

## Review

## Advances in phase equilibrium engineering of supercritical reactors

S. Pereda, E.A. Brignole, S.B. Bottini\*

PLAPIQUI, UNS-CONICET, Camino La Carrindanga km 7.5, Bahía Blanca, Argentina

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## ABSTRACT

This review summarizes the advances made in the last decade in understanding the effect of phase conditions in the performance of supercritical reactors and in the control of process outputs. The study covers heterogeneous-catalyzed and non-catalytic supercritical reactions and shows the experimental and modeling tools that have been applied to address the problem of keeping reactants and products in a homogeneous phase.

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## 1. Introduction

Since the appearance of the special issue of the Chemical Reviews edited by Noyori at the end of last decade (volume 99, 1999), over a thousand papers have been published in the field of supercritical reactors. Gas–liquid catalyzed reactions are one of the areas where the use of supercritical fluids is particularly attractive [1]. In general, these reactions are diffusion-controlled and the use of supercritical fluids increases the reaction rate by eliminating the gas–liquid interface. On top of this, the operation at supercritical conditions offers many interesting properties: higher solubility of reactants and products in the supercritical phase; reduced deposition of reacting components on the catalyst pores; diffusion

coefficients higher than liquids; independent control of the concentration of permanent gases like H<sub>2</sub> or O<sub>2</sub> or CO in the reaction mixture; higher thermal capacity and low interfacial tension. The hydrogenation of low volatile liquids using solid–fluid heterogeneous catalysts is a typical reaction where the use of supercritical conditions can be highly beneficial. Härröd et al. [2], for example, report large increases of the reaction rates during hydrogenation of vegetable oils and fatty esters under supercritical propane.

The selection of process conditions that guarantees operation under a supercritical single-phase state is considered a typical phase-equilibrium engineering problem. Wandeler and Baiker [3] and Baiker [1] have stressed the need of having knowledge and control of the phase conditions, to be able to understand the results obtained when operating high-pressure reactors. In this paper, advances in the design and control of the phase conditions in several supercritical reaction processes are discussed. The review covers heterogeneous-catalyzed and non-catalytic super-

\* Corresponding author. Tel.: +54 291 4861700; fax: +54 291 4861600.  
E-mail address: [sbottini@plapiqui.edu.ar](mailto:sbottini@plapiqui.edu.ar) (S.B. Bottini).

critical reactions, carried out under single-phase conditions of the reaction mixture.

## 2. The reactor phase-condition

The reactor phase-condition establishes the number of phases present under a certain degree of conversion, for a given feed, and operating temperature and pressure. To take advantage of the benefits of working in the supercritical state, phase-equilibrium engineering tools can be applied to determine the feed composition, supercritical solvent/feed mass ratio and operating pressure and temperature required to achieve complete homogeneous operation at all conversions.

There are several possible situations for the reaction system under consideration. One of the reactants may be a permanent gas like  $H_2$ ,  $O_2$  or  $CO$  in a heterogeneous catalytic process, while the other reactant/s is a liquid or a solid. This is the case of the hydrogenation of heavy substrates like vegetable oils and the alkylation of naphthalene with methanol. A different situation may arise if we have a system in which both reactants are partially miscible liquids, like in the transesterification of vegetable oils with methanol.

Another problem is related to reactions that are usually carried out in the gas phase, with components that have high volatility under the reaction conditions. A typical example of this type of reactions is the alkylation of isobutane with 1-butene.

