

PHASE EQUILIBRIUM ENGINEERING OF SUPERCRITICAL REACTORS

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INTRODUCTION

The phase behavior in supercritical reactors can be quite complex. Drastic changes in density and solubility with temperature, pressure and composition can be expected, due to the presence of a multicomponent mixture of a near-critical or supercritical solvent with reactants and products. In the case of hydrogenation or hydroformylation, permanent gases are mixed with a supercritical cosolvent to bring mixtures of liquid components to a single phase condition. The large difference in molecular size and volatility between these components is likely to give rise to liquid phase instability and multiphase behavior. Wandeler et al.[1] point out that in the analysis of results of reactions carried out under supercritical conditions that “although the importance of phase behavior in high pressure systems is generally accepted, the complexity of high pressure multicomponent systems is often underestimated”. The phenomenological behavior of high pressure fluids has been the subject of numerous studies, we can refer the reader to the works of Peters [2], Schneider [3] and Straver [4]. The classification of the phase behavior observed in binary mixtures by van Konynenburg and Scott [5] is of great value for the understanding of the phase behavior of supercritical reactors. Recently Pereda et al.[6] have introduced a systematic approach for finding the boundaries of the single phase region in supercritical reactors.

The use of supercritical conditions to carry out chemical reactions has attracted great interest during the last decade [7]. Some of the advantageous properties of supercritical reactors are: i) to combine all reactants and products in a single phase reducing the mass transfer and solubilities limitations, ii) to increase the selectivity of the process, iii) a reduction of environmental risk and iv) facilitated product separation and catalyst recovery. In many chemical processes a combination of the above properties justifies the use of supercritical conditions. Eventhough the potential for supercritical reactors is boundless, at present most of the experimental studies has concentrated in hydrogenation or hydroformylation reactions. The main goal has been to bring a gas – liquid heterogeneous catalytic process to a single phase in contact with a solid catalyst. The conceptual design of process conditions to determine the range of single phase operation for the supercritical reactor, is a problem of *phase equilibrium engineering*; i.e. the systematic study and application of phase equilibria to the development of chemical processes. For each process there will be a set of specifications, which represent the problem design restrictions. In the case of catalytic hydrogenation of liquid substrates these specifications are: a) components of the reactive mixture, i.e. reactants and products; b) operating temperature, given by the reaction kinetics and catalyst; c) degree of conversion. By applying phenomenological and modeling phase equilibrium engineering tools it is possible to find the reactor operating conditions which guarantee the existence of a

single fluid phase, at any reaction time or reactor location, subject to the above specifications. The solution to this problem requires the determination of the following process variables: a) supercritical solvent; b) operating pressure; c) solvent/feed ratio or system composition profile. The solution to this problem should be based on the understanding of the phase equilibria scenarios that may exhibit mixtures of the components of the system. For this purpose experimental studies on the systems of interest are required. Finally it is required a thermodynamic model for phase equilibria for the extrapolation and interpolation of limited experimental information over the whole range of conditions: compositions, pressures and temperatures. In the present work recent studies on selection of process conditions for hydrogenation and hydrogenolysis reactions are presented.

THERMODYNAMIC MODELING

The group contribution equation of state GC-EOS [8] is applied to predict the required phase equilibrium scenarios for solvent containing reactive mixtures. This equation has been updated by Gros et al [9] to handle associating components (GCA-EOS) and by Bottini et al [10] to deal size asymmetric mixtures. The group contribution character of the equation and the possibility of dealing with associating compounds make it possible to predict and correlate a great variety of multicomponent mixtures at high pressures [11].

