

Supercritical hydrogenolysis of fatty acid methyl esters: Phase equilibrium measurements on selected binary and ternary systems

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Received 30 July 2004; accepted 15 February 2005

Abstract

Fatty alcohols (FOH) are industrially obtained by heterogeneous catalytic hydrogenolysis of fatty acid methyl esters (FAME). Reaction rates are strongly dependent on hydrogen concentration at the catalyst surface, which is limited by the low solubility of hydrogen and high mass-transport resistance of the liquid substrate. The addition of a supercritical solvent can bring the reactive mixture into a single phase, increasing the reaction rate by several orders of magnitude. Propane has shown to be an adequate supercritical medium for these reactions. To find the homogeneous region and to determine the most favorable process conditions, it is a prerequisite to know the phase equilibrium boundaries of the reactive mixture as the reaction proceeds. This paper reports experimental phase equilibrium data on binary and ternary mixtures of propane with the reactants and reaction products of the hydrogenolysis of methyl palmitate: methyl palmitate, hydrogen, hexadecanol and methanol. A temperature region between 300 and 450 K, and pressures up to 15 MPa were covered. A liquid–liquid–vapor region was found in the system hexadecanol + hydrogen + propane, showing retrograde behavior of the lighter liquid phase.

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Keywords: Phase equilibria; Retrograde behavior; Propane; Hydrogen; Hexadecanol

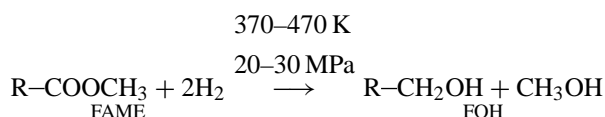
1. Introduction

Fatty alcohols (FOH) and their derivatives have numerous industrial applications and constitute one of the largest families of oleo chemicals [1]. They are mostly used as raw materials for the synthesis of surfactants and lubricants, with about 70% of higher alcohols being used in the first application. It is predicted that the total world fatty alcohol production will increase in the forthcoming years [1,2].

While the Zigler and Oxo processes are used to produce synthetic alcohols, the catalytic high-pressure hydrogenation of fats, oils and their methyl esters, is the most common process used for the preparation of natural fatty alcohols [3,4].

The main industrial route from natural materials to fatty alcohols is the hydrogenolysis (fission of the C–O bond + hydrogenation of both fragments) of fatty acid methyl esters

(FAME) over copper-based catalyst [5]. The stoichiometry of the reaction and the normal operating conditions of a trickle-bed or slurry-phase reactor are given below [4,6]:



The yield of FOH and the reaction rate depend on the pressure of hydrogen (H₂) in the reactor. Typical for this process is the large excess of hydrogen (20–100 mol H₂/mol ester) and, consequently, a high hydrogen recirculation required, a long reaction time and an excessive use of catalyst [4–8].

High pressures are required to increase the concentration of H₂ in the reaction mixture. The low solubility of this gas and the mass-transport resistance in the liquid phase limit the availability of H₂ at the catalyst surface [9–11]. Therefore, the reaction rate is diffusion-controlled.

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It is possible to overcome this problem by adding a supercritical solvent to the reacting species. The role of the supercritical fluid is to bring both the gas and the substrate into a homogeneous phase in which the transport resistance for hydrogen is minimized. The effective concentration of reactants can be controlled and increased significantly. As a consequence, the reaction rate is enhanced, achieving values of several orders of magnitude higher than the traditional process [10,12].

The use of propane (C_3H_8) as supercritical solvent for the hydrogenation of fatty acid methyl esters has been investigated by Van den Hark [13–15], Macher et al. [16] and Andersson et al. [17]. Reaction rates 500 times higher than those obtained in the traditional two-phase process have been reported [16]. Although supercritical hydrogenation has been proven to be very effective and offers significant advantages over the traditional process, their research demonstrates that this approach may lead to quite complex phase behavior.

As the reaction proceeds, the key issue in the supercritical process is to ensure that the reactive mixture always is in a homogeneous phase and in contact with the solid catalyst as well. For that purpose, it is necessary to know the phase behavior for the reactive system in the region of interest in terms of pressure, temperature and composition.

The information available in the literature on the phase behavior of these types of mixtures is very scarce. Brands [5] reports some phase equilibrium data in which the supercritical solvent is *n*-butane. In a previous paper [18], experimental phase equilibrium data on binary and ternary mixtures comprising the components propane, hydrogen and methyl palmitate have been reported. In the present paper we extend the information, given in the previous paper [18], by including the reaction products (i.e. hexadecanol and methanol) in the reacting system.

In this work, both a liquid–liquid two-phase split and retrograde behavior was observed in the system hydrogen + hexadecanol (HD) + propane. It is known that addition of a gas to a binary system showing already partial liquid–liquid immiscibility may cause that the original three-phase locus (L_1L_2V) in the binary system will extend to a three-phase region in the related ternary system [19].

Binary systems *n*-alkanol + propane, for *n*-alkanols with carbon number higher than 18, show type-V fluid phase behavior in the classification of van Konynenburg and Scott [20]. According to this, no liquid–liquid immiscibility is expected in the system hexadecanol + propane. Even though there is no liquid–liquid immiscibility in the original binary system, addition of hydrogen to the binary system HD + C_3H_8 induces the appearance of a second liquid phase, i.e., a three-phase L_1L_2V region will be present in the ternary system as a consequence of the anti-solvent effect of hydrogen. Because the third component (hydrogen) is dissimilar compared to the two other constituents, as a consequence, the three-phase region L_1L_2V will develop towards lower temperatures in a p – T diagram [19]. For some of the isopleths with high propane concentrations and a molar ratio of H_2 :HD = 4,

the boundary of the three-phase region L_1L_2V was determined, as well as its upper and lower critical endpoints, respectively, UCEP ($L_2 + V = L_1$) and LCEP ($V + L_1 = L_2$). Furthermore, retrograde behavior of the light liquid phase (L_1) [21] has been observed (i.e. a second liquid phase appears at certain temperature with increasing pressure and at further pressure increase this newly formed phase disappears again).

2. Experimental

All measurements were carried out in a Cailletet apparatus present at Delft University of Technology, which operates according to the synthetic method. A sample of known overall composition was brought into the closed top of a thick-walled Pyrex glass tube. After dosing the liquid and/or solid chemicals into tube, these substances were degassed under vacuum conditions. After that, gaseous species were dosed volumetrically. Then, the sample was confined at the closed end of the tube by pressing mercury into it. Finally, the open bottom-end of the tube was immersed in mercury already present in an autoclave. The autoclave was connected to a high-pressure hydraulic system applying oil as the pressure medium. Mercury was also used as the pressure-transmitting fluid between the hydraulic oil and the sample. The pressure inside the tube can be modified by means of a hand screw pump, while the pressure is measured with a dead weight pressure balance. Pressure measurements were as accurate as 0.03% of the reading. The Cailletet tube was jacketed, and silicon oil was used as the thermostatic fluid. A platinum resistance thermometer (Pt 100), located close to the sample, was used to measure the temperature, which was controlled within ± 0.02 K by a thermostat. The sample inside the tube was stirred by a stainless steel ball, which was moved up and down by two button magnets activated by a rotating disc mounted on a stirring motor.

The temperature of the experiments ranged from 312 up to 450 K (maximum operating temperature allowed of the apparatus). Pressures in the range from 2.5 up to 15 MPa were covered. The latter pressure is the upper limit allowed for the Pyrex glass Cailletet tube.

