructed by Machining and Technical Services at Clemson University. A modification to the original design was the addition of graphite gaskets (Graftech, Grafoil GTJ grade, 0.015” thick) on the sealing surfaces of the two end caps; the gaskets were found to help eliminate cell leakage. Within the cell is a piston (shown in **Fig. 2** as a black bar) that separates the working fluid from the “process fluid” (i.e., the mixture of interest) and is used to control the system pressure through changes in the process volume at constant temperature. The working fluid used was pure CO₂, which was delivered into the view cell via a syringe pump (Isco Series 500D) for pressures below 345 bar and via a pressure generator (High Pressure Equipment (HiP; model 37-6-30) at pressures above 345 bar. The guaiacol + CO₂ mixture was observed through the view port of the cell (i.e., a sapphire window) with a borescope (Olympus Ind., model R100-038-000-50) and associated light generator (Olympus, model ILK-5). Photographs in the vicinity of cloud points and bubble points were

taken with a camera attached to the borescope. Depending on their availability at the time, either a Watec 202D digital CCD color camera or an Amscope MU 300 series microscope digital camera was used. The cameras were interfaced to a PC computer, which was used to capture, view, and store the recorded pictures.

Unless otherwise noted, all tubing shown in **Fig. 2** was 1.59 mm o.d. x 0.762 mm i.d., and all valves were 1/16" HiP on/off valves (part no. 15-11AF1) initially in the closed position. A constant-temperature environment for the cell was provided by an isothermal bath (i.e., a nitrogen-purged oven) designed and constructed at Clemson. A nitrogen-purged cooling jacket (not shown) was built into the oven wall to maintain the borescope below its estimated maximum operating temperature of 80 °C. The oven is equipped with a rotating permanent magnet (Dexter Corp., model H-109) that provides mixing in the cell via a magnetic stir bar.

Before a phase-behavior experiment could begin, the cell had to be charged with the components of interest in their desired compositions. In order to charge the variable-volume high pressure cell with a known amount of CO₂, the flow rate of the syringe pump first had to be precisely calibrated. To this end, an empty sample cylinder (Swagelok Model DOT-3E 1800; not shown) of accurately known weight with attached on/off valve was connected to micro-metering valve MM1 in the almost closed position. The syringe pump was set to the constant pressure mode, and the process lines were filled with CO₂ up to valve WF2 to a pressure of 137.9 bar (2000 psig). The pump was then switched to the constant-fill mode at 2 mL/min, valve WF2 was opened to fill the sample cylinder with CO₂, and micro-metering valve MM1 was adjusted to maintain a constant pressure at the pump of 137.9 bar. After the syringe pump had run exactly 8 minutes in the constant-fill mode, the sample-cylinder on/off valve was closed, and the sample cylinder was removed and weighed. This process was repeated three times, and the

(average) weight of CO₂ delivered to the sample cylinder in 8 min at 2 mL/min and a pump delivery pressure of 137.9 bar was calculated. Using this weight of CO₂ (typically 12-13 g), the corresponding mass of guaiacol needed to achieve the desired overall solute concentration was determined and then injected into the empty view cell through a process port using a 5-mL syringe.

With the syringe pump having been calibrated, micro-metering valve MM1 was connected to valve PS1 on the process side of the view cell (see **Fig. 2**), and the view cell was purged several times with CO₂ via valve PS1 using the syringe pump. Then the exact same process as described above for filling the sample cylinder was repeated on the view cell, so that the amount of CO₂ charged to the cell was accurately known.

After the charging of CO₂ and guaiacol had been completed, the oven temperature was set, the rotating magnet was turned on to activate the stir bar, and about 8 h was allowed for the view cell to reach a steady-state temperature at moderate pressures (e.g., ~100 bar). The contents of the cell were then compressed with the pressure generator (see **Fig. 2**) under continuous mixing with the stir bar until a pressure was reached such that a homogeneous solution was obtained.

To determine a given cloud-point pressure, a preliminary measurement was initially taken to determine the approximate location of the cloud-point pressure. First, the pressure generator was used to increase the view cell pressure to 655 bar under stirring so as to obtain one phase; then the system was allowed to equilibrate, stirring was stopped to allow any possible phase separation to occur, and the pressure was lowered in increments of 13.8 bar. In between each increment, 30 s of waiting time was allowed for the mixture to equilibrate, the cell contents were photographed, and the pressure and temperature were recorded. This process of pressure

decrement and photographing was repeated until the CO₂-guaiacol mixture had clearly become darker when observed against the shiny, stainless-steel cell piston face located in the back of the process volume.

To obtain the final, reported, cloud-point measurement, the pressure was raised 68.9 bar above the cloud point noted during the above preliminary measurement. The pressure was then decreased in smaller, 3.45-bar increments; otherwise the process was identical to that described above. Photographs of the cell contents for each pressure decrement were then compared to determine the first point at which the mixture had darkened as defined above. This pressure was determined to be the cloud-point pressure. The above procedure was repeated three times at each temperature.