## 3. Thermodynamic tools for the analysis of phase conditions

In order to select the appropriate operating conditions of a supercritical reactor, it is necessary to determine the phase boundaries of the multicomponent mixture formed by the reacting system and the supercritical solvent. Particularly difficult systems to bring into homogeneous supercritical conditions are those found in the hydrogenation of heavy compounds. In these reactions, we have immiscibility in the binary hydrogen–heavy substrate at all conditions. In the search of a suitable solvent to attain supercritical homogeneous conditions, we need to consider the temperature or temperature range recommended for the particular reaction. The critical temperature of the solvent should be lower than the reactor operating temperature. In this way, the binary supercritical solvent + hydrogen will be completely miscible and it will be possible to find a region of complete miscibility in a type I ternary system (Fig. 1), having two miscible (solvent + hydrogen and sol-

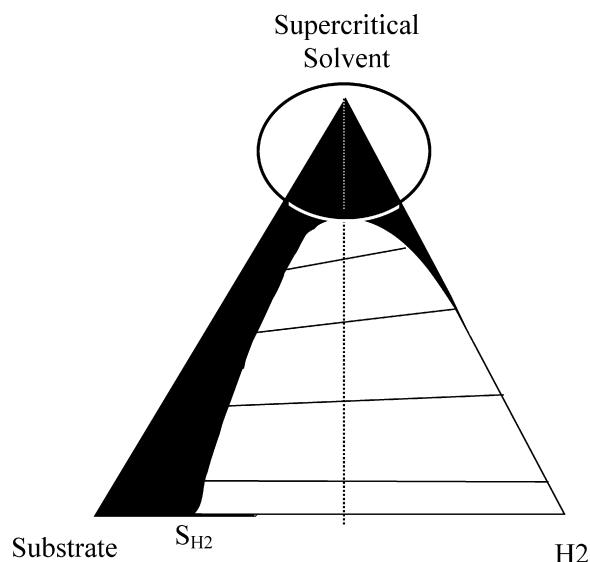


Fig. 1. Type I phase diagram showing the feasible operating region for supercritical hydrogenation [4].

vent + substrate) and one immiscible (hydrogen + substrate) pairs [4,5]. However, the miscibility between the supercritical solvent and the heavy substrate requires further analysis.

van Konynenburg and Scott [6] have classified the fluid phase behavior observed in binary mixtures into five main types. In type I phase behavior complete liquid miscibility is observed at all temperatures, and there is a continuous critical locus between the critical points of the two pure components. When there is partial liquid miscibility at low temperatures, the system is of type II. When the immiscibility persists at high pressures and temperatures, the systems are of type III.  $CO_2$  forms type III mixtures with heavy alkanes and triglycerides. For this reason  $CO_2$  is not a suitable solvent to carry out homogeneous supercritical reactions in which these components participate. When differences in molecular size become significant in near ideal systems, liquid–liquid immiscibility is observed close to the critical temperature of the light component. In this case, there is a discontinuity in the critical locus of the binary mixture. However, complete miscibility is recovered at lower temperatures or high pressures. This is the case of binary mixtures of propane with heavy alkanes and triglycerides.

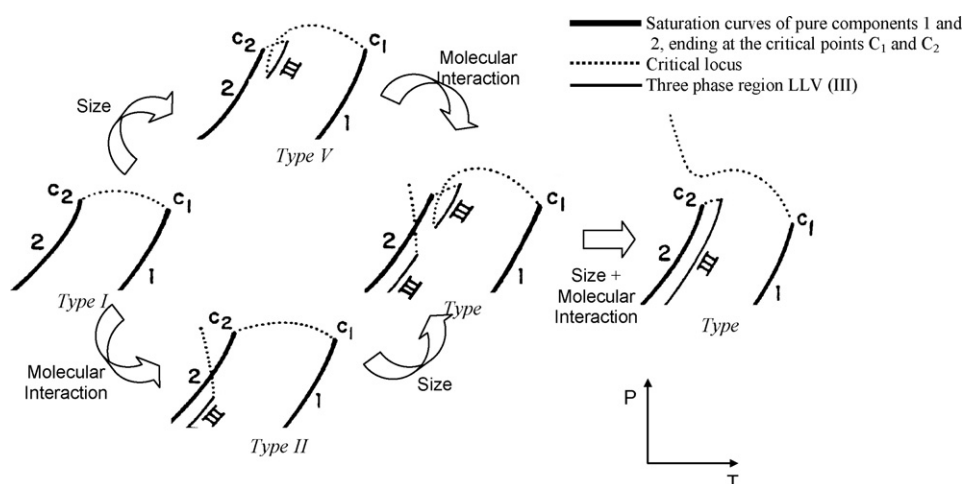


Fig. 2. Effect of molecular interactions and size differences in the types of binary fluid phase diagrams [7].

