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Niramol Juntarachat, Lucie Coniglio, Romain Privat, Jean-Noël Jaubert. Experimental determination of the critical locus of binary systems containing CO₂ and an ethyl ester. XXXIX JEEP - 39TH EDITION OF THE JOINT EUROPEAN DAYS ON EQUILIBRIUM BETWEEN PHASES, 2013, Nancy, France. 10.1051/mateconf/20130301020 . hal-01292158

HAL Id: hal-01292158

<https://hal.univ-lorraine.fr/hal-01292158>

Submitted on 12 Dec 2016

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Experimental determination of the critical locus of binary systems containing CO₂ and an ethyl ester

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1 Introduction

Progressive depletion of world oil resources, combined to increasing energy consumption as well as the negative environmental impact of fossil fuel use, led to a shift toward alternative renewable sources of energy. Biodiesel is among the most viable liquid transportation fuels for the foreseeable future, with the potential of contributing significantly to sustainable development in terms of socioeconomic and environmental concerns. Indeed, biodiesel is a mixture of alkyl esters obtained by transesterification (alcoholysis) of triglycerides from vegetable oils or animal fats with an alcohol (methanol or ethanol). The transesterification reaction is commonly carried out in the presence of a catalyst the main drawback of which is to be water sensitive, preventing the use of non-conventional feedstocks (such as waste cooking oils or algal biomass) [1]. Emerging non-catalytic alcoholysis methods based on supercritical fluids allow solving this problem. Nevertheless, their industrial scale application is limited because of the severe operating conditions required (high temperature, high pressure, and high alcohol to oil molar ratio) which can be successfully reduced by addition of a co-solvent, such as CO₂ [2-4]. To optimize the supercritical process via simulation, the phase behaviour under high temperatures and pressures for systems containing CO₂ and components involved in biodiesel production must be firstly investigated.

In this work, the critical properties of nine binary mixtures containing CO₂ and an ethyl ester are investigated. A synthetic-dynamic apparatus capable of measuring the critical points of pure compounds and mixtures is employed using the dynamic method. The critical points can be determined by visually observing the critical opalescence phenomenon in the view cell. Regarding the system CO₂ + ethyl acetate, the experimental results in this work are compared to those available in the open literature. Such a comparison is not possible for the eight other systems which are measured for the first time in this study.

2 EXPERIMENTAL

All compounds were purchased from commercial sources and used without any future purification. Their purity and the suppliers are listed in Table 1.

Table 1. Purity and supplier of the compounds used in this study.

Compound	Purity	Supplier
Carbon dioxide	99.998 vol. %	Messer
Ethyl acetate (E2)	≥99.8%	Sigma-Aldrich
Ethyl propionate (E3)	99%	Sigma-Aldrich
Ethyl butanoate (E4)	99%	Sigma-Aldrich
Ethyl pentanoate (E5)	99%	Sigma-Aldrich
Ethyl hexanoate (E6)	≥99%	Sigma-Aldrich
Ethyl heptanoate (E7)	99%	Sigma-Aldrich
Ethyl octanoate (E8)	≥99%	Sigma-Aldrich
Ethyl nonanoate (E9)	≥98%	Sigma-Aldrich
Ethyl decanoate (E10)	≥99%	Sigma-Aldrich

A schematic diagram of the apparatus used in this work is presented in Fig. 1. It has been developed by ARMINES, a company hosted by the *Ecole Nationale Supérieure des Mines de Paris*, for the measurement of the critical properties of pure substances and multi-component mixtures with known overall composition. This apparatus can work using two different modes: dynamic and static. Due to short residence time, the dynamic method enables to determine the critical points of substances likely to thermally decompose but needs a large amount of matter. On the other hand, the static method requires small amounts of substances but is limited due to possible thermal decomposition of substances. The temperature and pressure upper limits of application are 673 K and 20 MPa for the dynamic method and 493 K and 20 MPa for the static method. The temperature upper limits are different owing to the use of a magnetic stirrer, which withstands conditions up to 493 K, in the static method.

In this work, the measurements were carried out using the dynamic method in which circulation of fluid ensures an efficient stirring.

