Phase equilibria of CO_2 with components in the light naphtha cut of tyre derived oil

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ABSTRACT

Phase equilibria of CO_2 + limonene, CO_2 + 1,2,3-trimethylbenzene, CO_2 + *p*-cymene and CO_2 + *m*-cymene systems were measured to investigate the possibility of extraction of these components from tyre derived oil using supercritical CO_2. Measurements were conducted using variable-volume view cells at four temperatures between 313 and 358 K, with solute mass fractions ranging from 0.0159 to 0.635. The maximum total solubility pressure measured was 16.5 MPa. The phase behaviour of the systems indicated that an increase in system temperature leads to an increase in phase transition pressure at constant composition. The solubility differences between the components increase slightly with the temperature, however a sufficient pressure difference exists for 1,2,3-trimethylbenzene to be isolated at temperature higher than 343 K. Experimental data of four binary systems were satisfactory correlated by using the Redlich-Kwong-Soave equation of state, along with Mathias-Klotz-Prausnitz mixing rules, which include two temperature independent binary interaction parameters.

1. Introduction

The international increase in the number of vehicles along with a lack of effective and economical methods to recycle waste tyres, is causing serious waste tyre disposal problems [1,2]. Recent attempts to re-use and recycle waste tyres include the use of ground tyre rubber as an additive in artificial sport fields and floor mats, for example. Furthermore, waste tyres can be used as a solid fuel to power cement kilns and power plants [1]. Stricter regulation on waste tyre disposal has, however, prompted investigation into more efficient and environmental-friendly recycling methods such as pyrolysis [1–4]. Pyrolysis is a process in which the volatile components in tyres are thermally degraded in the absence of oxygen. The process produces three products namely pyrolytic char, flammable gas and tyre derived oil (TDO), all of which are potentially useable as energy sources [1,2]. A drawback of this recycling method is that the raw pyrolysis products are in low demand, mainly due to their physico-chemical complexity [2]. A possible method to improve the economic viability of waste tyre pyrolysis processes is to recover valuable chemicals from the TDO.

Limonene, present in TDO, is a valuable component with wide industrial application [5]. Therefore multiple studies have been conducted to investigate the effects of the pyrolysis conditions, such as temperature and pressure, on the yield of limonene, as reported in a review article by Danon et al. [3]. However, the extraction and recovery of high purity limonene from the limonene-enriched fraction,

also known as the light naphtha cut (normal boiling point below 473 K), is not a trivial tasks due to the complex composition of TDO [6,7]. Moreover, 1,2,3-trimethylbenzene, *m*-cymene and *p*-cymene, which are formed due to limonene thermal decomposition and aromatisation reactions, respectively [3,8], could be considered as major impurities. These components and limonene have very close normal boiling points (between 448 and 450 K) and as a consequence traditional separation techniques such as distillation are unable to achieve separation at high purity [8,9].

An alternative separation technique receiving much attention is supercritical fluid fractionation (SFF), due to the good solvent properties of supercritical solvents and the fact that the solvent can easily be regenerated with minimal solvent residue in the final product. Furthermore, the use of CO_2 as solvent, which is non-toxic, non-flammable, chemically stable and has suitable critical properties (P_c = 7.38 MPa, T_c = 304.2 K), increases the advantages associated with the process. In order to determine the technical viability of SFF processes, the phase equilibria needs to be characterised and an accurate thermodynamic model must be implemented before reliable equilibrium stage simulation can be performed [10]. To the best of our knowledge only phase equilibrium measurements of CO_2 + limonene [11–14] and CO_2 + *p*-cymene [15] systems are referenced in open literature. However, published data for the latter binary system present inconsistencies which need to be addressed.

This work aims to build on previous research [16] by further

Nomenclature

AAD	Average absolute deviation
AARD	Average absolute relative deviation
CO_2	Carbon dioxide
EoS	Equation of state
RKS	Redlich-Kwong-Soave
SFF	Supercritical fluid fractionation
TDO	Tyre derived oil
a	Energy parameter of the equation of state
b	Co-volume parameter of the equation of state
$k_{i,j}$ and $l_{i,j}$	Binary interaction parameters between two components i

	and j
P_c	Critical pressure
T_c	Critical temperature
u and u_r	Standard and relative uncertainty
V_m	Molar volume
w_i and w_j	Mass fraction of the components i and j
x_i and x_j	Molar fraction of the components i and j
α_i	Alpha function of the equation of state for the component i
ε	Dielectric constant
μ	Dipolar moment
ω_i	Acentric factor for the component i