SOLVENT AND OPERATING CONDITIONS SELECTION

The selection of a solvent is a key step in the design of supercritical reactors. When the solvent is required to achieve a single phase hydrogenation reaction, the basic principle is that the solvent should be above its supercritical temperature. In this way hydrogen, or the synthesis gas participating in the reaction, will be completely miscible with the high pressure supercritical solvent. Therefore the reaction temperature determines the range of suitable solvents. Besides the solvent should be inert with respect to reactants and products and the catalyst. CO₂ is considered an ultimate solvent for green chemistry however it offers some limitations with regard to interaction with the catalysts at high pressures, high acidity in aqueous systems at high pressures and partial miscibility with moderate and high molecular weight organic compounds. Also CO₂ may not be an inert component under the reaction conditions. On the basis of critical temperature and inertness propane has been chosen by Härröd and Møller [12] as a solvent for hydrogenation of unsaturated triglycerides and for hydrogenolysis [13] of fatty acid methyl esters. These reactions are carried out above the critical temperature of propane. In the hydrogenation of triglycerides, there is only a change in the degree of unsaturation of the triglycerides, in this case it is possible to model the phase conditions on the basis of a triangular diagram of hydrogen, the solvent and the hydrogenation substrate (triglyceride). The ultimate goal is to achieve a type I diagram in which there are two pairs that are completely miscible (propane + triglyceride) and (propane + hydrogen) and an immiscible pair (hydrogen + triglyceride). In Figure 1 is illustrated the ternary diagrams predicted by the GCA-EOS for near critical propane working at 360 K in mixtures with tripalmitin and hydrogen for increasing values of the operating pressure. In the first diagram (20 bar) propane is a superheated vapor completely miscible with hydrogen but depicting heterogeneous liquid – vapor equilibria with the tripalmitin. At 40 bar propane is a liquid that depicts liquid-liquid immiscibility with the tripalmitin and vapor-liquid equilibria with the hydrogen. Therefore a region of liquid-liquid-vapor equilibria exists at high propane concentrations. At higher pressures propane and tripalmitin become complete miscible and a

region of complete miscibility is found around the corner of high propane concentration. In this region we can obtain complete miscibility at any molar ratio between the oil and hydrogen. However a region of gas - liquid – liquid immiscibility is still observed because the temperature is below the critical temperature of propane.

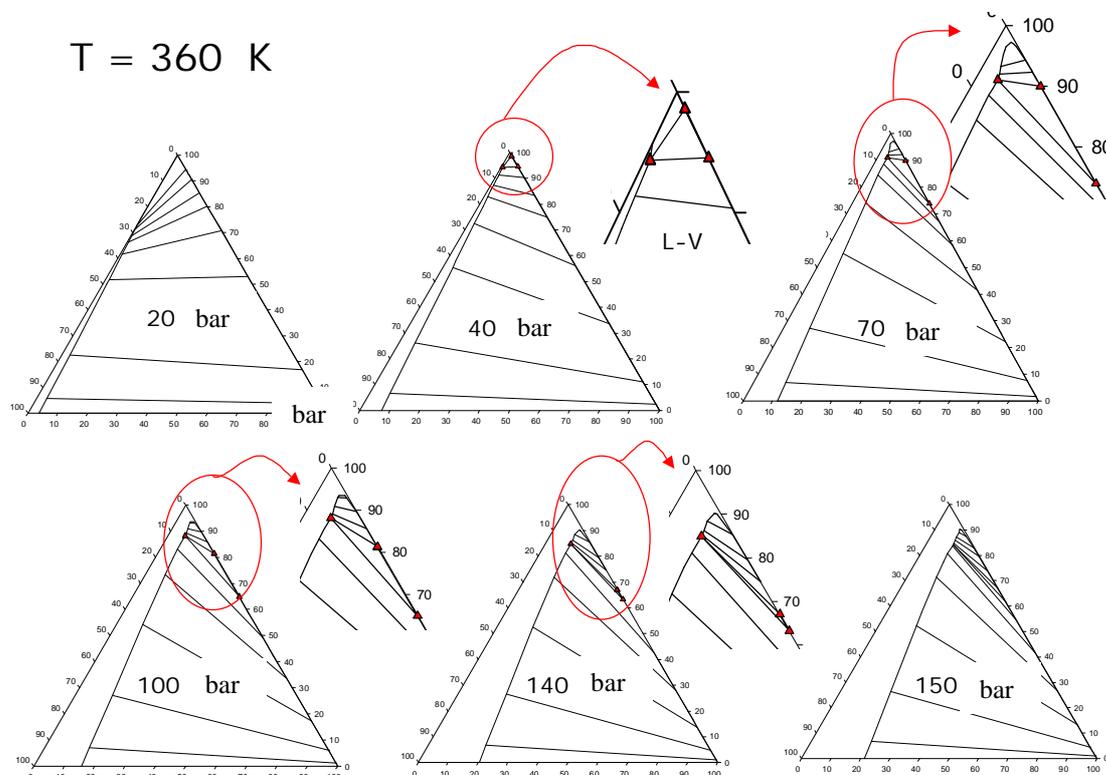


Figure 1: Predictions by the GCA-EOS for mixtures $\text{PPP} + \text{H}_2 + \text{C}_3\text{H}_8$ at 360K.