Samples were prepared by dosing gravimetrically the solid or liquid components (methyl palmitate, hexadecanol and methanol) into the Cailletet tube. Then, gases (hydrogen and/or propane) were dosed volumetrically into the tube via a gas-dosing device. For details of the experimental facility one is referred to Raeissi and Peters [22].

For each measurement the temperature was fixed and the pressure was varied (increased or decreased stepwise) until a phase change was observed. Bubble and dew points were determined as the points at which the last bubble of vapor or the last droplet of liquid disappeared, respectively. Critical points were determined visually using a number of criteria, including critical opalescence and the equality of volumes of the two phases. For a given sample, the whole procedure was

repeated at several temperatures to obtain the equilibrium curve of that particular isopleth.

2.1. Materials

Aldrich supplied methyl palmitate (purity better than 99 mol%); 1-hexadecanol (purity of approximately 99 mol%) was purchased from Fluka and dried methanol (purity of 99.5 mol%) from J.T. Baker. Propane (purity better than 99.95% molar) was obtained from Scott Specialty Gases and hydrogen (purity of 99.999% molar) from Hoek Loos. All chemicals were used without any further purification.

3. Results and discussion

3.1. Binary systems

3.1.1. Hexadecanol + hydrogen

The solubility of hydrogen (H_2) in 1-hexadecanol (HD) was measured as bubble point ($L+V \rightarrow L$) transitions. Table 1 reports the vapor–liquid equilibrium conditions obtained for four different isopleths with low hydrogen concentrations. The gas solubility increased with temperature. Due to the low solubility of H_2 in the liquid phase, a small increase in the mole fraction of hydrogen produced a large increase in the bubble point pressure of the mixture (see Fig. 1).

3.1.2. Hexadecanol + propane

The same procedure was followed for the binary system propane (C_3H_8) + hexadecanol (HD). Table 2 summarizes the results obtained for five different compositions. For the isopleth with 95.07 mol% of propane, not only bubble points ($L+V \rightarrow L$), but also dew ($L+V \rightarrow V$) and critical points ($L=V$) were determined. The experimental data are shown in Fig. 2.

Table 1

Vapor–liquid isopleths of the binary system hexadecanol (1)–hydrogen (2)

T (K)	p (MPa)	T (K)	p (MPa)	T (K)	p (MPa)	T (K)	p (MPa)
$x_2 = 0.0498$		$x_2 = 0.0805$		$x_2 = 0.1025$		$x_2 = 0.1203$	
$L+V \rightarrow L$		$L+V \rightarrow L$		$L+V \rightarrow L$		$L+V \rightarrow L$	
450.62	4.164	450.60	7.179	450.57	9.194	450.66	11.044
445.69	4.254	445.67	7.349	445.63	9.399	445.69	11.309
440.69	4.349	440.69	7.514	440.64	9.609	440.67	11.594
435.72	4.459	435.73	7.689	435.70	9.844	435.73	11.874
430.78	4.559	430.77	7.879	430.73	10.074	430.77	12.149
425.83	4.664	425.83	8.089	425.76	10.319	425.81	12.434
420.84	4.774	420.84	8.289	420.80	10.564	420.82	12.744
415.87	4.894	415.87	8.484	415.82	10.839	415.89	13.064
410.90	5.009	410.92	8.699	410.87	11.099	410.90	13.419
405.96	5.134	405.94	8.914	405.91	11.379	405.96	13.764
400.98	5.264	400.99	9.139	400.98	11.672	400.99	14.169
396.04	5.394	396.06	9.374	396.04	11.977		
391.08	5.534	391.06	9.624	391.12	12.297		
386.15	5.684	386.13	9.874	386.18	12.622		
381.20	5.839	381.18	10.134	381.28	12.967		
376.26	5.989	376.23	10.409	376.36	13.317		
371.33	6.159	371.30	10.694	371.45	13.721		

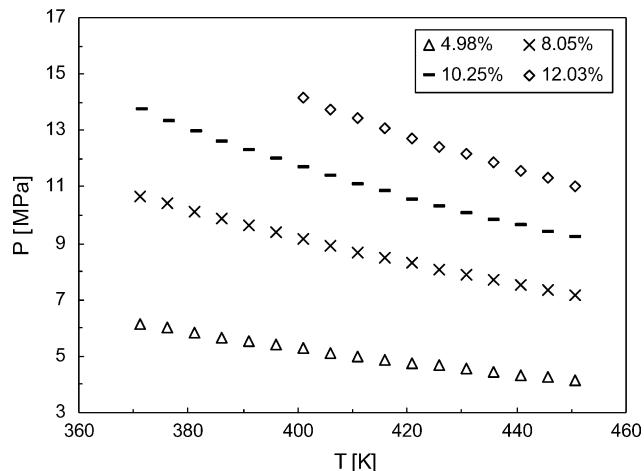


Fig. 1. Experimental bubble points of the binary system H_2 + hexadecanol for four different compositions. Concentrations are given in H_2 mol%.

3.2. Ternary systems

Previous research by Van den Hark and Härröd [15] and Macher et al. [16], along with model predictions by Pereda et al. [23] and Rovetto et al. [24], suggest that high propane concentrations are required to achieve single-phase conditions in the hydrogenation process. For that reason, all ternary systems were studied at high propane (C_3H_8) concentrations (>75 mol%).

3.2.1. Hexadecanol + methyl palmitate (MP) + propane

According to the stoichiometry of the reaction, all measurements were carried out at a molar ratio of MP:HD close to 1. Table 3 summarizes the bubble, dew and critical points measured for nine different isopleths. As the concentration of propane increased, the critical point of the mixtures moved gradually from higher towards lower temperatures

Table 2
Vapor–liquid isopleths of the binary system hexadecanol (1)–propane (2)

T (K)	p (MPa)	T (K)	p (MPa)	T (K)	p (MPa)
$x_1 = 0.0493$ L + V \rightarrow V		$x_1 = 0.0998$ L + V \rightarrow L		$x_1 = 0.1983$ L + V \rightarrow L	
450.51	10.163	450.60	10.192	450.51	9.129
440.63	9.633	440.72	9.612	440.62	8.554
430.70	9.018	430.82	8.957	430.72	7.929
420.82	8.328	420.88	8.227	420.82	7.269
410.85	7.553	410.96	7.432	410.91	6.584
405.94	7.143	401.03	6.577	401.03	5.894
402.99	6.888	391.13	5.692	391.08	5.194
402.67	6.863	381.22	4.857	381.16	4.534
	L = V	371.32	4.132	371.26	3.909
402.46	6.843	361.42	3.497	361.40	3.344
	L + V \rightarrow L	351.56	2.947	351.54	2.834
402.18	6.823	341.69	2.462	341.67	2.384
401.97	6.798	331.93	2.042	331.84	1.984
401.49	6.758	322.04	1.672	321.97	1.634
400.99	6.713	312.14	1.357	312.10	1.334
396.03	6.263				
		$x_1 = 0.3459$ L + V \rightarrow L		$x_1 = 0.5095$ L + V \rightarrow L	
391.06	5.798	450.55	7.077	450.62	4.887
381.14	4.923	440.68	6.682	440.70	4.607
371.27	4.188	430.78	6.257	430.77	4.337
361.36	3.548	420.83	5.807	420.86	4.067
351.53	2.988	410.93	5.357	410.97	3.777
341.67	2.498	401.01	4.897	401.02	3.492
331.84	2.073	391.11	4.437	391.14	3.202
321.96	1.698	381.19	3.992	381.21	2.907
312.12	1.378	371.30	3.557	371.33	2.632
		361.41	3.147	361.43	2.357
		351.58	2.757	351.58	2.097
				341.75	1.857
				331.89	1.632

and pressures, ending finally at the critical point of pure propane.