Luks [7] presented a diagram showing the transition between the different binary phase types, according to the differences in molecular size and/or molecular interactions between the components of the mixture (Fig. 2). Cismondi and Michelsen [8] have developed a very efficient algorithm for predicting global phase diagrams of binary mixtures, which can help in finding regions of complete miscibility of binary mixtures.

When the reacting system involves more than three components, including the supercritical solvent, the recommended approach is to compute the pressure–temperature phase envelopes of the multicomponent system, under different degrees of conversion [4,5].

Quite frequently experimental studies are carried out in fixed volume reactors, charged with solid or liquid reactants and pressurized with different gases. The composition inside the reactor can be estimated by an iterative procedure and using a suitable equation of state, from the information on the reactor volume and the pressure measured after charging each different gas [5].

#### 4. Phase equilibria in reacting systems

Many papers in the recent literature report the results of experimental studies and thermodynamic modeling of reacting systems. Camy et al. [9] measured and modeled the phase equilibrium conditions for the synthesis of dimethyl carbonate from methanol and carbon dioxide, with water as a by-product. The supercritical conditions were established by using the SRK equation with MHV2 mixing rules (Dahl and Michelsen) [10]. These authors predicted that a large excess of CO<sub>2</sub> is required to operate the reactor under single-phase conditions. Andreatta et al. [11] and Hegel et al. [12] measured the phase equilibria of mixtures related to the production of biodiesel using supercritical methanol. In this case, the experimental data were correlated with the GCA-EOS model (Gros et al.) [13]. Hu et al. [14] made a thorough study of the critical properties of binary and multicomponent mixtures found in the supercritical synthesis of ethyl acetate. These authors examine the changes in the critical pressure and temperature caused by the addition of CO<sub>2</sub> to the reacting mixture. Ji et al. [15] on the other hand, studied the critical properties in the acylation of anisole with acetic anhydride, using CO<sub>2</sub> or propane as supercritical cosolvents. The effect of the extent of the reaction on the critical properties was also investigated. Ke et al. [16] studied experimentally and with the Peng Robinson EoS, the changes in the critical properties of mixtures of H<sub>2</sub>, propylene, propane and CO<sub>2</sub> under hydrogenation conditions. The experimental fluid phase behavior during hydrogenation of vegetable oils and hydrogenolysis of fatty esters under supercritical propane was studied by Rovetto et al. [17–19]. Pereda et al. [20] carried out the thermodynamic modeling of these mixtures using the GCA-EOS equation. Li et al. [21] measured the critical temperature and pressure of various binary and ternary mixtures related to the alkylation of 2-methylpropane with 1-butene; the effect of methane and CO<sub>2</sub> in the system behavior was investigated. Wang et al. [22] on the other hand, report the results of an experimental study on the critical properties of the reacting mixtures found during alkylation of benzene with propylene to obtain cumene. Zhang et al. [23] carried out a similar study for the oxidation of cyclohexane in supercritical CO<sub>2</sub>. Yermakova and Anikeev [24] have made a careful analysis of the phase behavior of multicomponent mixtures in connection with the design of chemical reactors. They applied the SRK equation of state to represent the operation of a Fischer–Tropsch reactor. Jiang et al. [25] measured bubble pressures of mixtures typical of the hydroformylation of 1-hexene under supercritical CO<sub>2</sub>, covering different degrees of conversion. Later, Pereda et al. [5] correlated these data with the GCA-EOS model and studied the effect, not only

of supercritical CO<sub>2</sub>, but also of supercritical propane on the phase conditions.

All these papers study the changes of the critical properties with conversion, and highlight the importance of finding the boundaries of the critical region in order to identify the phase condition in the supercritical reactors.

