

Supercritical hydrogenation processes

Experimental results on the fluid phase behavior of binary and ternary mixtures of hydrogen, propane and tripalmitin

L.J. Rovetto^a, S.B. Bottini^{a,*}, E.A. Brignole^a, C.J. Peters^b

^a *PLAPIQUI, Universidad Nacional del Sur-CONICET, Camino La Carrindanga Km 7, Casilla 717, 8000 Bahía Blanca, Argentina*

^b *Laboratory of Applied Thermodynamics and Phase Equilibria, Faculty of Applied Sciences, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands*

Received 2 January 2002; received in revised form 10 June 2002; accepted 21 June 2002

Abstract

The problems of low reaction rate and *cis*–*trans* isomerization encountered in the gas–liquid catalyzed hydrogenation of vegetable oils can be overcome by using a supercritical fluid to bring the reactive mixture into a homogeneous phase. For that purpose, experimental phase equilibrium data on mixtures of high molecular weight substrates with hydrogen and a supercritical fluid are needed in order to evaluate optimum process conditions. In this work vapor–liquid and liquid–liquid equilibria in mixtures of hydrogen + propane + tripalmitin have been measured. A temperature region between 323 and 453 K, and pressures up to 15 MPa were covered.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Phase equilibria; Hydrogen; Propane; Tripalmitin; Supercritical hydrogenation

1. Introduction

Margarine and shortenings are produced by hydrogenation of vegetable oils. The traditional heterogeneous catalytic process takes place in a reactor where the slurry of oil (liquid), H₂ (gas) and catalyst (solid) is mixed intensively. The low solubility of H₂ and the high mass transfer resistance in the liquid phase lead to a depletion

of H₂ at the catalyst surface, which, in turn, slows down the reaction rate and gives rise to double bond migration and *cis*–*trans* isomerization [1].

These problems can be overcome by using a supercritical solvent in which both reactants are soluble, bringing the mixture of H₂ + solvent + oil into a homogeneous phase [2–9]. The main role of the supercritical solvent is to get the homogeneous phase in contact with the solid catalyst, at the required molar ratio of the reactants. If a single phase is achieved, the various process parameters (temperature, pressure, H₂ concentration, etc.) can be adjusted independently. With respect to this process, supercritical fluids have some advantages:

* Corresponding author. Tel.: +54-291-486-1700; fax: +54-291-486-1600

E-mail address: sbottini@plapiqui.edu.ar (S.B. Bottini).

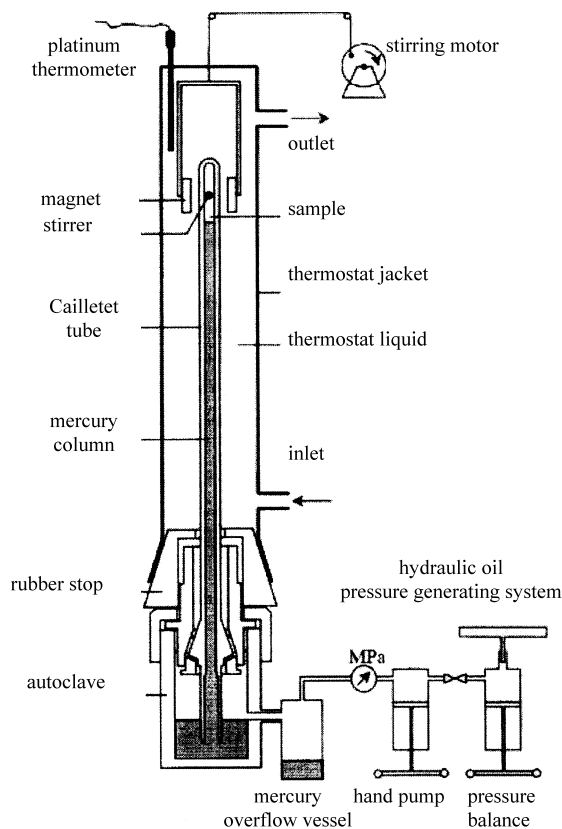


Fig. 1. The Cailletet apparatus.

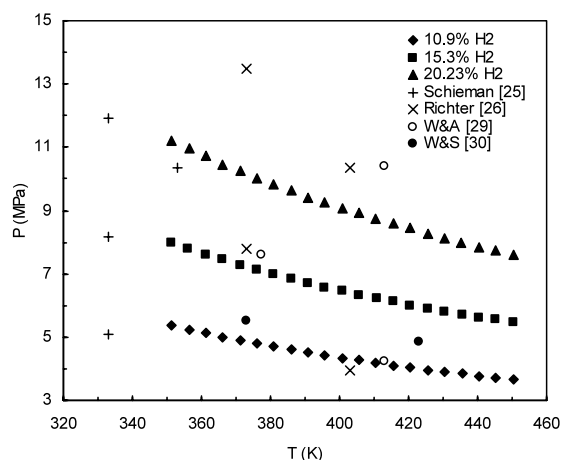


Fig. 2. Bubble pressures of certain isopleths in the binary system H_2 +PPP (compositions in mol%). Comparison with literature data: \circ Wisniak and Albright [25]; \bullet Wisniak and Shoshanah [26]; $+$ Schieman [27]; \times Richter [28].