Changes in the MP:HD molar ratio did not result in significant variation in the equilibrium pressure of the ternary system, which is in accord with expectations because the solubility of MP and HD in propane is very similar and both com-

pounds have comparable molecular sizes and are aliphatic. Measurements were carried out varying the HD:MP molar ratios between 0.6 and 2.6 at a fixed molar fraction of propane equal to 93%, corresponding to concentrations that would occur in the reacting mixture. Table 4 summarizes the vapor pressure data of these mixtures. From the data in Table 4 it

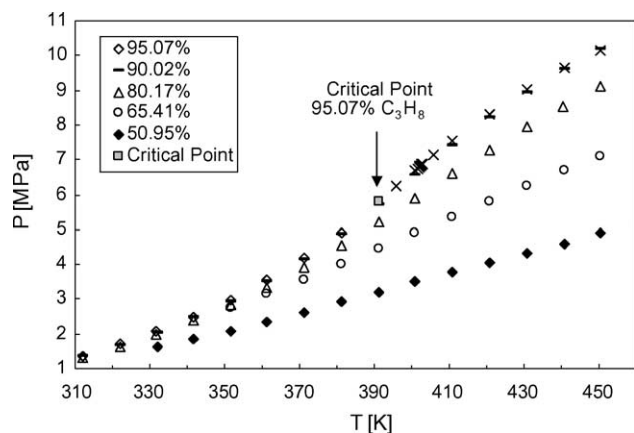


Fig. 2. Experimental bubble points of the binary system C_3H_8 + hexadecanol. The isopleth with 95.07 mol% of C_3H_8 has bubble points, a critical point and dew points. Concentrations are given in C_3H_8 mol%.

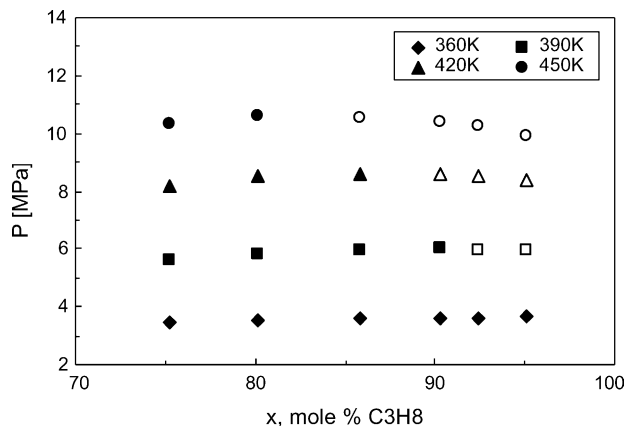


Fig. 3. P - x diagram of the ternary system hexadecanol + methanol + C_3H_8 at a hexadecanol:methanol molar ratio equal to 1, at four selected temperatures. Filled symbols are bubble points and open symbols dew points.

Table 3
Vapor–liquid isopleths of the ternary system hexadecanol (1) + methyl palmitate (2) + propane (3)

T (K)	p (MPa)	T (K)	p (MPa)	T (K)	p (MPa)
$x_1 = 0.1284, x_3 = 0.7744$		$x_1 = 0.1013, x_3 = 0.8015$		$x_1 = 0.1019, x_3 = 0.8193$	
L + V → L		L + V → L		L + V → L	
450.55	8.226	450.55	8.663	450.53	8.922
448.10	8.086	445.58	8.358	448.06	8.772
445.59	7.941	440.65	8.053	445.61	8.622
443.14	7.796	435.67	7.738	443.13	8.467
440.65	7.656	430.75	7.418	440.67	8.312
438.18	7.506	425.82	7.080	438.21	8.152
435.72	7.362	420.82	6.763	435.73	7.997
433.23	7.207	415.87	6.428	433.26	7.827
430.74	7.057	410.93	6.093	430.77	7.662
428.29	6.902	405.98	5.758	428.28	7.492
425.79	6.747	401.01	5.423	425.80	7.322
423.31	6.597	396.06	5.098	423.32	7.152
420.84	6.437	391.07	4.778	420.85	6.977
418.36	6.282	386.13	4.468	418.35	6.802
415.87	6.122	381.17	4.168	415.88	6.628
413.37	5.967	376.22	3.878	413.41	6.453
410.92	5.807	371.28	3.598	410.90	6.273
405.95	5.492	361.41	3.083	405.95	5.923
401.02	5.182	351.56	2.618	401.01	5.573
396.05	4.877	341.68	2.203	396.05	5.228
391.06	4.572			391.09	4.894
386.12	4.282			386.15	4.564
381.17	4.002			381.22	4.254
376.25	3.727			376.28	3.949
371.31	3.462			371.34	3.664
366.36	3.212			366.41	3.389
361.40	2.967			361.48	3.124
$x_1 = 0.0729, x_3 = 0.8730$		$x_1 = 0.0493, x_3 = 0.9035$		$x_1 = 0.0492, x_3 = 0.9136$	
L + V → L		L + V → L		L + V → L	
450.55	9.688	450.58	9.929	450.49	9.924
448.10	9.543	445.64	9.644	448.03	9.789
445.63	9.398	440.70	9.339	445.58	9.649
443.17	9.233	435.71	9.014	443.12	9.499
440.66	9.073	430.75	8.669	440.65	9.349
438.19	8.903	425.80	8.304	438.15	9.189
435.71	8.733	420.85	7.924	435.67	9.029
433.22	8.563	415.89	7.534	433.19	8.864
430.78	8.384	410.94	7.129	430.74	8.694
428.27	8.199	405.95	6.709	428.26	8.514
425.82	8.019	401.00	6.294	425.77	8.334
423.33	7.829	396.08	5.879	423.26	8.144
420.83	7.639	391.10	5.474	420.82	7.954
418.37	7.444	386.17	5.079	7.764	
415.86	7.249	381.21	4.709	415.85	7.564
413.37	7.054	376.26	4.354	413.36	7.359
410.91	6.859	371.32	4.019	410.91	7.154
405.94	6.459	361.40	3.414	405.91	6.734
400.94	6.049	351.56	2.879	400.93	6.304
396.05	5.659	341.74	2.414	395.99	5.884
391.05	5.274			391.07	5.469
386.10	4.898			386.14	5.069
381.35	4.541			381.20	4.689
376.25	4.206			376.26	4.334
371.32	3.891			371.30	3.994
366.38	3.586			366.34	3.679
361.44	3.306			361.39	3.379
$x_1 = 0.0256, x_3 = 0.9503$		$x_1 = 0.0250, x_3 = 0.9563$		$x_1 = 0.0150, x_3 = 0.9735$	
L + V → V		L + V → V		L + V → V	
450.54	9.953	450.58	9.881	450.50	9.533
445.58	9.688	448.12	9.756	448.03	9.438
440.61	9.408	445.60	9.626	445.61	9.338

Table 3 (Continued)