#### 5. Experimental tools to determine the phase scenario

The direct observation of phase conditions during the course of a reaction is strongly recommended to verify operation under single-phase conditions and to detect any changes in the phase scenario with the advancement of the reaction. Experimental studies with direct control of phase conditions have been reported by Caravatti et al. [26,27] for the oxidation of benzyl alcohol in scCO<sub>2</sub>. Baiker and co-workers [28–30] discuss the application of spectroscopic and related techniques for the control of the phase condition and reaction mechanisms in various supercritical reactions. Martin et al. [31] used an optical cell to obtain critical points of mixtures of olefins and ammonia in the synthesis of amines by hydroaminomethylation. Moreover, Novitskiy et al. [32] recently presented a new continuous method to perform quick phase equilibrium measurements in multicomponent systems at high temperature and pressure. This method is similar to that presented by Wu et al. [33] and applied also by Hyde et al. [34] However, instead of detecting changes in the refractive index of the mixture that is undergoing a phase transition, the new method detects changes in the signal of a flame ionization detector (FID).

#### 6. Gas–liquid reactions

##### 6.1. Hydrogenation

Chouchi et al. [35] presented results on the hydrogenation of alpha-pinene, which seems to indicate that operation under a near critical two-phase region performs better than supercritical single-phase reactions. However, these results may be explained by the dilution of hydrogen in the reacting mixture when working in the supercritical region [5].

Burgener et al. [36] have raised an interesting question regarding the inertness of CO<sub>2</sub> in supercritical hydrogenation processes. Attenuated total reflection infrared (ATR-IR) spectroscopic studies were carried out in a variable volume cell, and in batch and continuous reactors with windows. The results indicate the formation of CO when Pt catalysts are used. However, this is a minor side-reaction and CO<sub>2</sub> may be considered a relatively “inert” solvent in many practical applications.

Chatterjee et al. [37] studied the Pd-catalyzed selective hydrogenation of citral in supercritical CO<sub>2</sub>. They found that it is possible to achieve a selective hydrogenation of the conjugated and isolated C=C double bond, obtaining a fully saturated aldehyde. Burgener et al. [38] studied also the hydrogenation of citral over Pd/alumina catalyst. They found that operating under scCO<sub>2</sub> gives a rate of hydrogenation about two orders of magnitude higher than in organic solvents.

Pillai and Sahle-Demessie [39] have investigated the selective hydrogenation of ketoisophorone to 4-hydroxyisophorone under different organic solvents, scCO<sub>2</sub> and CO<sub>2</sub> expanded solvents. Phase equilibrium studies showed that at 373 K and 15 MPa total pressure, with 1.7 MPa hydrogen partial pressure, the mixture (substrate + H<sub>2</sub> + CO<sub>2</sub>) forms a single-phase system. Under these conditions good conversion and selectivity were obtained, comparable to those in liquid cyclohexane and better than those in CO<sub>2</sub>

expanded solvents. Also the deactivation of the Pd/Al<sub>2</sub>O<sub>3</sub> catalyst in scCO<sub>2</sub> was lower.

Wandeler et al. [40] found very good enantioselectivity and high reaction rates in the continuous hydrogenation of ethyl pyruvate under supercritical ethane. These authors measured the phase behavior of the reactive mixture at different compositions, in the temperature range of 288–323 K and pressures up to 140 bar, using a computer-controlled view cell with on-line video imaging and recording. Based on the experimental results obtained for the multicomponent reactive mixtures, they found that the phase diagram of a binary system representative of the ethyl pyruvate and ethane-rich phases was an appropriate and useful guide to understand the high-pressure reaction process.

van den Hark and Härröd [41] and Härröd et al. [2] have studied experimentally the hydrogenation of vegetable oils and fatty esters, under supercritical conditions. These authors report an increase of several orders of magnitude in the reaction rate and improved selectivity, compared to conventional hydrogenation, when the reacting system is in a single homogeneous phase. Piqueras et al. [42,43] have studied the hydrogenation of sunflower oil on Pt/TiO<sub>2</sub> catalysts, under supercritical and conventional conditions. The addition of propane as supercritical solvent allows the reaction to be performed in a homogeneous phase, in contact with the solid catalyst. Also, the supercritical hydrogenation produced a lower amount of triglyceride *trans*-isomers than the conventional process. Ramírez et al. [44] also carried out the hydrogenation of sunflower oil on Pd/C under supercritical propane. The operating conditions were selected following the recommendations of Pereda et al. [4] to work under a single supercritical fluid phase.