To measure bubble points (i.e., the onset of a vapor phase in equilibrium with liquid-liquid equilibrium, or LLV equilibrium) the pressure was set to about 75 bar, where the mixture was already below the cloud point determined above, that is, in the liquid-liquid equilibrium region. The pressure was then lowered by 0.35 bar, the system was allowed to equilibrate for 30 s, the contents of the cell were photographed, and the pressure and temperature were recorded. This process was repeated until the formation of a bubble in the view cell was observed. Photographs were then reviewed for the first evidence of a bubble, and this point was determined to be the bubble-point pressure. This was repeated for a total of three times at each temperature.

The pressure inside the view cell was determined indirectly by measuring the pressure of the working fluid via pressure gauge P1 (Heise, model CM-109834, 0-10,000 psig) shown in **Fig. 2**; the pressure drop across the piston has been found to be no more than 0.689 bar. Pressure gauge P1 was calibrated to an accuracy of better than ± 0.0689 bar for the bubble points and ± 0.5 bar for the cloud points. The temperature in the view cell (T2) was measured with a platinum

resistance thermometer (Burns Engineering 200 Series RTD) that had been calibrated to an accuracy of ± 0.02 °C.

4. Results and Discussion

The pressure vs. temperature (P-T) diagram for CO₂ + guaiacol is given for six different concentrations of guaiacol in the mixture in **Fig. 3**. Here the curves at higher pressures (i.e., above 200 bar) are cloud-point curves, with one liquid phase existing above the curve for a given mixture composition (e.g., for 1.13 mol % guaiacol), and two liquid phases existing below the curves. At pressures below 100 bar, the LLV line (whose pressure was measured by the presence of a bubble point in the presence of two liquid phases) is given, along with selected vapor pressures and the critical point for pure CO₂ [12]. Mixture compositions, temperatures, and pressures for the guaiacol + CO₂ binary at the measured liquid–liquid cloud points (LL) and bubble points (BP) are listed in **Table 1**. Uncertainties in the reported compositions were ± 0.015 mol %, temperatures ± 0.15 °C, cloud-point pressures ± 1.75 bar, and bubble-point pressures ± 0.25 bar. The above results are also plotted in the form of pressure vs. composition diagrams in **Fig. 4** in order to determine the location of the mixture critical points at the temperatures measured for this binary system. Here we see that the mixture critical compositions (i.e., the maxima in the P-x curves) were all in the range of 0.80 to 0.90 mol % guaiacol, with the critical composition increasing slightly with temperature.

Referring to **Fig. 3**, measurements were first made only at ambient and higher temperatures to generate the cloud-point and bubble-point curves. However, those measurements did not provide enough information to determine the type of critical-curve behavior that the guaiacol + CO₂ binary exhibits per the classification system of van Konynenburg and Scott [13]. That is, a continuous critical curve was observed over the temperature range from 25 to 80 °C,

closely following the curve for the 0.90 mol % isopleth shown in **Fig. 3**. But the question of what direction the critical curve would take at lower temperatures remained unresolved. That is, would the vapor-liquid critical curve extend to lower pressures and eventually intersect the three-phase liquid-liquid-vapor (LLV) line at the lower critical end point L, as is characteristic of Type V phase behavior, see **Fig. 5** [14,15]? Or would the critical curve go through a minimum and then turn to higher pressures, as is characteristic of Type III phase behavior?

In order to access sub-ambient temperatures for the required cloud-point and bubble-point measurements, we added a cold nitrogen-gas purge from a nitrogen Dewar into the oven (see **Fig. 2**). Because the ambient and higher-temperature measurements shown in **Fig. 3** had demonstrated that the 0.90 mol% guaiacol solution was close to the mixture critical composition for all of the temperatures measured to this point, we extended only this isopleth to sub-ambient temperatures. The results for this isopleth given in **Fig. 3** clearly indicate that the critical curve for the CO₂ + guaiacol binary mixture goes through a minimum with decreasing temperature, and then extends to higher pressures as the temperature is decreased further. Such behavior is a classic characteristic of many Type III systems [14,15], with the observed minimum in pressure being common in binary mixtures of CO₂ with high molecular weight alkanes, such as hexadecane and squalane, for example [15]. At lower temperatures (not shown), the critical curve will eventually intersect the solid guaiacol–liquid CO₂–liquid guaiacol line [16].

At lower pressures below 100 bar, the LLV line and the vapor-pressure curve for CO₂ are given. As shown in the expanded inset, the vapor-pressure curve consistently lies above the LLV line, with the difference becoming noticeable near the critical point of CO₂. This is consistent with the cartoons depicted in **Fig. 5** and was expected, because systems with CO₂ +

another nonpolar compound would not be expected to exhibit heterogeneous azeotropic behavior, which would give an LLV line above both pure component vapor pressure curves [14].