<i>T</i> (K)	<i>p</i> (MPa)	<i>T</i> (K)	<i>p</i> (MPa)	<i>T</i> (K)	<i>p</i> (MPa)
435.68	9.108	443.16	9.496	443.10	9.233
430.71	8.783	440.69	9.356	440.65	9.118
425.75	8.448	438.18	9.211	438.16	9.003
420.75	8.088	435.75	9.066	435.71	8.873
418.34	7.908	433.25	8.911	433.20	8.738
417.84	7.873	430.78	8.751	430.73	8.603
417.54	7.848	428.32	8.586	428.27	8.453
	L = V	425.80	8.416	425.79	8.303
417.34	7.833	423.33	8.241	423.30	8.148
	L + V → L	420.84	8.066	420.82	7.983
417.03	7.813	418.38	7.886	418.36	7.818
416.85	7.798	415.88	7.696	415.90	7.643
416.53	7.773	413.37	7.506	413.42	7.463
416.33	7.758	412.90	7.466	410.92	7.278
415.83	7.718	412.40	7.426	408.43	7.083
410.87	7.333	411.89	7.396	405.96	6.898
405.92	6.928	411.41	7.351	403.45	6.688
400.99	6.518	410.90	7.311	400.95	6.488
396.02	6.093	410.41	7.276	396.03	6.083
391.07	5.663	409.91	7.231	394.52	5.958
386.12	5.253	409.42	7.196	394.03	5.918
381.18	4.858	409.13	7.171	393.92	5.908
	$x_1 = 0.0256, x_3 = 0.9503$	$x_1 = 0.0250, x_3 = 0.9563$		$x_1 = 0.0150, x_3 = 0.9735$	
	L + V → L	L = V		L + V → V	
376.21	4.493	409.02	7.161	393.82	5.903
371.26	4.148		L + V → L		L = V
361.37	3.513	408.94	7.156	393.73	5.893
351.49	2.958	408.74	7.141		$x_1 = 0.0150, x_3 = 0.9735$
341.62	2.473	408.46	7.116		L + V → L
		408.16	7.091	393.60	5.883
		407.95	7.076	393.53	5.878
		406.96	6.996	393.05	5.838
		405.97	6.911	391.06	5.673
		403.47	6.706	386.10	5.278
		401.00	6.491	381.17	4.893
		396.07	6.071	376.22	4.523
		391.11	5.646	371.26	4.173
		386.16	5.231	366.29	3.843
		381.22	4.836	361.37	3.528
		376.26	4.466		
		371.31	4.116		
		366.37	3.786		
		361.44	3.476		

can be observed that over the entire temperature range, no significant changes occurred in the equilibrium pressure as a function of the HD:MP molar ratio.

3.2.2. Hexadecanol + methanol (MeOH) + propane

The ternary system of propane with the reaction products (i.e. hexadecanol and methanol), was also studied. The molar ratio of both alcohols was set equal to 1, which is in agreement with the stoichiometry of the reaction. Six different isopleths were measured and the data are summarized in Table 5. It can be observed that all isopleths in the region from 75 up to 95 mol% of propane have approximately the same vapor pressure, i.e., all isopleths in these mixtures almost coincide. Fig. 3 shows the corresponding

P–*x* diagram with four different temperatures. From this figure it became clear that the bubble point pressures of each isotherm remained almost constant with composition. From the few critical point data summarized in Table 5, it can be observed that with increasing propane concentration, the critical points gradually moved towards the critical point of pure propane.

3.2.3. Hexadecanol + hydrogen + propane

In this ternary system, equilibrium pressures should increase with increasing H₂ concentration. As an additional feature, it is known that H₂ may have an anti-solvent effect, leading to a reduction of the solubility of hexadecanol. To make a systematic comparison of the results

Table 4

Vapor–liquid isopleths of the ternary system hexadecanol (1) + methyl palmitate (2) + propane (3) as a function of the ratio hexadecanol:methyl palmitate, i.e., the progress of the reaction

T (K)	p (MPa)	T (K)	p (MPa)	T (K)	p (MPa)
$x_1 = 0.0499, x_3 = 0.9310$		$x_1 = 0.0387, x_3 = 0.9328$		$x_1 = 0.0243, x_3 = 0.9390$	
HD:MP = 2.61		HD:MP = 1.36		HD:MP = 0.66	
L + V → V		L + V → V		L + V → V	
450.46	10.020	450.60	9.972	450.49	9.867
447.96	9.885	448.11	9.837	448.05	9.737
445.52	9.750	445.60	9.702	445.53	9.602
444.57	9.695	443.13	9.557	443.10	9.462
443.08	9.610	442.15	9.507	440.60	9.317
L = V		442.09	9.497	438.15	9.167
442.99	9.605	442.00	9.492	436.65	9.077
L = V → L		L = V		436.37	9.057
442.87	9.600	441.91	9.487	436.15	9.042
442.59	9.580	L = V → L		436.03	9.037
442.09	9.550	441.82	9.482	L = V	
440.63	9.465	441.69	9.472	435.95	9.032
438.12	9.310	440.73	9.417	L = V → L	
435.65	9.155	438.22	9.262	435.84	9.027
433.15	8.995	435.76	9.107	435.65	9.012
430.69	8.830	433.24	8.947	433.17	8.857
428.21	8.655	430.81	8.782	430.72	8.692
425.74	8.485	428.31	8.612	428.25	8.527
423.25	8.300	425.84	8.437	425.76	8.357
420.79	8.120	423.35	8.257	423.27	8.177
418.28	7.925	420.87	8.072	420.80	7.997
415.81	7.729	418.38	7.882	418.33	7.812
410.85	7.329	415.91	7.692	415.83	7.622
405.90	6.909	413.42	7.492	410.87	7.227
400.82	6.460	410.94	7.292	405.93	6.822
395.92	6.025	408.47	7.082	400.87	6.386
391.00	5.595	405.99	6.872	395.96	5.966
386.05	5.175	403.50	6.657	391.01	5.546
381.13	4.785	401.02	6.442	386.06	5.141
376.18	4.415	396.00	6.003	381.14	4.756
371.23	4.070	391.07	5.578	376.19	4.391
366.32	3.750	386.14	5.168	371.26	4.046
361.39	3.445	381.18	4.779	366.33	3.726
		376.27	4.409	361.38	3.426
		371.32	4.064		
		366.38	3.744		
		361.43	3.439		

possible, measurements were conducted in ternary mixtures of HD + H₂ + C₃H₈ with a fixed molar ratio of H₂:HD equal to 1.0 and with variable propane concentrations. A total of seven isopleths were measured and the data are reported in Table 6. From Fig. 4 the following can be observed:

- The H₂ solubility increased with increasing propane concentration in the mixture, i.e., the equilibrium pressures decreased.
- The shape of the ternary isopleths, which represents the solubility of a mixture of H₂ + HD in propane, easily can be related to the solubility of both gaseous compounds in their respective binary mixtures with HD, as shown in Figs. 1 and 2.

The low solubility of H₂ in the liquid substrate is a bottleneck in the traditional gas–liquid hydrogenation pro-

cess. For that reason, in the process, H₂:substrate molar ratios larger than 4 are normally applied. Taking this into account, measurements were carried out for ternary mixtures of C₃H₈ + H₂ + HD at H₂:HD molar ratios equal to 4. Six isopleths were measured and the results are summarized in Table 7 and some of them are depicted in Fig. 5. As can be seen in this figure, a three-phase region L₁L₂V occurred for the three isopleths lowest in propane concentration. As was pointed out already, binary systems of *n*-alkanols + propane show fluid multiphase behavior with alcohols containing more than 18 carbon atoms. From these experiments, it became apparent that the addition of H₂ drives the C₃H₈–HD binary system into a three-phase region L₁L₂V in the ternary system. In the range of compositions studied, the L₁L₂V region became smaller when the concentration of propane

Table 5
Vapor–liquid isopleths of the ternary system hexadecanol (1) + methanol (2) + propane (3)