If the temperature is increased above the critical temperature of propane to 373 K the gas-liquid – liquid region disappears and a type I phase diagram is recovered (Fig.2). The evidence of gas-liquid-liquid equilibria has been verified experimentally as can be seen from Fig.3. [14]. It can be observed that at the reaction temperature and pressure there is a concentration of propane above which the system is always in a single phase condition. This concentration as well as the solvent/feed ratio decreases with pressure at a given temperature. Depending on the operating temperature Pereda et al [6] shows that eventhough there is an exponential decrease in the solvent feed ratio in the low pressure range there is a pressure for each temperature, beyond which no significant reduction of the solvent requirements is achieved by increasing the pressure. In the case of hydrogenation of sunflower oil the GCA-EOS predictions indicate that these pressures are 120 bar at 373K, 150 bar at 398 K and 220 bar at 425 K. For example at 373 K and 120 bar, 2.3 Kg of propane are required per Kg of oil to achieve complete miscibility.

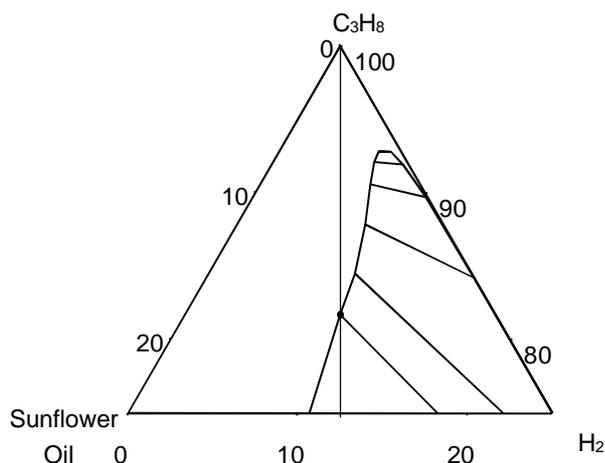


Figure 2: Propane requirement for the homogeneous hydrogenation of sunflower oil

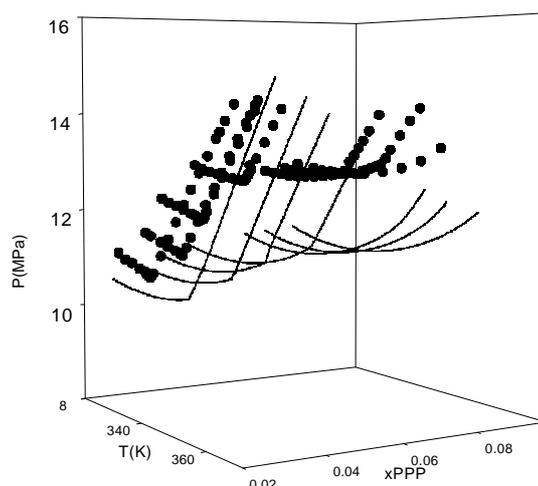


Figure 3: $H_2+C_3H_8+PPP$. Exp Data [•], — GCA-EOS

In the case of hydrogenolysis of fatty acid methyl esters (FAME), the products of the reactions are fatty alcohols and methanol. Therefore a five component system is obtained.. Recent experimental results [15] indicate good agreement with the predictions of the GCA-EOS. In this case the phase behavior varies with the degree of conversion of the reaction and the solubilities of the components of the mixture in the supercritical phase decrease with conversion. Again the identification of a minimum pressure for all ratios of reactants at a given temperature allows an efficient identification of the pressure required to achieve a single phase behavior as a function of the molar fraction of propane in the system. Recently van der Hark and Harrod [16] have presented data of selective hydrogenation of unsaturated fatty esters (methylated sunflower oil) to obtain unsaturated alcohols. The experimental conditions of two runs are indicated in Fig.4 together with predictions of phase envelopes curves for zero and full conversion of the ester group to alcohol.

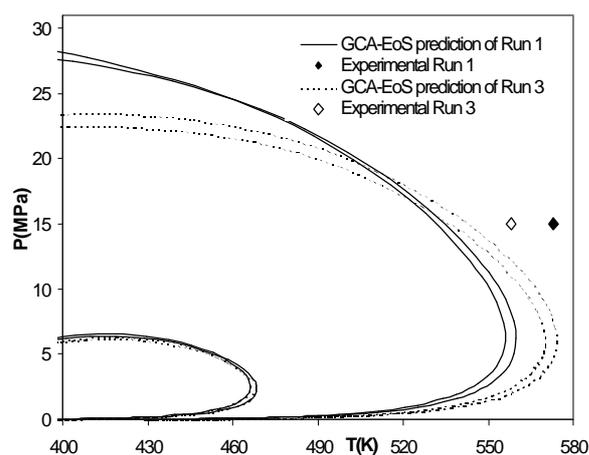


Figure 4: Phase envelopes in selective hydrogenations of fatty esters.