With respect to the LLV data given in **Table 1**, only the results at 0.90 mol % guaiacol were plotted. Even though the LLV line must occur at the same pressure for a given temperature, we did note that the BP pressures for compositions below 0.90 mol % guaiacol did occur at slightly higher pressures than for the guaiacol data 0.90 mol % and above. Thus, the possibility exists that we were actually measuring the onset of the very small VL region that exists near the vapor pressure of CO₂ instead of the true LLV bubble point. The BP measurements for 0.90 mol % guaiacol at the highest measured temperatures and pressures (see **Table I**) provide our best estimate of the upper critical end point U. Note that the estimated U for the system occurred at a temperature and pressure only 2.1 °C and 2.2 bar above the critical point of pure CO₂ (T_c = 31.0 °C, P_c = 73.8 bar). The proximity of these two endpoints is a characteristic of binaries where the two components differ significantly in their molecular properties [17], such as is the case for CO₂ and guaiacol.

5. Conclusions

The recovery of lignin from biomass for use as a renewable biopolymer or as a precursor for carbon fibers is becoming of significant interest in the scientific community. Supercritical fluids can play a role in this effort, but few fundamental phase-behavior measurements exist for lignin model compounds with supercritical fluids. Herein are presented results for supercritical CO₂ with guaiacol, a model lignin monomer with a melting point close to ambient. This system has been found to exhibit Type III fluid-phase behavior according to the classification of Scott and Van Konynenburg, so guaiacol can only be regarded as being slightly soluble in CO₂. However, at 15 °C the liquid–liquid critical curve does exhibit a pressure minimum at just under

500 bar, where the two liquid phases become one miscible liquid. Thus, lignin should be able to be effectively processed with CO₂ as long as the appropriate co-solvent(s) are also employed.

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Figure captions.

Fig. 1. (a) Coniferyl alcohol, the dominant monomer in softwoods; (b) sinapyl alcohol, a major monomer unit in hardwoods along with coniferyl alcohol [6]; (c) guaiacol, a model lignin monomer.

Fig. 2. Experimental apparatus used for phase-behavior measurements, including variable-volume view cell, borescope, isothermal N₂ bath, and CO₂ delivery system.

Fig. 3. Pressure–temperature isopleths for molar concentrations of guaiacol at conditions encompassing the liquid–liquid critical curve and the three-phase LLV line. CO₂ vapor-pressure data (✕) [12]; LLV data (+); critical point of CO₂(○). All lines shown are only to guide the eye.

Fig. 4. Pressure-vs-composition diagrams of the liquid–liquid region; generated from the liquid–liquid cloud-point results given in **Table 1** and **Figure 3**.

Fig. 5. The CO₂ + guaiacol system exhibits Type III fluid-phase behavior, as the vapor-liquid critical curve first goes through a minimum and then turns to higher pressures.

Table 1. Temperatures, pressures, and types of phase transitions for CO₂+ guaiacol binary at various mixture compositions*.

Composition (mole% guaiacol)	Temperature (°C)	Pressure (bar)	Transition	Composition (mole% guaiacol)	Temperature (°C)	Pressure (bar)	Transition
0.30	25.3	356	LL	0.90	25.1	502	LL
	30.3	385	LL		30.2	518	LL
	40.3	420	LL		39.9	515	LL
	50.1	450	LL		50.0	561	LL
	64.9	511	LL		64.5	584	LL
	80.0	571	LL		79.9	623	LL
	25.1	65	BP		1.5	36	BP
	30.0	72	BP		10.3	45	BP
0.50					19.9	56	BP
	25.7	412	LL		25.3	63	BP
	30.2	445	LL		30.0	70	BP
	40.1	479	LL		33.1	75	U
	50.2	512	LL	1.13			
	65.2	557	LL		25.4	408	LL
	80.0	596	LL		30.3	431	LL
	25.3	65	BP		40.6	457	LL
0.65	30.1	72	BP		50.3	493	LL
					64.5	540	LL
	26.0	480	LL		80.0	600	LL
	30.3	488	LL		25.2	63	BP
	40.4	511	LL		30.1	70	BP
	50.5	536	LL	1.41			
	65.0	574	LL		25.9	334	LL
	79.8	608	LL		30.2	365	LL
0.90	26.3	66	BP		40.3	404	LL
	29.8	72	BP		50.1	431	LL
					64.7	483	LL
	1.6	539	LL		80.0	526	LL
	11.2	496	LL		25.4	62	BP
	15.0	493	LL		30.1	70	BP
	20.4	500	LL				

*LL is a liquid–liquid cloud-point phase transition, BP is a bubble-point on the LLV line, and U is estimate of the upper critical end point.

END OF TABLE 1

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5