T (K)	p (MPa)	T (K)	p (MPa)	T (K)	p (MPa)
$x_1 = 0.1258, x_3 = 0.7525$		$x_1 = 0.1000, x_3 = 0.8013$		$x_1 = 0.0721, x_3 = 0.8586$	
L + V → L		L + V → L		L + V → V	
450.63	10.349	450.59	10.615	450.55	10.551
448.20	10.184	448.16	10.470	449.15	10.469
445.71	10.024	445.69	10.315	448.92	10.459
443.23	9.859	443.16	10.155		L = V
440.72	9.689	440.71	9.995	448.82	10.454
438.26	9.514	438.24	9.820		L + V → L
435.75	9.334	435.69	9.645	448.74	10.449
433.29	9.154	433.23	9.470	448.67	10.444
430.81	8.969	430.75	9.290	448.54	10.439
428.34	8.779	428.29	9.100	448.45	10.434
425.86	8.584	425.81	8.910	448.16	10.414
423.37	8.389	423.33	8.715	445.73	10.279
420.87	8.189	420.85	8.515	443.21	10.134
418.38	7.984	418.34	8.304	440.73	9.989
415.83	7.784	415.87	8.099	438.28	9.834
413.44	7.574	413.41	7.884	435.82	9.679
410.96	7.364	410.92	7.669	433.27	9.509
406.00	6.939	405.95	7.224	430.85	9.344
401.06	6.504	401.00	6.774	428.35	9.169
396.10	6.074	396.07	6.304	425.85	8.989
391.15	5.644	391.09	5.834	423.38	8.809
361.45	3.460	386.14	5.384	420.89	8.619
366.42	3.770	381.16	4.954	418.43	8.429
371.37	4.105	376.25	4.559	415.94	8.229
376.31	4.455	371.34	4.194	413.39	8.016
381.22	4.830	366.38	3.849	410.91	7.806
386.17	5.230	361.47	3.534	405.98	7.376
		356.54	3.234	401.04	6.926
		351.62	2.954	396.08	6.451
				391.15	5.971
				386.19	5.486
				381.25	5.031
				376.31	4.621
				371.35	4.246
				366.46	3.901
				361.52	3.576
$x_1 = 0.0485, x_3 = 0.9031$		$x_1 = 0.0381, x_3 = 0.9245$		$x_1 = 0.0250, x_3 = 0.9509$	
L + V → V		L + V → V		L + V → V	
450.53	10.411	450.62	10.241	450.57	9.898
448.04	10.286	448.06	10.126	448.12	9.813
445.65	10.156	445.60	10.006	445.61	9.708
443.16	10.021	443.15	9.881	443.16	9.603
440.71	9.881	440.68	9.746	440.66	9.488
438.22	9.736	438.24	9.611	438.17	9.373
435.70	9.581	435.72	9.466	435.70	9.248
433.26	9.426	433.22	9.316	433.23	9.118
430.74	9.266	430.73	9.161	430.75	8.978
428.29	9.096	428.26	9.001	428.27	8.838
425.81	8.926	425.81	8.836	425.80	8.683
423.32	8.746	423.31	8.670	423.31	8.528
420.85	8.566	420.80	8.495	420.82	8.368
418.37	8.381	418.32	8.310	418.34	8.198
415.91	8.191	415.86	8.125	415.85	8.023
413.41	7.991	413.36	7.930	413.39	7.848
410.94	7.791	410.88	7.735	410.91	7.663
406.00	7.371	408.38	7.530	405.96	7.278
403.62	7.161	405.89	7.325	401.00	6.868
403.54	7.156	401.01	6.895	396.05	6.433
403.32	7.136	396.05	6.440	391.07	5.972

Table 5 (Continued)

T (K)	p (MPa)	T (K)	p (MPa)	T (K)	p (MPa)
	L = V	391.09	5.965	386.12	5.501
403.04	7.111	389.61	5.820	384.66	5.356
	L + V \rightarrow L	389.52	5.810	384.17	5.311
402.83	7.091		L = V		L + V \rightarrow L
402.62	7.076	389.42	5.805	384.08	5.301
402.49	7.061		L + V \rightarrow L	383.99	5.296
402.43	7.056	389.33	5.795	383.69	5.266
402.33	7.046	389.12	5.775	381.25	5.061
402.22	7.036	388.63	5.725	376.28	4.671
402.05	7.021	386.16	5.480	371.37	4.306
401.20	6.946	381.22	5.025	366.40	3.956
401.04	6.926	376.29	4.625	361.51	3.641
400.85	6.911	371.35	4.255	356.55	3.341
400.51	6.876	366.42	3.940	351.64	3.056
396.07	6.466	361.49	3.585		
391.06	5.986	356.57	3.285		
386.16	5.491	351.65	3.005		
381.22	5.031				
376.29	4.626				
371.29	4.251				
366.37	3.901				
361.44	3.581				
356.52	3.276				
351.61	2.996				

Ratio: hexadecanol:methanol = 1.

was increased, i.e. at lower concentration of H_2 in the mixture its anti-solvent effect is less pronounced (see Fig. 5).

For the three isopleths lowest in propane concentration for the system hexadecanol + hydrogen + propane, it was possible to determine the boundaries of the three-phase region L_1L_2V , as well as the upper and lower critical endpoints, UCEP ($L_2 + V = L_1$) and LCEP ($V + L_1 = L_2$), respectively.

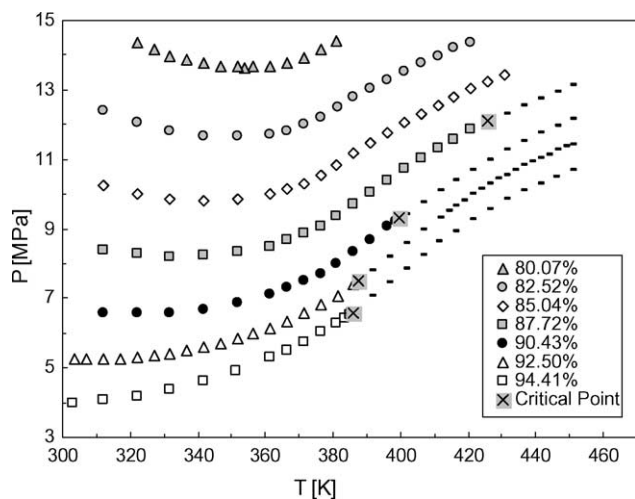


Fig. 4. Experimental pressure–temperature isopleths of the ternary system hexadecanol + H_2 + C_3H_8 at a H_2 :hexadecanol molar ratio equal to 1. Concentrations are given in C_3H_8 mol%. Symbols represent the bubble point curve for each isopleth, and its continuation in dashed line represent the dew point curves for the corresponding composition. Isopleths with C_3H_8 concentration of 87.72% and higher also show their critical point (x).

In Table 8, the data are summarized for the three measured isopleths.

Fig. 6 is an enlargement of the isopleth with 85.04 mol% of C_3H_8 , which clearly shows the various transitions around the three-phase region L_1L_2V . This figure also shows that the lower part of the three-phase region L_1L_2V is a retrograde region. At constant temperature moving from lower to higher pressures (see the arrow in Fig. 6), the following sequence of phase transitions occur: $L_2V \rightarrow L_1L_2V \rightarrow L_2V$, i.e., the L_1 phase shows retrograde behavior. This behavior will occur at

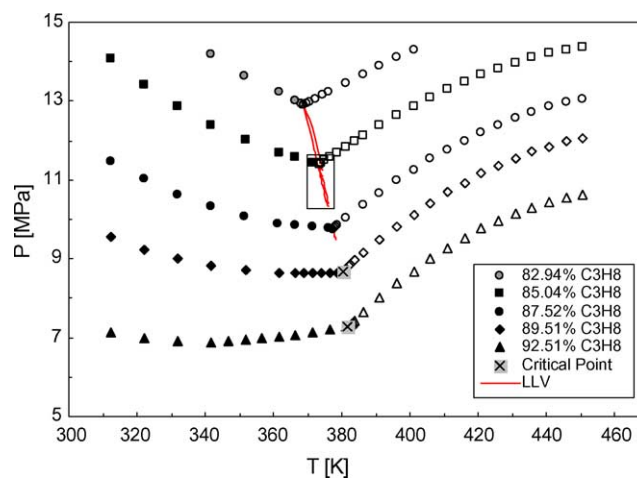


Fig. 5. Phase equilibria of the ternary system hexadecanol + H_2 + C_3H_8 at a fixed H_2 :hexadecanol molar ratio equal to 4. Filled symbols are bubble points for each isopleth and open symbols their corresponding dew points. The lines enclose the three-phase region $L_1 + L_2 + V$. The C_3H_8 compositions are in mol%.

