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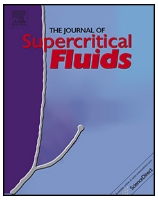

Fluid-phase behavior of the guaiacol + CO_2 system at high pressures

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ABSTRACT

The binary phase behavior of supercritical CO_2 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. CO_2 + 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 CO_2-rich liquid phase extends to temperatures and pressures 2.1 °C and 2.2 bar above the critical point of CO_2.

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 Science^{TM} 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 Fig. 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 (CO_2). 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, CO_2 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 CO_2. Because vanillin has a melting point of 81.5 °C, the focus of their measurements was on the solid–liquid–gas phase equilibria that exist for this system. To our knowledge, no other phase-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 CO_2 (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

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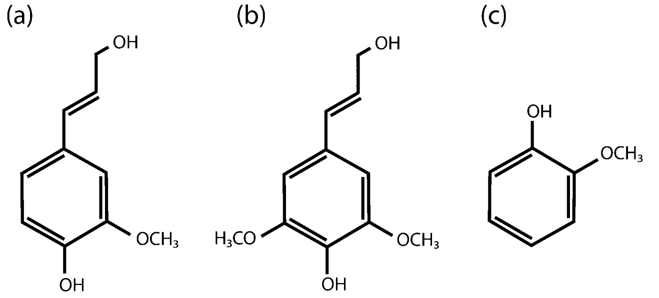

Fig. 1. (a) Coniferyl alcohol, the dominant monomer in softwoods; (b) sinapyl alchohol, a major monomer unit in hardwoods along with coniferyl alcohol [6]; (c) guaiacol, a model lignin monomer.

view cell (1.59 cm i.d. × 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 CO_2, 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 + CO_2 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. × 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 CO_2, 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 CO_2 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 CO_2, 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 min 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 CO_2 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 CO_2 (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 CO_2 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 CO_2 charged to the cell was accurately known.

After the charging of CO_2 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.

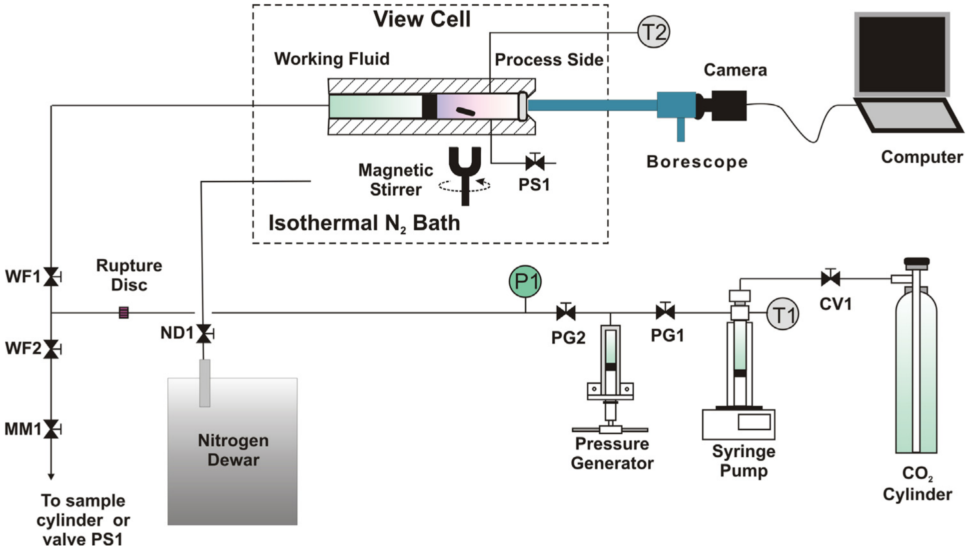

Fig. 2. Experimental apparatus used for phase-behavior measurements, including variable-volume view cell, borescope, isothermal N_2 bath, and CO_2 delivery system.