Table 1
Vapor–liquid boundaries of the binary system hydrogen–tripalmitin at fixed molar compositions

x, H_2	T (K)	P (MPa)	T (K)	P (MPa)
0.109	450.33	3.68	395.85	4.42
	445.38	3.73	390.87	4.51
	440.40	3.78	385.93	4.61
	435.44	3.84	380.98	4.71
	430.50	3.90	376.05	4.80
	425.52	3.97	371.14	4.90
	420.56	4.04	366.24	5.01
	415.61	4.11	361.29	5.12
	410.64	4.18	356.37	5.24
	405.70	4.26	351.45	5.37
0.1526	450.30	5.46	395.81	6.58
	445.41	5.55	390.87	6.71
	440.43	5.63	385.91	6.84
	435.45	5.72	380.99	6.98
	430.52	5.82	376.04	7.13
	425.56	5.91	371.13	7.28
	420.57	6.01	366.21	7.44
	415.64	6.12	361.24	7.62
	410.67	6.22	356.25	7.80
	405.70	6.34	351.40	7.98
0.2018	450.32	7.61	395.81	9.26
	445.35	7.73	390.85	9.43
	440.36	7.86	385.91	9.62
	435.43	8.00	380.96	9.81
	430.39	8.14	376.03	10.03
	425.49	8.29	371.11	10.24
	420.50	8.44	366.22	10.44
	415.60	8.59	361.27	10.71
	410.65	8.74	356.35	10.96
	405.67	8.91	351.42	11.23
400.75	9.09			

- Favorable transport properties, which improves the mass transfer;
- Better thermal properties improve also the reaction, because hydrogenation is a highly exothermic process;
- Easier separation from the product.

Although carbon dioxide is an attractive supercritical solvent because it is environmentally benign, cheap, non-toxic and non-flammable, propane draws special attention as a solvent. The hydrocarbon nature of vegetable oils makes C_3H_8 a better solvent for vegetable oils than CO_2 .

Table 2

Vapor–liquid boundaries for the ternary system H₂–PPP–C₃H₈ at fixed molar composition (PPP/C₃H₈ ≈ 0.14)

x , PPP	x , H ₂	PPP/C ₃ H ₈	T (K)	P (MPa)	T (K)	P (MPa)
0.1215	–	0.1383	322.81	1.49	358.72	3.03
			326.67	1.63	365.69	3.44
			330.70	1.77	373.66	3.95
			334.75	1.92	383.65	4.70
			338.69	2.08	394.72	5.66
			343.79	2.29	405.78	6.70
			347.80	2.47	416.74	7.78
			352.74	2.71	430.75	9.11
0.1209	0.047	0.1452	429.93	13.54	356.31	8.57
			420.64	12.73	351.41	8.42
			410.36	11.95	346.53	8.27
			401.00	11.19	341.55	8.16
			391.01	10.44	336.67	8.06
			381.00	9.74	331.74	8.00
			371.05	9.17	326.79	7.97
			361.22	8.73	321.88	7.94
0.1172	0.075	0.1451	371.06	12.51	339.12	11.79
			363.66	12.28	336.68	11.79
			361.20	12.17	334.20	11.79
			356.32	12.04	331.73	11.80
			351.40	11.94	326.80	11.82
			346.49	11.87	321.87	11.89
			341.62	11.81		

Binary data are taken from Coorens et al. [34].

Mixtures of CO₂ and *n*-paraffins with carbon number greater than 7 display a liquid–liquid phase split [10], whereas C₃H₈ and *n*-paraffins of

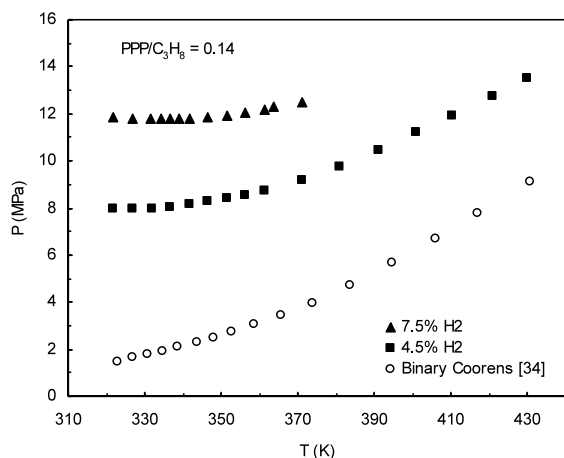


Fig. 3. Effect of the addition of H₂ to C₃H₈ + PPP mixtures (○ Coorens et al. [34]), keeping the ratio PPP/C₃H₈ = 0.14.

up to 30 carbon atoms are completely miscible in the liquid state [11]. Even though propane–triglyceride mixtures exhibit a region of partial liquid miscibility at high solvent concentrations and temperatures close to the critical temperature of C₃H₈, complete miscibility is achieved by increasing the pressure [12–14]. In the mixtures CO₂ + triglyceride, on the other hand, the partial miscibility persists until very high pressures [15] and the region of complete miscibility is limited to mixtures of high triglyceride concentrations.