Table 6
Vapor–liquid isopleths of the ternary system hexadecanol (1) + hydrogen (2) + propane (3)

T (K)	p (MPa)	T (K)	p (MPa)	T (K)	p (MPa)
$x_1 = 0.1006, x_3 = 0.8007$		$x_1 = 0.0881, x_3 = 0.8252$		$x_1 = 0.0765, x_3 = 0.8504$	
L + V → L		L + V → L		L + V → L	
381.21	14.393	420.82	14.384	430.71	13.441
376.27	14.163	415.88	14.194	425.82	13.246
371.36	13.943	410.93	13.994	420.85	13.036
366.41	13.783	405.99	13.779	415.83	12.811
361.46	13.688	401.03	13.549	410.92	12.571
356.54	13.654	396.08	13.309	405.91	12.316
354.06	13.649	391.14	13.054	400.99	12.046
351.62	13.654	386.18	12.794	396.04	11.766
346.69	13.684	381.25	12.509	391.04	11.466
341.77	13.754	376.33	12.229	386.14	11.161
336.82	13.859	371.37	11.994	381.19	10.836
331.88	13.989	366.47	11.839	376.22	10.526
326.94	14.149	361.51	11.734	371.30	10.301
322.00	14.344	351.66	11.650	366.33	10.141
		341.77	11.670	361.42	10.016
		331.88	11.815	351.58	9.866
		322.01	12.070	341.73	9.821
		312.14	12.424	331.86	9.876
				321.99	10.026
				312.13	10.250
$x_1 = 0.0620, x_3 = 0.8772$		$x_1 = 0.0492, x_3 = 0.9043$		$x_1 = 0.0382, x_3 = 0.9250$	
L + V → V		L + V → V		L + V → V	
450.59	13.129	450.57	12.160	450.60	11.448
445.65	12.949	445.61	11.960	448.13	11.368
440.65	12.754	440.64	11.745	445.66	11.263
435.77	12.549	435.70	11.515	443.18	11.153
430.79	12.304	430.71	11.265	440.70	11.053
426.02	12.104	425.79	10.995	438.22	10.938
	L = V	420.80	10.710	435.76	10.818
425.91	12.099	415.83	10.410	433.28	10.688
	L + V → L	410.91	10.095	430.77	10.558
425.81	12.094	405.94	9.765	428.31	10.423
420.86	11.844	400.95	9.415	425.84	10.278
415.89	11.579	399.88	9.340	423.36	10.138
410.93	11.304		L = V	420.85	9.988
405.88	11.014	399.80	9.335	418.38	9.828
401.02	10.719		L + V → L	415.91	9.663
396.02	10.399	399.70	9.325	413.43	9.498
391.12	10.069	399.51	9.310	410.95	9.328
386.11	9.719	398.51	9.240	405.98	8.973
381.18	9.364	396.01	9.070	401.05	8.603
376.23	9.064	391.07	8.705	396.08	8.213
371.30	8.854	386.13	8.330	391.13	7.813
366.34	8.679	381.20	7.975	388.16	7.563
361.40	8.494	376.26	7.710	387.77	7.538
351.60	8.344	371.29	7.490		L = V
341.73	8.234	366.37	7.300	387.65	7.528
331.86	8.209	361.42	7.135		L + V → L
321.99	8.269	351.57	6.875	387.57	7.523
312.12	8.409	341.73	6.690	387.17	7.488
		331.86	6.585	386.20	7.408
		321.98	6.555	381.23	7.062
		312.13	6.590	376.29	6.797
$x_1 = 0.0287, x_3 = 0.9441$				371.32	6.557
L + V → V				366.40	6.342
450.57	10.697			361.46	6.157
445.58	10.517			356.54	5.987
440.63	10.312			351.64	5.837
435.69	10.087			346.69	5.707
430.72	9.837			341.76	5.592
425.72	9.557				

Table 6 (Continued)

T (K)	p (MPa)	T (K)	p (MPa)	T (K)	p (MPa)
420.80	9.262			336.80	5.492
415.81	8.947			331.87	5.407
410.87	8.612			326.94	5.346
405.93	8.250			321.98	5.296
400.99	7.870			317.05	5.266
396.02	7.465			312.13	5.251
391.09	7.050			307.21	5.247
386.10	6.625			303.48	5.262
386.06	6.620				
385.96	6.610				
	L = V				
385.86	6.600				
	L + V → L				
385.75	6.590				
385.15	6.550				
383.70	6.450				
381.17	6.295				
376.23	6.015				
371.27	5.755				
366.33	5.520				
361.40	5.300				
351.55	4.925				
341.72	4.615				
331.87	4.370				
321.99	4.185				
312.12	4.060				
303.03	3.990				

Ratio: H_2 :hexadecanol = 1.

any temperature between the UCEP and the maximum temperature for the three-phase region for a certain composition of the mixture.

Fig. 7 shows a p – T projection of the upper (UCEP) and lower (LCEP) critical endpoints with each type of critical endpoints being connected by a dashed line. The point of intersection of both loci results in the phenomenon $L_1 = L_2 = V$, i.e., a tricritical point, and towards higher temperatures, the

three-phase region L_1L_2V ceases to exist. In the p – T projection, these critical endpoint loci represent the limits of the three-phase region L_1L_2V in terms of pressure and temperature. This region broadens at lower concentrations of propane (i.e., at higher concentrations of H_2), towards the high-pressure, low-temperature corner, as discussed elsewhere [19,25]. Eventually, the L_1L_2V region will end at lower temperatures with the formation of a solid hexadecanol phase.

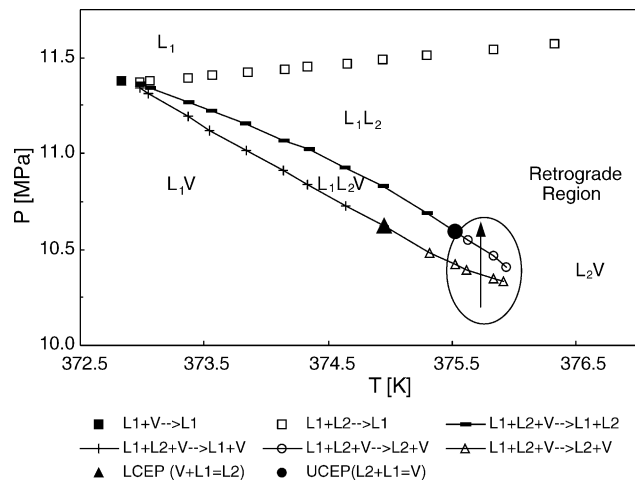


Fig. 6. Magnification of the isopleth with 85.04 mol% of propane in the system hexadecanol + H_2 + C_3H_8 at a fixed H_2 :hexadecanol molar ratio equal to 4, showing the boundaries and type of coexisting phases in the three-phase region L_1L_2V .