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investigating the binary phase behaviour of the major TDO components with supercritical CO_2. Firstly, this paper provides phase behaviour data of CO_2 with limonene and its close boiling point impurities from TDO light naphtha cut, namely 1,2,3-trimethylbenzene, *p*-cymene and *m*-cymene at temperatures just above the critical temperature of CO_2. Secondly, the ability of using CO_2 as a solvent in SFF to distinguish between limonene and the above mentioned impurities is investigated. Lastly, thermodynamic modelling is reported for the CO_2 + limonene, CO_2 + 1,2,3-trimethylbenzene and CO_2 + *p*-cymene systems in both the vapour-like and liquid-like regions by correlating experimental measurements with the Redlich-Kwong-Soave (RKS) equation of state (EoS) along with the mixing rules of Mathias-Klotz-Prausnitz. [17]. Note that the number of vapour-like data points measured for the CO_2 + *m*-cymene system were insufficient to apply the correlation method used in this work.

2. Method and materials

2.1. Experimental set-up and measurement method

The high pressure phase transition measurements were conducted using the synthetic visual phase detection method and the experiments were conducted using two previously constructed equilibrium view-cells [18,19]. A similar design, based on a movable piston-cylinder, was used for both view-cells, which only differ by their maximum internal volume, 45 cm³ [18] and 80 cm³ [19], respectively. The larger cell was generally used for measurements at low solute concentrations to ensure a more accurate determination of the mass fraction. The view-cells allow for experiments within a temperature range of 300–460 K, measured by 4-wire Pt 100-probes and pressures up to 28 MPa, measured by OneHalf20 transducers.

The accuracy of the measurements mainly depends on temperature, pressure and mass fraction determination [18]. Based on the accuracy of the measuring equipment, the standard uncertainty of the temperature measurement is determined to be better than 0.2 K, i.e. $u(T)$ = 0.2 K. Taking into account the accuracy of the measuring equipment and inaccuracies derived from visual determination of phase transition pressure, the standard uncertainty of the pressure measurement is determined to be better than 0.06 MPa, i.e. $u(T)$ = 0.06 MPa. The relative standard uncertainty associated with the mass fraction is estimated to be 1% of the value, i.e. $u(w_i) = 0.01 \times w_i$, taking into account the accuracy of the balances used to weigh the materials.

Experimental measurements are started by adding a weighted amount of liquid solute to the equilibrium view-cell, along with a magnetic stirrer to ensure good mass and energy transfer during measurements. The cell is closed and repeatedly flushed with CO_2, to remove air before gravimetrically adding a known mass of CO_2. The cell is heated up to the required temperature using a water recirculating thermostat bath and the studied system is pressurised to the one-phase region. Measurements of the phase transition point are determined by slowly decreasing the pressure until the system moves from the one-

phase region to the two-phase region at constant temperature. The phase transition detection procedure is then duplicated to ensure correct pressure measurement. Then the temperature is increased, the cell content is pressurised to reach the one-phase region and the measuring procedure is repeated. Comprehensive description of the experimental set-ups and measurement method, as well as comparison of results with reliable literature data, can be found in previous publications [11,16,18–20].
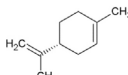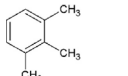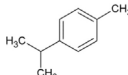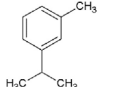
2.2. Materials

CO_2 was obtained from Air Products at a purity level of 99.995%. The molar purities, supplier, CAS Registry Numbers (CAS RN) and chemical structures of materials used as solutes are listed in Table 1. All components were used without further purification.

3. Results and discussions

3.1. Experimental phase equilibrium data

The phase transition pressure (bubble and dew points) were measured at four temperatures between 313 and 358 K, mass fractions ranging from 0.0159 to 0.635 and pressures up to 16.5 MPa. Experimental data of the systems CO_2 + limonene, CO_2 + 1,2,3-trimethylbenzene, CO_2 + *p*-cymene and CO_2 + *m*-cymene are reported in Tables 2–5, respectively. Although the temperature remained constant throughout measurements, temperature fluctuations between the different data-sets were unavoidable due to changes in ambient conditions. Therefore, not all data-sets could be measured at exactly the same temperature. In order to generate isothermal phase transition data, polynomial curves were fitted to the experimental pressure and

Table 1
List of materials used and their sources.

Chemicals	CAS RN number	Chemical structure	Supplier	Purity (Molar %)
Limonene	5989−27-5		Sigma Aldrich	≥99
1,2,3-trimethylbenzene	526−73-8		Finetech Industry Limited	98
p-cymene	99−87-6		Sigma Aldrich	99
m-cymene	535−77-3		Tokyo Chemical Industry	> 99