The solubility of gaseous hydrogen is relatively low in organic solvents but the reaction temperature is close to or greater than the critical temperature of C₃H₈ and under these conditions H₂ and C₃H₈ are completely miscible [16,17]. In the hydrogenation process, complete miscibility of the ternary mixture is required at a ratio H₂/oil fixed by product specification, that is generally greater than one. Recently, single-phase reaction

Table 3
 Vapor–liquid boundaries of the ternary system H₂–PPP–C₃H₈ at fixed molar compositions (PPP/H₂ ≈ 4.1)

x , PPP	x , C ₃ H ₈	PPP/H ₂	T (K)	P (MPa)	T (K)	P (MPa)
0.7982	0	3.95	351.42	11.23	405.67	8.91
			356.35	10.96	410.65	8.74
			361.27	10.71	415.6	8.59
			366.22	10.44	420.5	8.44
			371.11	10.24	425.49	8.29
			376.03	10.03	430.39	8.14
			380.96	9.81	435.43	8.00
			385.91	9.62	440.36	7.86
			390.85	9.43	445.35	7.73
			395.81	9.26	450.32	7.61
			400.75	9.09		
			0.7366	0.0887	4.2152	450.1
440.26	7.55	390.89				8.97
430.47	7.79	380.93				9.33
420.6	8.05	371.1				9.76
410.66	8.33	361.22				10.21
0.6774	0.1608	4.1868	450.07	7.52	390.92	8.99
			439.34	7.73	381.44	9.25
			430.23	7.94	371.22	9.59
			420.44	8.21	361.39	9.98
			410.48	8.45	351.44	10.42
400.5	8.71					
0.5847	0.2759	4.1931	450.2	7.86	390.92	8.95
			440.01	8.00	381.04	9.21
			430.42	8.15	371.28	9.51
			420.6	8.32	361.35	9.84
			410.64	8.50	351.66	10.22
400.65	8.72					
0.3949	0.5103	4.1673	451.73	8.60	392.308	8.67
			441.889	8.58	382.4	8.76
			431.995	8.56	372.487	8.86
			422.067	8.55	362.597	9.01
			412.164	8.57	352.702	9.21
402.214	8.61					
0.3313	0.5892	4.1694	449.85	9.17	391.18	8.67
			440.17	9.05	380.84	8.67
			430.43	8.94	371.11	8.70
			420.51	8.85	360.21	8.77
			410.42	8.76	351.46	8.87
400.87	8.71					
0.2581	0.6799	4.156	449.77	10.08	390.81	8.72
			440.16	9.82	380.9	8.58
			430.41	9.57	371.09	8.48
			420.44	9.32	361.27	8.42
			410.57	9.09	351.46	8.39
400.73	8.90					
0.2214	0.7275	4.3337	449.83	10.30	390.93	8.10
			440.22	9.90	380.93	7.81
			430.37	9.51	371.14	7.57

Table 3 (Continued)

x , PPP	x , C ₃ H ₈	PPP/H ₂	T (K)	P (MPa)	T (K)	P (MPa)
			420.51	9.12	361.28	7.38
			410.79	8.76	351.49	7.24
			400.76	8.41		

conditions were achieved by using propane as a co-solvent [18–23]. Also, regions of homogeneous phase behavior for the system H₂–C₃H₈–triglyceride have been predicted by means of a group contribution equation of state [24]. Experimental data are needed in order to corroborate predictions and to explore single-phase process conditions.

In this work, experimental phase equilibrium data on binary mixtures of H₂+tripalmitin (PPP) and ternary mixtures of H₂+C₃H₈+PPP have been measured, covering a temperature region between 323 and 453 K, and pressures up to 15 MPa. Tripalmitin (PPP) was used as a representative model triglyceride for vegetable oil. A saturated triglyceride was chosen in order to avoid premature hydrogenation.

In literature, no experimental information is available on the H₂+PPP system. The only information available in literature on related systems is from Wisniak and Albright [25] and

Wisniak and Shoshanah [26]. Recently Schieman [27] reported data for binary mixtures of H₂+sunflower oil, while Richter [28] measured data for the system H₂+soy oil. Schieman [27] and Richter [28] also report some data on the ternary systems with propane.

2. Experimental apparatus and procedure

All measurements were carried out in a Cailletet apparatus, shown in Fig. 1. Essentially, a Cailletet tube is a thick-walled Pyrex glass tube with one open end and an inner and outer diameter of about 3 and 8 mm, respectively. A sample of known overall composition is brought under vacuum conditions in the closed top of the high-pressure tube. After filling the tube with mercury, again under vacuum conditions, the open end of the tube is immersed in mercury present in an autoclave. The sample inside the tube is stirred by

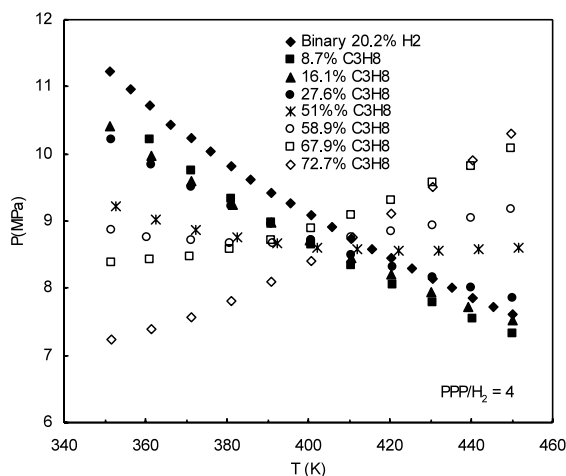


Fig. 4. Bubble pressures of certain isopleths in the ternary system H₂+C₃H₈+PPP, keeping the ratio PPP/H₂ = 4.