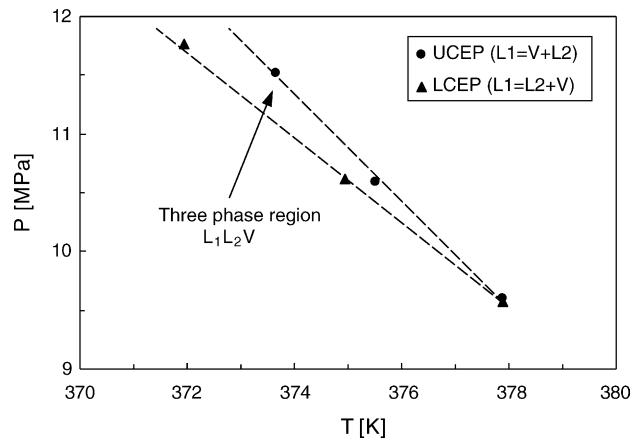


Fig. 7. Critical endpoints UCEP ($L_2 + V = L_1$) and LCEP ($V + L_1 = L_2$), in the ternary system HD + H_2 + C_3H_8 at various concentrations of propane and H_2 :hexadecanol molar ratio equal to 4.

Table 7
Vapor–liquid isopleths of the ternary system hexadecanol (1) + hydrogen (2) + propane (3)

T (K)	p (MPa)	T (K)	p (MPa)	T (K)	p (MPa)
$x_1 = 0.0340, x_3 = 0.8294$		$x_1 = 0.0292, x_3 = 0.8504$		$x_1 = 0.0249, x_3 = 0.8752$	
$L_2 + V \rightarrow V$		$L_2 + V \rightarrow V$		$L_2 + V \rightarrow V$	
(or) $L_1 + L_2 \rightarrow L_1$		(or) $L_1 + L_2 \rightarrow L_1$		(or) $L_1 + L_2 \rightarrow L_1$	
400.98	14.300	450.57	14.374	450.58	13.059
396.03	14.110	445.58	14.304	445.63	12.969
391.07	13.905	440.69	14.214	440.65	12.859
386.12	13.690	435.69	14.104	435.72	12.724
381.17	13.470	430.80	13.979	430.74	12.574
376.24*	13.245	425.77	13.829	425.76	12.399
374.29*	13.151	420.85	13.669	420.82	12.204
373.32	13.116	415.90	13.494	415.84	11.994
372.33	13.064	410.93	13.299	410.91	11.779
371.33	13.030	405.96	13.084	405.94	11.529
370.47	12.974	400.98	12.864	400.99	11.264
369.66	12.934	396.09	12.630	396.04	10.979
368.87	12.905	391.12	12.380	391.08	10.679
	$L + V \rightarrow L$	386.17	12.115	386.15	10.364
368.37	12.914	383.72	11.985	381.17	10.024
367.84	12.944	381.22	11.845	378.71*	9.855
366.39	13.025	378.77	11.705	378.23*	9.804
361.45	13.220	376.32*	11.570	378.03	9.799
351.57	13.640	375.83*	11.545	377.93	9.794
341.75	14.195	375.29	11.510	377.86	9.784
		374.94	11.490	377.74	9.775
		374.65	11.470	377.64	9.764
		374.33	11.455	377.53	9.754
		374.15	11.440		$L + V \rightarrow L$
		373.85	11.425	377.45	9.749
		373.56	11.411	377.24	9.759
		373.37	11.396	376.24	9.775
		373.06	11.376	371.27	9.815
		372.98	11.371	366.33	9.865
			$L + V \rightarrow L$	361.37	9.898
		372.83	11.376	351.49	10.080
		371.36	11.436	341.69	10.340
		366.44	11.566	331.86	10.640
		361.51	11.696	321.99	11.020
		351.65	12.011	312.13	11.485
		341.76	12.396		
		331.89	12.851		
		322.00	13.411		
		312.13	14.065		
$x_1 = 0.0210, x_3 = 0.8951$		$x_1 = 0.0198, x_3 = 0.9008$		$x_1 = 0.0148, x_3 = 0.9251$	
$L_2 + V \rightarrow V$		$L_2 + V \rightarrow V$		$L_2 + V \rightarrow V$	
450.52	12.071	450.56	11.910	450.59	10.621
445.64	11.981	445.66	11.825	445.61	10.546
440.68	11.851	440.64	11.710	440.67	10.441
435.73	11.711	435.70	11.575	435.70	10.294
430.76	11.546	430.73	11.415	430.73	10.149
425.80	11.371	425.78	11.280	425.79	9.969
420.84	11.161	420.80	11.025	420.84	9.764
415.90	10.936	415.87	10.800	415.89	9.534
410.94	10.686	410.92	10.550	410.90	9.279
405.98	10.416	405.98	10.285	405.96	8.999
401.03	10.126	401.01	9.995	401.01	8.694
396.09	9.816	396.05	9.680	396.04	8.369
391.12	9.481	390.89	9.350	391.11	8.014
386.20	9.136	386.17	9.000	386.16	7.634
383.75	8.956	381.20	8.620	383.70	7.439
382.56	8.866	379.71	8.480	383.18	7.399
381.96	8.816	379.66	8.470	382.73	7.354
381.28	8.761		$L = V$	382.24	7.319
381.26	8.756	379.55	8.470	381.89	7.294

Table 7 (Continued)

T (K)	p (MPa)	T (K)	p (MPa)	T (K)	p (MPa)
380.57	8.701	L + V → V		381.74	7.289
380.36	8.681	379.45	8.470	L = V	
380.27	8.676	379.25	8.465	381.62	7.284
380.18	8.666	378.76	8.465	L + V → L	
		376.25	8.455	381.54	7.279
L + V → L		371.33	8.440	381.21	7.269
380.08	8.661	366.35	8.435	376.29	7.189
379.96	8.656	361.46	8.435	371.34	7.134
379.90	8.656	351.58	8.475	366.43	7.074
379.68	8.651	341.74	8.570	361.51	7.018
379.28	8.646	331.87	8.720	356.57	6.968
378.80	8.640	321.98	8.945	351.67	6.933
376.30	8.635	312.08	9.245	346.74	6.903
373.84	8.630			341.79	6.888
371.36	8.625			331.90	6.908
368.90	8.625			322.01	6.988
366.43	8.630			312.15	7.133
361.47	8.640				
351.66	8.700				
341.80	8.816				
331.91	8.996				
322.03	9.246				
312.16	9.571				

Ratio: H₂:hexadecanol = 4. Liquid–vapor and liquid–liquid equilibria. The dew curve of this kind of systems show two different type of transitions. Close to the three-phase region the character of the curve is L + V and at higher temperatures change its character towards L₂ + V. This change is a continuous transition but it can be bounded between the temperatures with the asterisks.

