

Supporting Information

Experimental Section

Chemicals: Hydrogen and carbon dioxide were supplied by Air Liquide, with a stated purity of 99.998 mol%. *R*-(+)-limonene (purity: 98%), (+)-*p*-menth-1-ene (purity: $\geq 97\%$), terpinolene (purity: $\geq 97\%$), α -terpinene (purity: $\geq 95\%$) and nonane (purity: $\geq 99\%$) were supplied by Fluka. *cis-p*-menthane (purity: $\geq 97\%$) and *trans-p*-menthane (purity: $\geq 97\%$) were supplied by Fluorochem Limited.

Equipment for hydrogenation: The hydrogenations were performed in an apparatus consisting of one sapphire-windowed cell (VC) connected by a pump (CP) to a tubular reactor (TR) that encloses a catalyst bed. This apparatus is a modification of the one described by Milewska et al.⁵ The reactants were continuously withdrawn from the bottom of the view cell, circulated through the catalyst bed, and sent back to the upper entrance of the cell. Samples have been taken at regular intervals through a system of two valves with a sampling loop (S), at the top of the reactor. CO₂ in the loop was carefully vented to the atmosphere. The contents of the loop were bubbled through a measured amount of hexane, used as solvent. Initial product identification was carried out by a nominal mass GC-MS (Fisons MD800) apparatus equipped with a column of the GS-Molesieve (30 m \times 0.541 mm) type. Analyses were performed using gas chromatography by HRGC-3000C gas chromatograph. Column: 30 m \times 0.32 mm i.d. fused silica capillary column coated with a 0.25 μ m thickness film of 5 % phenyl groups in the dimethylpolysiloxane (CP-Sil 8 CB) from Varian Inc. Oven temperature program: 87-91 $^{\circ}$ C ramp at 0.5 $^{\circ}$ Cmin⁻¹, and 91-240 $^{\circ}$ C ramp 20 $^{\circ}$ Cmin⁻¹. Injector and detector temperature was 250 $^{\circ}$ C. The identification of products was based on GC comparisons with authentic samples (response factor for *R*(+)-limonene: 1.42, (+)-*p*-menth-1-ene: 1.26, terpinolene: 1.44, α -terpinene: 3.52, *cis-p*-menthane: 1.44, and *trans-p*-menthane: 1.43; precision of the method: better than 10%), yields were detected by GC.

Equipment for VLE measurements: The phase equilibrium measurements were made by analytical method using a visual high-pressure cell with variable volume, described by Stoldt et al.⁹ The mixture components were successively introduced into the heated cell, stirred for 1h and then left to equilibrate for 30 min. Samples were taken both from the liquid and vapour phases into the cooled glass traps. The amount of gas (CO₂ + H₂) in each sample was measured and analysed by GC. Perkin Elmer 8500 Gas Chromatograph with column Poropak

Q 100 - 120 mesh (2m, 2mm i.d.). Oven temperature program: isothermal – 150 °C for 1.6 minutes. Injector and thermoconductive detector temperatures were 200 °C. During the sampling, the pressure inside the cell was maintained constant by moving the piston and decreasing the volume. Each experimental composition value is the average of values obtained for at least six different samples. Reproducibility is better than $\pm 3\%$ of the mean value.

Table 1. Physical parameters of pure components.

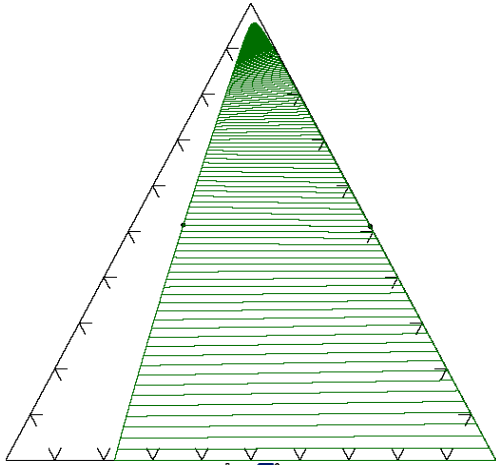
Compound	T_c/K	p_c/MPa	ω
CO ₂	304.10	7.38	0.225
limonene	653.00	2.82	0.381
H ₂	332.00	1.30	-0.218

Table 2. Optimised interaction parameters of the ternary system with the Peng-Robinson equation of state and the Mathias-Klotz-Prausnitz mixing rule.

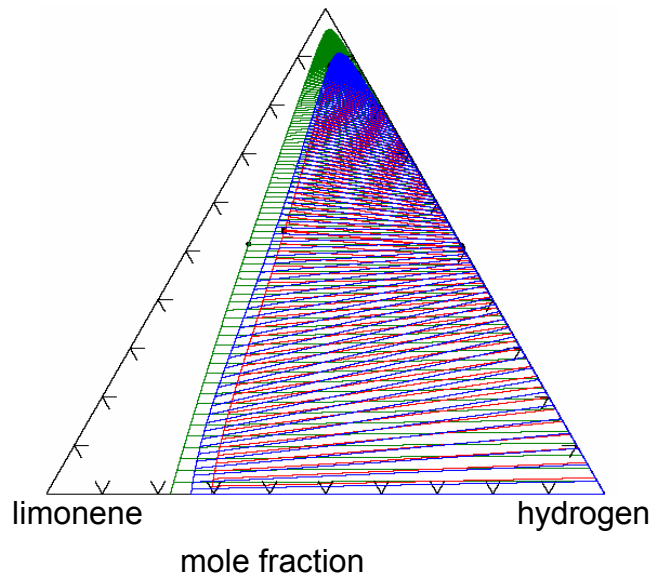
323.15 K			
	1-2	1-3	2-3
k_{ij}	-0.0038	-0.0108	-0.1779
l_{ij}	-0.0968	0.0597	0.1279
λ_{ij}	0.1058	0.0889	-0.0372

Figure 1. Correlation of the p_{xy} experimental and calculated data with the Peng-Robinson equation of state and the Mathias-Klotz-Prausnitz mixing rule at 323.15K for isobars at 11.0MPa (green), 12.5MPa (blue) and 13.0MPa (red).

carbon dioxide



carbon dioxide



limonene

hydrogen

mole fraction