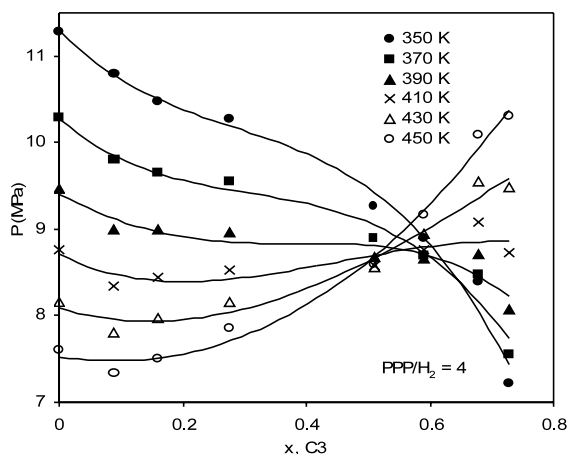


Fig. 5. Isothermal P-x data in the ternary system H₂+C₃H₈+PPP with PPP/H₂ = 4.

Table 4
 Vapor–liquid boundaries for the ternary system H₂–PPP–C₃H₈ at fixed molar compositions (H₂/C₃H₈ ≈ 0.1)

x , PPP	x , C ₃ H ₈	H ₂ /C ₃ H ₈	T (K)	P (MPa)	T (K)	P (MPa)
0.1172	0.8078	0.0928	371.06	12.51	339.12	11.79
			363.66	12.28	336.68	11.79
			361.20	12.17	334.20	11.79
			356.32	12.04	331.73	11.80
			351.40	11.94	326.80	11.82
			346.49	11.87	321.87	11.89
			341.62	11.81		
0.1029	0.8156	0.0998	363.80	13.76	339.17	13.25
			361.42	13.67	336.74	13.25
			358.90	13.57	334.25	13.26
			356.34	13.50	331.74	13.27
			353.97	13.44	329.26	13.29
			351.61	13.38	326.82	13.32
			349.03	13.34	324.38	13.35
			346.58	13.30	321.90	13.40
			344.13	13.28	319.41	13.45
341.67	13.26	316.95	13.50			
0.0797	0.8371	0.0993	361.31	13.58	334.18	12.90
			356.41	13.29	332.88	12.90
			351.48	13.12	331.71	12.91
			346.56	13.01	329.24	12.92
			341.61	12.94	326.78	12.95
			340.13	12.92	321.86	13.02
			339.13	12.91	319.41	13.07
			336.68	12.91	316.94	13.12
0.0711	0.8451	0.0991	352.60	13.18	339.15	12.93
			351.42	13.14	336.69	12.92
			350.12	13.10	334.23	12.92
			348.96	13.07	332.94	12.92
			346.52	13.01	331.75	12.93
			344.07	12.97	329.29	12.95
			341.62	12.94	326.81	12.97
0.0651	0.8506	0.0991	348.87	13.04	334.30	12.88
			347.68	13.00	331.80	12.89
			346.47	12.98	329.41	12.91
			344.24	12.94	326.90	12.94
			341.74	12.91	321.90	13.02
			339.23	12.89	316.99	13.13
			336.83	12.88		
0.0492	0.8648	0.0994	337.91	12.84	326.79	12.95
			336.63	12.84	324.31	13.00
			334.17	12.86	321.89	13.06
			331.70	12.88	319.38	13.12
			329.28	12.92	316.97	13.19
0.0407	0.8722	0.0999	334.43	12.04	325.71	12.23
			333.18	12.06	323.22	12.28

Table 4 (Continued)

x , PPP	x , C ₃ H ₈	H ₂ /C ₃ H ₈	T (K)	P (MPa)	T (K)	P (MPa)
			331.94	12.09	320.72	12.35
			330.68	12.12	318.22	12.43
			328.21	12.17		
0.0352	0.8775	0.0995	334.67	11.32	323.72	11.59
			333.62	11.35	322.04	11.64
			332.18	11.38	319.53	11.71
			329.63	11.44	317.13	11.80
			327.19	11.50		
0.0278	0.8841	0.0996	332.43	10.91	326.96	11.09
			333.28	10.88	324.49	11.14
			331.78	10.94	321.98	11.24
			329.49	11.01	316.88	11.39

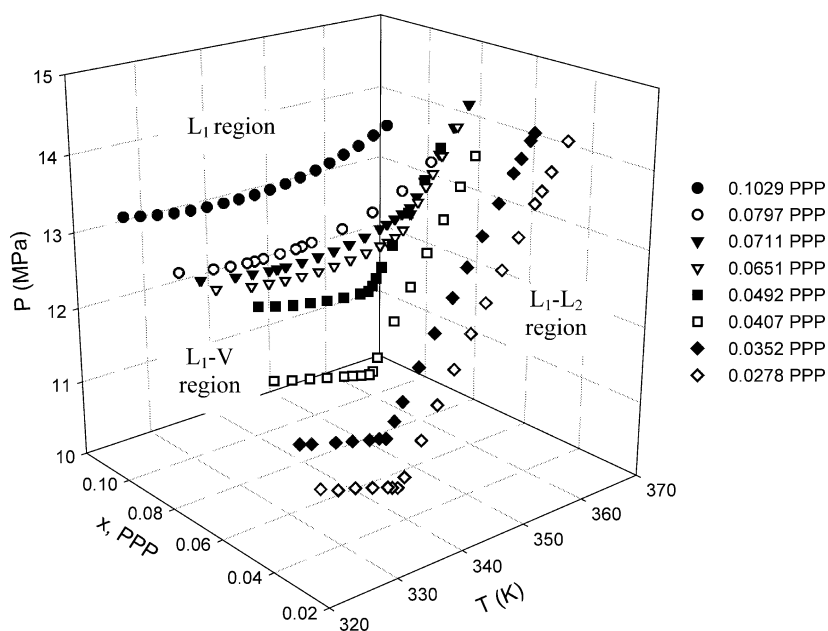


Fig. 6. Selected vapor–liquid isopleths (Table 4) and liquid–liquid isopleths (Table 5) in molar fractions, in the ternary system H₂ + C₃H₈ + PPP with the ratio H₂/C₃H₈ = 0.099.