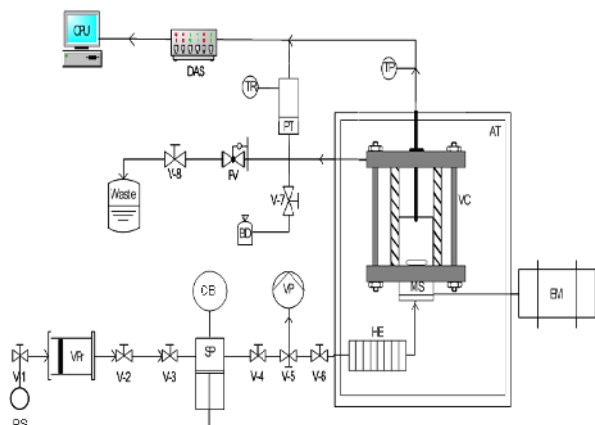


Figure 1. Schematic diagram of the apparatus. PS: Pressurized source; VPr: volumetric press; SP: syringe pump; CB: cryostat bath; VP: vacuum pump; HE: heat exchanger; EM: electric motor; MS: magnetic stirrer; VC: view cell; AT: air thermostat bath (oven); TP: platinum resistance temperature probe; PT: pressure transducer; TR: temperature regulator; BD: bursting disc; FV: flow regulation valve; DAS: data acquisition system; CPU: central processor unit; V: valve.

The state of the art of critical point measurements can be found in the book edited by Weir and de Loos [5] (in particular chapter 16 by Teja and Mendez-Santiago – entitled *Critical Parameters* – is notably well-documented). It is thus not necessary to recall it in this paper. A critical point can be determined by visually observing the critical opalescence and the simultaneous disappearance and reappearance of the meniscus (i.e. of the liquid-vapour interface from the middle of the view cell).

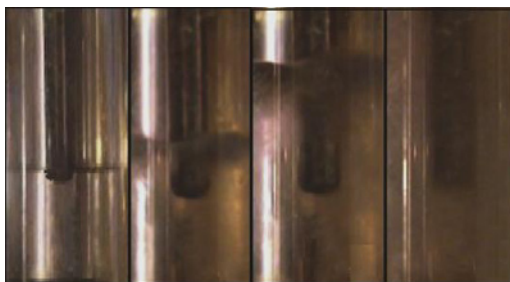


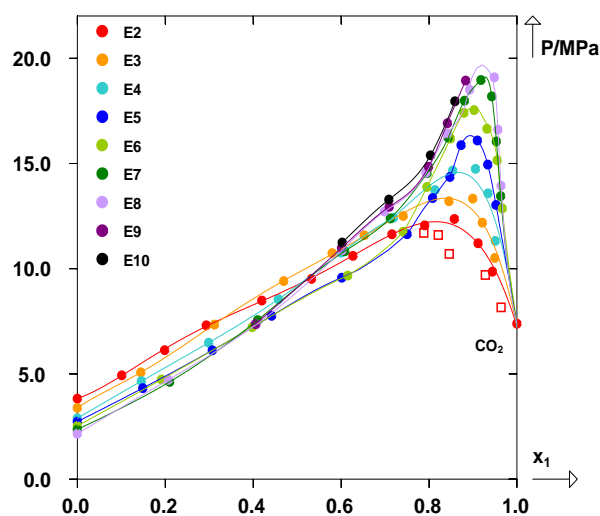
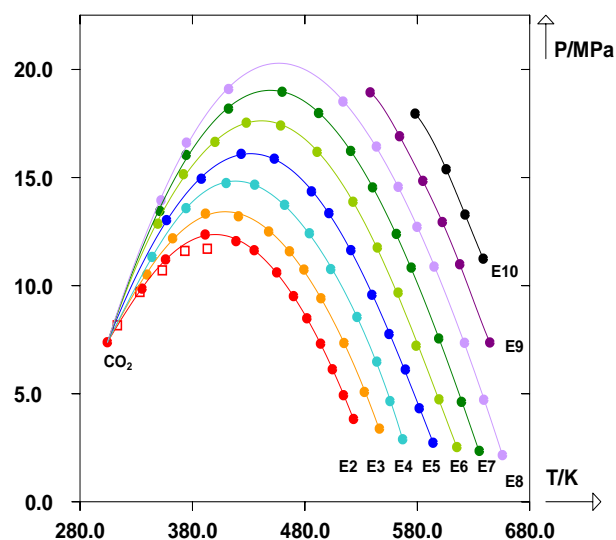
Figure 2 The transition of a fluid from the subcritical state to the critical state on temperature increase. From left to right: classical liquid–vapour mixture (the two phases are perfectly separated by a thin meniscus); cloudy subcritical state (the meniscus is not thin any more, it is coloured in orange which characterizes the critical opalescence); a thick and cloudy subcritical state (the meniscus becomes thicker and thicker); disappearance of the liquid–vapour interface (the meniscus occupies the entire view cell which is orange: we are at the critical point).