## 6.2. Fischer–Tropsch synthesis

Yokota et al. [45] were the first to propose the use of supercritical solvents in order to improve the reaction medium to carry out the Fischer–Tropsch synthesis. In the last decade Fujimoto and co-workers have published various studies, including: (i) comparison of different solvents like pentane, hexane and their mixtures with decane [46]; (ii) control of product distribution [47,48]; (iii) effect of the solvent recycle composition on the steady-state operation [49]. In this last work, it is shown that the average CO conversion decreases when fresh *n*-hexane is replaced by solvent recycling. Moreover, the use of solvent recycle lowers the contents of alpha-olefins in the products.

Bochniak and Subramanian [50] studied the Fischer–Tropsch synthesis in supercritical *n*-hexane. This work shows that by operating in the supercritical region with a heterogeneous catalyst, an increase in yield and selectivity is obtained, due to the higher solubility of the reaction products in the liquid-like densities of supercritical hexane. A similar conclusion is obtained by Irankhah [51]. These authors recommend the use of a mixture of hydrocarbon products of the Fischer–Tropsch synthesis as the supercritical media for this reaction.

Ermakova et al. [52] studied the effect of the non-ideality of the reaction medium on the rate of reaction, using the Soave Redlich Kwong EoS over a large range of pressures (6–100 atm). The reaction rate and yield of olefins under supercritical conditions was found to be much higher than those of a reference process carried out in the absence of supercritical solvent.

Elbashir and Roberts [53] did an extensive study on the effect of phase behavior on the product distribution. These authors measured the critical conditions of the hexane + syngas + product mixture at the outlet of a Fischer–Tropsch reactor, using a variable volume view cell. They showed the high sensitivity of the critical point to the mixture composition, which is typical of asymmetric mixtures. Therefore, the selection of the adequate solvent and

operating conditions should be based on the desired product distribution (high or low content of heavy cuts). The main advantages of operating under supercritical hexane conditions were in situ extraction of heavy hydrocarbons from the catalyst pores, coupled with enhanced incorporation of olefins in the chain growth process.

Huang et al. [54] made an interesting study of the effect of supercritical fluid density on the C<sub>6</sub>+ hydrocarbon product distribution and selectivity, in a fixed-bed Fischer–Tropsch reactor. The use of pentane and hexane were compared at the same density (ca 0.3 g/cm<sup>3</sup>) and 240 °C. Similar product distribution was obtained with both solvents, although pentane required higher pressures to obtain the same density.

## 6.3. Oxidation

Increasing environmental concern makes the use of traditional stoichiometric oxidants such as dichromate or permanganate no longer acceptable. The general trend is the direct application of molecular oxygen in heterogeneous or homogeneous catalytic processes. Water and dense CO<sub>2</sub> are the preferred reaction media, as oxidations will take place without formation of any solvent by-products.

Armbruster et al. [55] carried out batch and continuous experiments on the heterogeneous catalyzed partial oxidation of cyclohexane to cyclohexanol and cyclohexanone under scCO<sub>2</sub>, and accompanied their results with experimental and modeling studies on the phase behavior of CO<sub>2</sub> + cyclohexane + air mixtures. The reactions were carried out at supercritical conditions, reaching maximum selectivities of 26% and 16% for cyclohexanone and cyclohexanol, respectively, at 10% conversion.