a stainless steel ball, which is moved up and down by two button magnets activated by the rotating disc mounted on a stirring motor. The autoclave is connected to a hydraulic oil system. The pressure inside the tube can be modified by means of a hand screw pump and it is measured with a dead weight pressure balance. Mercury is used as the sealing

and pressure-transmitting fluid between the hydraulic oil and the sample. The Cailletet tube is jacketed, and silicon oil is used as the thermostatic fluid. A platinum resistance thermometer (Pt 100) measures the temperature, which is controlled within ± 0.02 K by a thermostat. Pressure measurements are as accurate as 0.03% of the reading.

Table 5
Liquid–liquid boundaries for the ternary system H₂–PPP–C₃H₈ at fixed molar compositions (H₂/C₃H₈ ≈ 0.1)

x , PPP	x , C ₃ H ₈	H ₂ /C ₃ H ₈	T (K)	P (MPa)	T (K)	P (MPa)
0.0711	0.8451	0.0991	363.68	14.38	356.31	13.53
			361.22	14.13	355.04	13.35
			358.77	13.83	353.93	13.23
0.0651	0.8506	0.0991	358.97	14.24	352.57	13.41
			356.48	13.92	351.36	13.28
			354.97	13.72	350.16	13.10
			353.87	13.58		
0.0492	0.8648	0.0994	348.93	14.35	339.88	13.09
			346.50	14.01	339.08	12.98
			343.98	13.66	338.49	12.90
			341.53	13.32		
0.0407	0.8722	0.0999	350.49	14.32	340.64	12.95
			348.17	14.00	338.18	12.59
			345.63	13.66	335.67	12.21
			343.14	13.31	334.99	12.06
0.0352	0.8775	0.0995	357.35	14.53	346.93	13.12
			356.69	14.45	344.74	12.80
			355.26	14.26	342.01	12.43
			354.08	14.11	339.63	12.07
			351.80	13.79	337.16	11.71
			349.26	13.45	335.94	11.50
0.0278	0.8841	0.0996	359.11	14.48	346.52	12.80
			356.54	14.16	344.27	12.48
			355.06	13.96	341.73	12.11
			353.98	13.83	339.22	11.74
			351.48	13.48	336.80	11.37
			348.96	13.14	334.29	10.98

For details on the experimental facility one is referred to elsewhere [29].

Samples are prepared by dosing a weighed amount of the solid component (PPP) into the Cailletet tube. To remove trapped air from the PPP, the solid material is molten several times along with vacuuming simultaneously. Afterwards, gases are dosed volumetrically into the Cailletet tube via a gas-dosing device. For details one is referred to elsewhere [30].

Bubble pressures, for instance, were measured for different samples of known overall composition. The temperature ranged from 313 (close to the mixture solidification point) to 453 K (maximum operating temperature of the apparatus).

Pressures in the range from 0.5 to 15 MPa were covered. The latter pressure is the upper limit allowed for the glass Cailletet tube. For each measurement the temperature is fixed and the pressure is varied until a two-phase vapor–liquid region is present. The pressure is then increased stepwise, consequently causing a decrease in the vapor phase volume. This procedure is continued until the vapor phase disappears after a final small increase in pressure (0.005 MPa). This final pressure is the bubble pressure of the mixture at the fixed temperature. For a given sample, the whole procedure is repeated at several temperatures until the bubble-point curve of that particular isopleth is obtained. A similar experimental

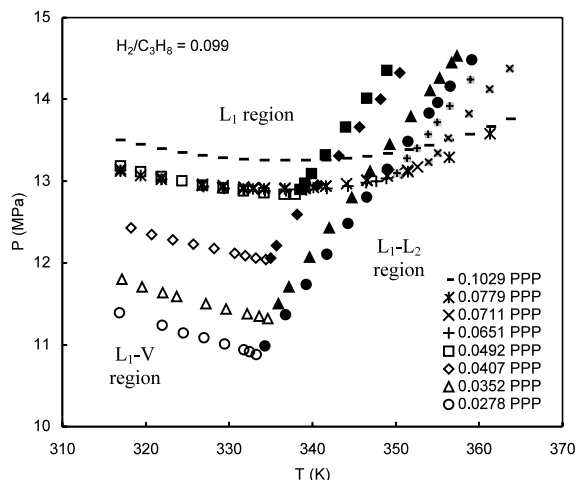


Fig. 7. P-T projection derived from Fig. 6. The vapor–liquid boundaries (Table 4: open symbols) and liquid–liquid boundaries (Table 5: filled symbols) in the ternary system $H_2 + C_3H_8 + PPP$ with the ratio $H_2/C_3H_8 = 0.099$.

procedure applies for liquid–liquid equilibrium measurements.

Fluka supplied tripalmitin (purity better than 99% on a molar basis), Scott Specialty Gases propane (purity better than 99.95% molar), and Hoek Loos hydrogen (purity of 99.999% molar).