Table 8

Three phase region of the ternary system hexadecanol (1) + hydrogen (2) + propane (3) for three different overall compositions

T (K)	p (MPa)	T (K)	p (MPa)	T (K)	p (MPa)
$x_1 = 0.0340, x_3 = 0.8294$		$x_1 = 0.0292, x_3 = 0.8504$		$x_1 = 0.0249, x_3 = 0.8752$	
L ₁ + V → V + L ₁ + L ₂		L ₁ + V → V + L ₁ + L ₂		L ₁ + V → V + L ₁ + L ₂	
368.89	12.825	372.98	11.346	377.53	9.714
369.67	12.544	373.05	11.316	377.65	9.670
370.45	12.264	373.37	11.196	377.74	9.630
371.34	11.970	373.54	11.121	377.85	9.594
L ₂ = L ₁ + V ^a		373.84	11.015	L ₂ + V → V + L ₁ + L ₂	
371.93	11.760	374.14	10.910	377.94	9.555
L ₂ + V → V + L ₁ + L ₂		374.33	10.840	378.04	9.519
372.15	11.695	374.64	10.730	378.09	9.494
372.33	11.624	L ₂ = L ₁ + V ^a		V + L ₁ + L ₂ → L ₂ + L ₁	
373.31	11.300	374.95	10.620	377.53	9.724
374.10	11.095	L ₂ + V → V + L ₁ + L ₂		377.65	9.694
374.19	11.120	375.32	10.485	377.74	9.660
V + L ₁ + L ₂ → L ₂ + L ₁		375.52	10.420	377.84	9.619
368.86	12.860	375.62	10.395	V + L ₁ + L ₂ → L ₂ + V	
369.66	12.689	375.83	10.350	377.93	9.579
370.43	12.519	375.91	10.330	378.04	9.534
371.34	12.315	V + L ₁ + L ₂ → L ₂ + L ₁		378.10	9.509
372.32	12.029	372.98	11.366		
373.31	11.675	373.06	11.346		
373.49	11.590	373.37	11.271		
373.61	11.540	373.55	11.226		
V + L ₁ + L ₂ → L ₂ + V		373.83	11.155		
373.70	11.500	374.14	11.070		
373.81	11.455	374.34	11.020		
374.08	11.305	374.63	10.925		

Table 8 (Continued)

<i>T</i> (K)	<i>p</i> (MPa)	<i>T</i> (K)	<i>p</i> (MPa)	<i>T</i> (K)	<i>p</i> (MPa)
374.19	11.245	374.94	10.830		
		375.29	10.690		
		$V = L_1 + L_2^b$			
		375.52	10.595		
		$V + L_1 + L_2 \rightarrow L_2 + V$			
		375.63	10.550		
		375.83	10.470		
		375.93	10.410		

Ratio: H₂:hexadecanol = 4.

^a L₂ = L₁ + V: lower critical end point (L₂ and L₁ are critical in presence of the vapor phase).

^b V = L₁ + L₂: upper critical end point (V and L₁ are critical in presence of the heavy liquid phase).

4. Conclusions

Experimental phase equilibrium data were obtained for the binary systems H₂ + HD and C₃H₈ + HD. In addition, also data of the ternary systems MP + HD + C₃H₈, HD + MeOH + C₃H₈, and HD + H₂ + C₃H₈ were measured.

Not only bubble points but also dew and critical points could be determined for some of the isopleths. In general, it can be concluded that increasing propane concentration increases the solubility of the reaction mixture, which means that propane is an adequate solvent to be used for the homogeneous hydrogenation of fatty acid methyl esters.

Measurements on the ternary system MP + HD + C₃H₈ show that, for a given propane molar fraction, the equilibrium pressure does not change significantly with the composition of the heavy components; this means that no significant influence on the solubility of the reactive mixture has to be expected as the reaction proceeds from reactant into product. On the other hand, the mixtures of propane with both reaction products, i.e. the ternary mixture HD + MeOH + C₃H₈, exhibit higher equilibrium pressures than the corresponding binary system HD + C₃H₈. This means that the presence of methanol as a by-product will decrease the solubility of the reactive mixture in the supercritical solvent.

The presence of H₂ at high concentrations induces liquid–liquid immiscibility in the ternary system HD + H₂ + C₃H₈, and high pressures are required to achieve a homogeneous phase. The boundaries of the three-phase region L₁L₂V were determined, and retrograde behavior of the light liquid phase (L₁) was observed.

As a general conclusion it was established that the phase behavior of the reactive mixture can be quite complex, i.e., multiphase equilibria easily may occur. Therefore, the boundaries of the single-phase region should be very carefully determined in order to assure operation of the reactor under homogeneous conditions.

Acknowledgement

The authors gratefully acknowledge financial support from the Argentine Research Council (CONICET) and Universidad Nacional del Sur.

References

- [1] R.A. Peters, Natural alcohol production and use, *INFORM* 7 (1996) 502–504.
- [2] R. Tsushima, Surfactants products from oleochemicals, *INFORM* 8 (1997) 362–370.
- [3] 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.
- [4] T. Voeste, H. Buchold, Production of fatty alcohols from fatty acids, *J. Am. Oil Chem. Soc.* 61 (2) (1984) 350–352.
- [5] D.S. Brands, The hydrogenolysis of esters to alcohols over copper containing catalyst, Ph.D. Thesis, University of Amsterdam, Amsterdam, 1998.
- [6] H. Buchold, Natural fats and oils route to fatty alcohols, *Chem. Eng.* 90 (1983) 42–43.
- [7] U.R. Kreutzer, Manufacture of fatty alcohols based on natural fats and oils, *J. Am. Oil Chem. Soc.* 61 (2) (1984) 343–348.
- [8] K. Noweck, H. Ridder, Fatty Alcohols Ullman's Encyclopedia, vol. 5, Weinheim–Wiley, 1999, p. 2533.
- [9] J.W. Veldsink, M.J. Bouma, N.-H. Schöön, A.A.C.M. Beenackers, Heterogeneous hydrogenation of vegetable oils: a literature review, *Catal. Rev.-Sci. Eng.* 39 (3) (1997) 253–318.
- [10] A. Baiker, Supercritical fluids in heterogeneous catalysis, *Chem. Rev.* 99 (1999) 453–473.
- [11] R.R. Allen, Hydrogenation research, *J. Am. Oil Chem. Soc.* 63 (10) (1986) 1328–1332.
- [12] P.G. Jessop, W. Leitner, *Chemical Synthesis Using Supercritical Fluids*, Wiley–VCH, Weinheim, 1999.
- [13] 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.
- [14] 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: Gen.* 210 (2001) 207–215.
- [15] 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.
- [16] 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.
- [17] 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.
- [18] L.J. Rovetto, S.B. Bottini, C.J. Peters, Phase equilibrium data on binary and ternary mixtures of methyl palmitate, hydrogen and propane, *J. Supercrit. Fluids* 31 (2004) 111–121.

- [19] D.J. Fall, K.D. Luks, Effect of additive gases on the liquid–liquid–vapor immiscibility of the carbon dioxide + *n*-nonadecane mixture, *J. Chem. Eng. Data* 3 (1986) 332–336.
- [20] C.J. Peters, Multiphase equilibria in near-critical solvents, in: E. Kiran, J.M.H. Levelt Sengers (Eds.), *Supercritical Fluids: Fundamental for Application*, Kluwer Academic Publishers, 1994.
- [21] C.J. Peters, Th.W. de Loos, J. de Swaan Arons, On the retrograde condensation of one or two liquids, *Fluid Phase Equilib.* 70 (1991) 179–185.
- [22] S. Raeissi, C.J. Peters, Bubble point pressures of the binary system carbon dioxide + linalool, *J. Supercrit. Fluids* 20 (2001) 221–228.
- [23] S. Pereda, S.B. Bottini, E.A. Brignole, Gas–liquid reactions under supercritical conditions—phase equilibria and thermodynamic modeling, *Fluid Phase Equilib.* 194 (2002) 493–499.
- [24] L.J. Rovetto, S. Pereda, S.B. Bottini, C.J. Peters, Phase equilibria in mixtures of hydrogen, propane and fatty oil derivatives at supercritical conditions, in: *Proceedings of the Sixth International Symposium on Supercritical Fluids*, Versailles, France, Tome 2, 2003, pp. 825–830.
- [25] K.D. Luks, R.C. Merrill, J.P. Kohn, Partial miscibility behavior in cryogenic natural gas systems, *Fluid Phase Equilib.* 14 (1983) 193–201.