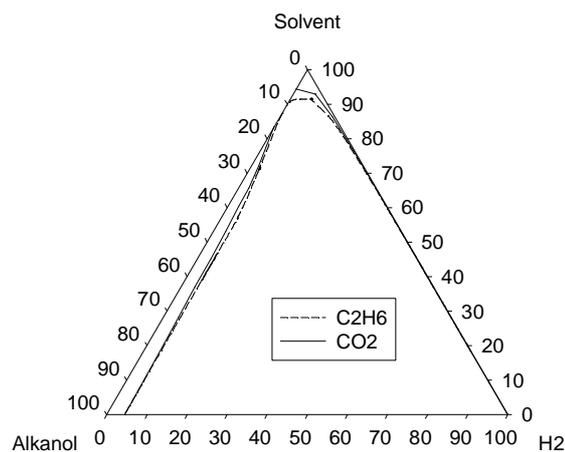


Figure 5: Ternary diagram for the hydrogenation of crotonaldehyde at 313 K

The smaller set of phase envelopes corresponds to the solvent feed ratio used for these authors and larger phase envelopes corresponds to mixtures much richer (10 to 15 times more) in the reactants but that still predict single phase for the reaction conditions studied. For this problem the temperature of the reactor is in the range of 285/300 °C. The potential of rigorous modeling of the phase equilibria of multicomponent mixtures to identify single phase conditions in supercritical reactors is illustrated for the selective hydrogenation of crotonaldehyde to unsaturated alcohols [17]. In this case the reaction takes place at low temperatures 313 to 353 K. In this temperature range the use of propane is not possible, because the temperatures are well below the critical temperature of propane. CO₂ and ethane have critical temperatures of about 304K and are in principle suitable solvents for this system. The more severe conditions to achieve single phase behavior are given for the alcohol + solvent + hydrogen ternary mixture. The triangular diagram for this system is shown in Fig.5, for the two solvents. The experimental studies of Bhanage et al. were carried out at 180 bar with a molar fraction of hydrogen of 0.22. The predictions of Fig.5 indicate that for this hydrogen molar fraction the system is within the two phase binodal curve. The phase envelope for this system for CO₂ and ethane indicate that pressures above 300 bar are required to avoid the two phase behavior (Figs.6 and 7) at 313K.

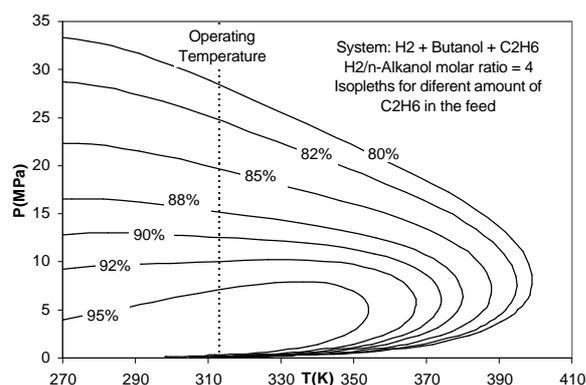


Figure 6: Phase envelopes for the system H₂ + octanol + ethane

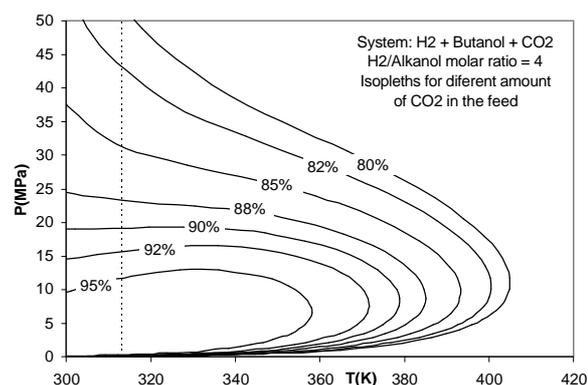


Figure 7: Phase envelopes for the system H₂ + octanol + CO₂

CONCLUSIONS

In this work is illustrated the potential of thermodynamic modeling with the GCA-EOS to obtain information on the phase behavior of complex mixtures undergoing chemical reactions and to select conditions for single phase operation. The thermodynamic modeling of the phase equilibria, combined with experimental information is of critical importance to understand the results obtained in supercritical reactors.

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