3. Results and discussion

In this work, first the vapor–liquid equilibrium of the $H_2 + PPP$ system was measured for three different compositions. The experimental results are summarized in Table 1 and shown in Fig. 2. For comparison, some of the data measured by Schieman [27], Richter [28] and Wisniak et al. [25,26] at similar compositions are included in Fig. 2.

During the measurements a problem in the reproducibility of the data was faced. For the same composition and temperature, the measured bubble pressure decreased with time. This behavior was particularly noticeable at the higher temperatures and pressures. NMR analysis on samples that had been subject to high temperatures and pressures during a certain period did not show any chemical changes in the mixture. The observed behavior can be ascribed to a slight change in the

concentration of H_2 in the sample, due to the diffusion of H_2 through the glass walls of the Cailletet tube [31–33]. The high diffusivity of H_2 makes the total pressure in the cell highly sensitive to the composition of H_2 in the liquid phase. Also the higher the triglyceride concentration, the more viscous the system became, which, in turn, could slow down the equilibration time of the phase change. Nevertheless, the variation of pressure with time was never higher than 0.06 MPa, which represents a maximum overall uncertainty in the experimental pressures of the order of 0.5%.

The main objective of this work was to measure data on the ternary system $H_2 + C_3H_8 + PPP$. The vapor–liquid data collected in Table 2 and shown in Fig. 3 indicate the effect of adding H_2 to a binary mixture of $C_3H_8 + PPP$. Due to the low solubility of H_2 in the liquid phase, a small increase in the hydrogen mole fraction produces a large increase in the bubble pressure of the ternary mixture. In heterogeneous hydrogenation processes the ratio H_2 /substrate should be higher than the stoichiometric ratio in order to reduce the time to attain chemical equilibrium. This means that reaction is preferred at higher concentrations of H_2 in the reactive mixture, which lead to operation at elevated pressures.

In order to see the effect of propane as a co-solvent in the hydrogenation process, eight ternary isopleths were measured, increasing the amount of propane in the mixture and keeping a PPP/H_2 ratio close to 4. The measured bubble pressures for the different isopleths are collected in Table 3 and depicted in Fig. 4. This figure shows that approximately up to propane concentrations as high as about 60 mol% in the liquid phase the experimental isopleths have a systematic negative slope (hydrogen-like behavior), while at higher concentrations of propane the slope of the isopleths change sign systematically and become positive (propane-like behavior). As an additional feature, it can be observed in Fig. 4 that all isopleths intersect at about 400 K and 8.5 MPa. From Fig. 4 it also can be observed that at a propane concentration of approximately 50 mol% the influence of the temperature on the equilibrium pressure becomes almost negligible. Of course, this effect can be assigned to the change of sign in the slope of the

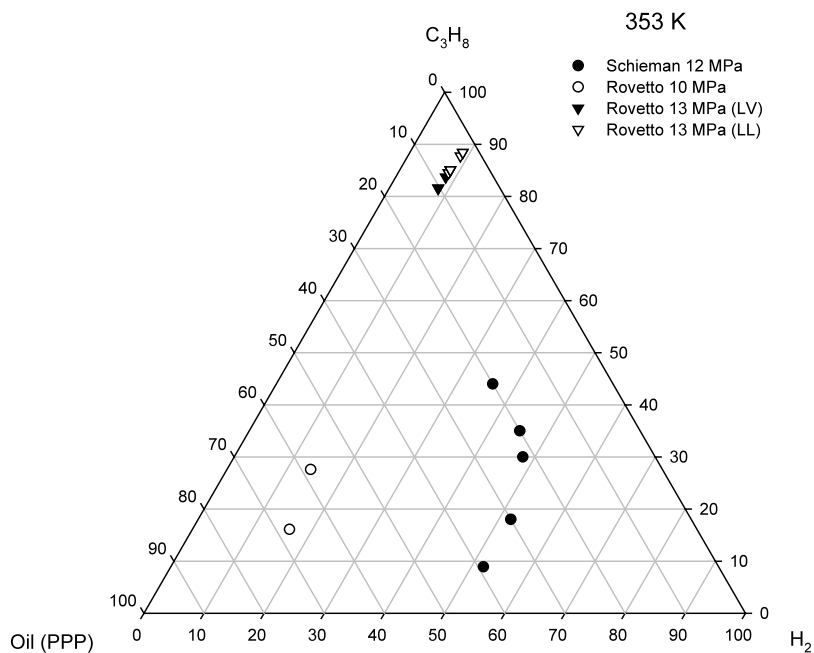


Fig. 8. Comparison of some experimental data points with those of Schieman [27] at 353 K and at different pressures (composition in mol%).