Fig. 2 illustrates the transition of a fluid from the subcritical state to the critical state on temperature increase. The apparatus was calibrated and validated by the measurement of critical points for pure compounds and binary mixtures [6-8] for which data were available

in the open literature. The experimental setup used in this work is the same as that described in one of our previous studies [7]. The uncertainties obtained in the critical temperature and critical pressure for pure compounds and mixtures at different mole fractions were ≤ 0.14 K and ≤ 0.0135 MPa, respectively. Likewise, a mean value uncertainty in the mole fraction, $u(x_i) = \pm 0.00006$ was obtained.

3 RESULTS

In this work, the vapour-liquid critical points for nine binary systems containing CO_2 and an ethyl ester (ethyl acetate, ethyl propionate, ethyl butyrate, ethyl valerate, ethyl hexanoate, ethyl heptanoate, ethyl octanoate, ethyl nonanoate and ethyl decanoate) were experimentally determined. The experimental results in this work and literature data are graphically presented in Figs. 3a, 3b and 3c which correspond to pressure – temperature, pressure – composition and temperature – composition diagrams, respectively.



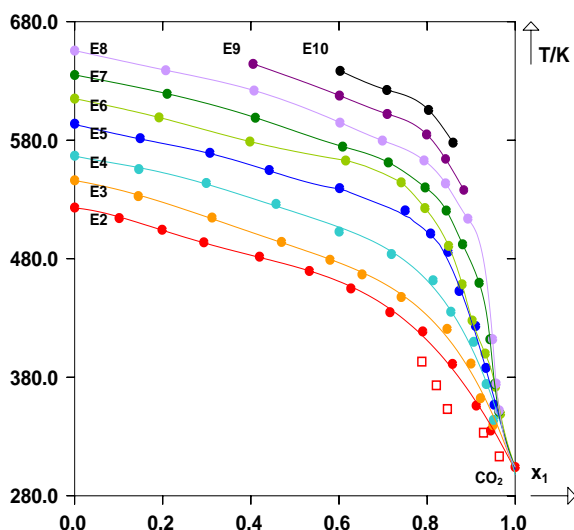


Figure 3 Experimental critical points of the binary systems: (●): CO₂ (1) + ethyl acetate (2), (●): CO₂ (1) + ethyl propionate (2), (●): CO₂ (1) + ethyl butyrate (2), (●): CO₂ (1) + ethyl valerate (2), (●): CO₂ (1) + ethyl hexanoate (2), (●): CO₂ (1) + ethyl heptanoate (2), (●): CO₂ (1) + ethyl octanoate (2), (●): CO₂ (1) + ethyl nonanoate (2) and (●): CO₂ (1) + ethyl decanoate (2). Literature data: (□): CO₂ (1) + ethyl acetate (2) collected by Byun et al. Solid lines: polynomial regression of the data. P-T (a), (P-x₁) (b) and (T-x₁) (c) projections.

As can be seen in Fig. 3a, the critical points of the first six systems (i.e. from the system CO₂ + ethyl acetate to the system CO₂ + ethyl heptanoate) could be determined throughout the entire range of composition. Such systems exhibit a continuous vapour-liquid critical locus. For the three other systems, the temperature and pressure upper limits of the apparatus prevented some critical points from being measured. Furthermore, six overall compositions ($0.92 \leq x_1 \leq 1.00$) of the CO₂ (1) + ethyl nonanoate (2) and CO₂ (1) + decanoate (2) systems were prepared and introduced in the view cell but no critical state could be found. As a consequence, these two systems are suspected to exhibit a discontinuous vapour – liquid critical locus.

Additionally, the experimentally determined critical points of the CO₂ (1) + ethyl acetate (2) can be compared to literature data [9] whereas the critical loci of the eight other binary systems are measured for the first time in this study. Fig 3b and 3c illustrate that, at a same composition, the critical pressures and temperatures measured in this study are a bit higher than those from the collection of Byun et al. These authors used the Peng-Robinson equation of state to correlate the critical locus of the CO₂ (1) + ethyl acetate (2) system. Although they concluded to an accurate correlation, it is noticeable that the calculated values are higher than their experimental data which were measured using a static – type experimental apparatus. Such an apparatus enables to accurately determine bubble and dew points but is often said not to be accurate enough for critical point measurements due to an iterative process.

4 Conclusions

In this work, the critical properties of nine binary systems containing CO₂ and an ethyl ester were studied. The measurements were carried out using a synthetic – dynamic apparatus which was employed in the dynamic mode. For six binary mixtures, the critical loci were experimentally determined over the whole composition range. For the three other systems, the critical loci were only determined in a smaller composition range due to the cell's capacity. The experimental results were compared to literature data. Some variations were found owing to different experimental methods used.

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