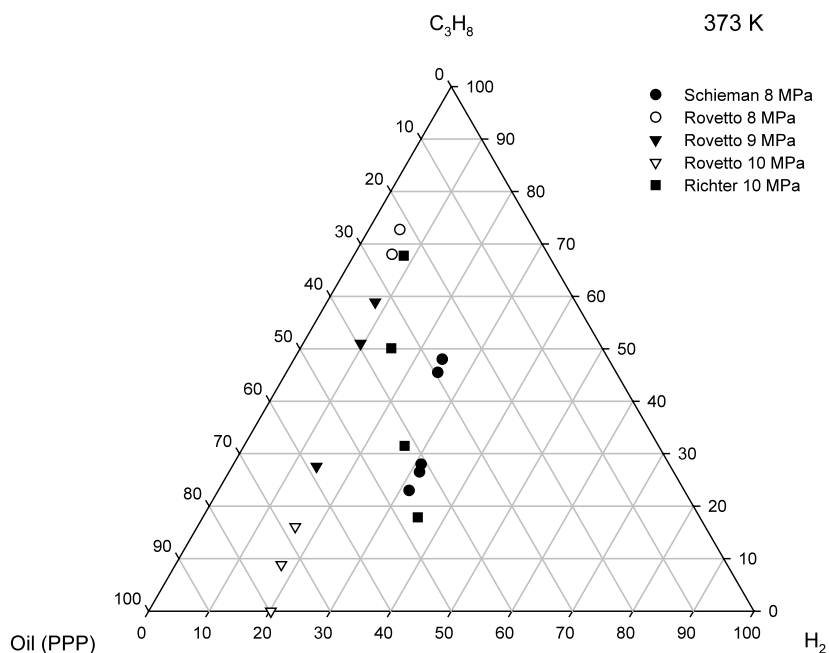


Fig. 9. Comparison of some experimental data points with those of Schieman [27] and Richter [28] at 373 K and at various pressures (composition in mol%).

isopleths with increasing propane concentration. The same data are shown in Fig. 5 as an isothermal pressure–composition diagram. The points in this figure have been obtained by interpolating the primary experimental data with a second order polynomial.

It is known that C_3H_8 +PPP mixtures present a region of partial liquid miscibility at high propane concentrations and at temperatures close to the critical point of propane [34]. It is expected that this behavior is also present in the ternary H_2 + C_3H_8 +PPP system [24,35]. Measurements were carried out for nine different isopleths having a molar fraction ratio of H_2/C_3H_8 of around 0.1. Table 4 summarizes the corresponding vapor–liquid experimental data. It was observed that six of these isopleths (with PPP molar fractions lower than 0.07) showed a liquid–liquid two-phase split. In Table 5, the experimental data of the liquid–liquid equilibria are collected. Fig. 6 shows in a 3D figure some of the experimental results as presented in both Tables 4 and 5. A p–T projection of these results is shown in Fig. 7.

The data of Schieman [27] on the ternary system H_2 + C_3H_8 +sunflower oil show that a slight addition of C_3H_8 to a H_2 +oil mixture causes a sudden increase in the solubility of H_2 in the liquid phase. This phenomenon was not observed in the experiments carried out in this work. In order to check this observation further, extra samples were prepared with the concentrations at which Schieman [27] reports to have found saturated liquid conditions. In the temperature range from 323 to 423 K, the mixtures were pressurized up to 14.8 MPa, and saturation of the liquid phase could not be reached, i.e. it is believed that Schieman's data are erroneous. Figs. 8 and 9 compare our experimental data at temperatures of 353 and 373K (± 2 K) with data of Schieman [27] and Richter [28] at comparable pressures. From these figures the discrepancy becomes apparent.

4. Conclusions

Experimental phase equilibrium data were obtained for the binary system H_2 +PPP and the ternary system H_2 + C_3H_8 +PPP. Both vapor–

liquid and liquid–liquid equilibria were determined, i.e. the partial miscibility behavior found in the C_3H_8 +PPP system [34] is also present in the ternary mixtures with hydrogen. From this study it can be concluded that the composition of the reaction mixture and the operating process conditions have to be carefully selected in order to ensure single-phase hydrogenation processes.

References

- [1] P.N. Rylander, Hydrogenation Methods, Academic Press, London, 1985, Chapter 2, pp. 29–52.
- [2] P.E. Savage, S. Gopalan, T.I. Mizan, C.J. Martino, E.E. Brock, Reactions at supercritical conditions: applications and fundamentals, Am. Inst. Chem. Eng. J. 41 (7) (1995) 1723–1778.
- [3] M.G. Hitzler, M. Poliakoff, Continuous hydrogenation of organic compounds in supercritical fluids, Chem. Commun. 17 (1997) 1667–1668.
- [4] A. Bertucco, P. Canu, L. Devetta, A.G. Zwahlen, Catalytic Hydrogenation in supercritical CO_2 : kinetic measurements in a gradientless internal-recycle reactor, Ind. Eng. Chem. Res. 36 (1997) 2626–2633.
- [5] M.G. Hitzler, F.R. Smail, S.K. Ross, M. Poliakoff, Selective catalytic hydrogenation of organic compounds in supercritical fluids as a continuous process, Organic Process Res. Dev. 2 (1998) 137–146.
- [6] A. Baiker, Supercritical fluids in heterogeneous catalysis, Chem. Rev. 99 (1999) 453–473.
- [7] P.G. Jessop, W. Leitner, Chemical Synthesis Using Supercritical Fluids, Wiley-VCH, Weinheim, 1999, Chapter 1, 29–30, Chapter 4, 358–411.
- [8] S. van den Hark, M. Härröd, P. Møller, Hydrogenation of fatty acid methyl esters to fatty alcohols at supercritical conditions, J. Am. Oil Chem. Soc. 76 (1999) 1363–1370.
- [9] A. De Jong, A. Eftaxias, F. Trabelsi, F. Recasens, J. Sueiras, F. Stüber, Solvent screening for the supercritical hydrogenation of polyunsaturated hydrocarbons using VLE calculations, Ind. Eng. Chem. Res. 40 (2001) 3225–3229.
- [10] D.J. Fall, J.L. Fall, K.D. Luks, Liquid–liquid–vapor immiscibility limit in carbon dioxide+*n*-paraffins mixtures, J. Chem. Eng. Data 32 (1985) 201.
- [11] C.J. Peters, H.J. van der Kooij, J.L. de Roo, J. de Swaan Arons, J.S. Gallagher, J.M.H. Levelt Sengers, The search for tricriticality in binary mixtures of near-critical propane and normal paraffins, Fluid Phase Equilibria 51 (1989) 339.
- [12] E.J.M. Straver, C.J. Peters, J. de Swaan Arons, On the phase behavior of mixtures of certain triglycerides and palm oil with propane as the near critical solvent, Proc. 5th Meeting on Supercritical Fluids, Materials and Natural Products Processing, vol. 2, Nice, France, Tome, 1998, pp. 943–948.

- [13] E.J.M. Straver, J.L. de Roo, C.J. Peters, J. de Swaan Arons, Phase behavior of the binary system propane and tristearin, *J. Supercritical Fluids* 11 (1998) 139–150.
- [14] J. de la Fuente Badilla, G.D. Mabe, E.A. Brignole, S.B. Bottini, Phase equilibria in binary mixtures of ethane and propane with sunflower oil, *Fluid Phase Equilibria* 101 (1994) 247–257.
- [15] T. Klein, S. Schulz, Measurement and model prediction of vapor–liquid equilibria of mixtures of rapeseed oil and supercritical carbon dioxide, *Ind. Eng. Chem. Res.* 28 (1989) 1073.
- [16] W.L. Burriss, N.T. Hsu, H.H. Reamer, B.H. Sage, Phase behavior of the hydrogen–propane system, *Ind. Eng. Chem.* 45 (1953) 210–213.
- [17] D.B. Trust, F. Kurata, Vapor–liquid phase behavior of the hydrogen–propane and hydrogen–carbon monoxide–propane systems, *Am. Inst. Chem. Eng. J.* 17 (1971) 86–91.
- [18] M.-B. Macher, J. Högberg, P. Møller, M. Härröd, Partial Hydrogenation of fatty acid methyl esters in supercritical propane, *Fett/Lipid* 101 (1999) 301–305.
- [19] M.B.O. Andersson, J.W. King, L.G. Blomberg, Synthesis of fatty alcohol mixtures from oleochemicals in supercritical fluids, *Green Chem.* 2 (2000) 230–234.
- [20] S. Van der Hark, M. Härröd, Hydrogenation of oleochemicals at supercritical single-phase conditions: influence of hydrogen and substrate concentrations on the process, *Appl. Catal. A: General* 210 (2001) 207–215.
- [21] M.-B. Macher, A. Holmqvist, Hydrogenation of palm oil in near-critical and supercritical propane, *Eur. J. Lipid Sci. Technol.* 103 (2001) 81–84.
- [22] S. van den Hark, M. Härröd, Fixed-bed hydrogenation at supercritical conditions to form fatty alcohols: the dramatic effects caused by phase transitions in the reactor, *Ind. Eng. Chem. Res.* 40 (2001) 5052–5057.
- [23] M. Härröd, M.-B. Macher, S. van den Hark, P. Møller, Hydrogenation at supercritical conditions. *Proc. 5th Conference on Supercritical Fluids and Their Applications*, Garda, Italy, 1999, pp. 319–324.
- [24] S. Pereda, L. Rovetto, S.B. Bottini, E.A. Brignole, Modeling phase equilibria for hydrogenation processes at supercritical conditions, in: D. Bush (Ed.), *Proc. 5th International Symposium on Supercritical Fluids, ISSF:Atlanta, GA*, 2000.
- [25] J. Wisniak, L.F. Albright, Hydrogenating cottonseed oil at relatively high pressure, *Ind. Eng. Chem.* 53 (1961) 375–380.
- [26] J. Wisniak, S. Shoshanah, Hydrogen solubility in jojoba oil, *JAOCS* 51 (1974) 482–485.
- [27] H. Schieman, Interfacial tension of lipids in the presence of dense gases, Ph.D. Thesis; Univ. Erlangen-Nurnberg, Erlangen, 1993.
- [28] D. Richter, Phasenverhalten und Viscositat in Systems aus Triglyceriden, Wasserstoff Kohlendioxid, Propan und Dimethylether; Ph.D. Thesis; Univ. Erlangen-Nurnberg, Erlangen, 2000.
- [29] S. Raciassi, C.J. Peters, Bubble-point pressures of the binary system carbon dioxide+linalool, *J. Supercritical Fluids* 20 (2001) 221–228.
- [30] K. Gauter, Fluid multiphase behavior in ternary systems of near-critical CO₂, Ph.D. Thesis, Delft University of Technology, 1999.
- [31] Ch.M. Hartwig, Raman scattering from hydrogen and deuterium dissolved in silica as a function of pressure, *J. Appl. Phys.* 47 (1976) 956–959 Chapter 2, 15–60.
- [32] J.E. Shelby, *Handbook of Gas Diffusion in Solids and Meals*, AMS International, 1996.
- [33] R. Hull, *Properties of Crystalline Silicon*, London IEE, 1999.
- [34] H.G.A. Coorens, C.J. Peters, J. de Swaan Arons, Phase equilibria in binary mixtures of propane and tripalmitin, *Fluid Phase Equilibria* 40 (1988) 135–151.
- [35] L.J. Rovetto, S.B. Bottini, E.A. Brignole, C.J. Peters, Experimentally determined fluid phase equilibria for supercritical hydrogenation processes, *Proc. 4th Brazilian Meeting on Supercritical Fluids, Salvador-Bahia, Brazil*, 2001, pp. 221–228.