Zhang et al. [23] on the other hand, measured the critical properties of nominal mixtures, representative of the oxidation of cyclohexane under scCO<sub>2</sub>, using nitrogen as the homomorphous of oxygen. Cyclohexanol, cyclohexanone and water in a 1:1:1 molar ratio, were assumed to be the products of the reaction. The experimental data show that the critical temperature increases with the initial ratio of cyclohexane to nitrogen, but decreases with the increase of carbon dioxide content, which proves that the addition of carbon dioxide and the adjustment of the ratio of alkane to oxygen are effective measures to regulate the critical temperature of the reacting mixture. The authors used this experimental data to follow the changes in the phase behavior of a series of reactions carried out in a constant volume cell at 394 K, covering a 110–222 bar pressure range [56]. The results show a decrease in cyclohexane conversion from 9% to 4% when the global density in the reactor increased from 0.27 to 0.61 g/cm<sup>3</sup>. This change in conversion was accompanied by an increase in the selectivity towards the formation of cyclohexanone.

In the case of water-soluble alcohols, water has been the favored option for oxidation with air. However, when working with heterogeneous catalytic processes, the presence of bulk water can lead to rapid formation of geminal diols on the metal surface, which will undergo dehydrogenation to form an undesirable acid product [57]. With CO<sub>2</sub> as the solvent medium, this problem is in principle overcome, as no bulk water phase will be in contact with the metal surface. Baiker and co-workers have extensively studied the air oxidation of various alcohols in scCO<sub>2</sub> media, using 0.5% Pd-supported catalysts in a continuous reactor. The oxidation of primary and secondary octyl alcohols [58] and benzyl alcohol [59,60] gave high turnover frequencies and increased rate of partial oxidation compared to conventional gas phase oxidation. In the case of 2-octanol and benzyl alcohol, 2-octanone and benzaldehyde were obtained with selectivities higher than 99.5% and 95%, respectively.

One problem found during heterogeneous catalytic oxidation of alcohols under scCO<sub>2</sub> is the behavior of the solid–fluid interface.

CO<sub>2</sub> is a non-polar solvent, with a poor capacity to dissolve the polar products or by-products formed during reaction. In particular, the relatively hydrophilic nature of the catalytic surface compared to scCO<sub>2</sub>, prevents desorption of water from the catalyst into the non-polar fluid phase, leading to potential catalyst deactivation [61,62]. Tsang and co-workers [62,63] have circumvented this problem by using a Teflon-coated metal catalyst during air oxidation of 9-anthracene methanol and *m*-hydrobenzoin. The Teflon-modified catalyst prevents water formed during the oxidation process from being retained on the metal surface, increasing catalyst activity and lifetime.

Caravati et al. [64] on the other hand, carried out the oxidation of a solid alcohol (cinnamyl alcohol) in a continuous fixed-bed reactor under scCO<sub>2</sub>, by dissolving the alcohol in a small amount of toluene. These authors found that at pressures above 130–150 bar (according to the toluene/alcohol molar ratio) the reactor is under homogeneous conditions, but at lower pressures (90–120 bar) the reactive mixture formed a two-phase system, with a CO<sub>2</sub>-rich phase (containing also part of the cinnamyl alcohol and almost all of the toluene) in equilibrium with an alcohol-rich, liquid-like phase. The greatest activity was measured at biphasic conditions. ATR-IR spectroscopic investigations suggest that inside the catalyst pores conditions are similar to the bulk phase under single-phase conditions (e.g., rich in carbon dioxide). In this case, the solvation power of the liquid-like alcohol-rich phase in the bulk around the solid particles is probably beneficial for desorption and transport of the aldehyde and reaction by-products, including water. The addition of toluene to the scCO<sub>2</sub> media has also been applied to the aerobic oxidation of benzyl alcohol [27].

## 7. Processes where the supercritical fluid takes part in the reaction

This type of processes is found, for example, in the transesterification of triglycerides with supercritical alcohols, in direct amination with ammonia and in alkylation using olefins or alcohols.

The non-catalytic transesterification of vegetable oils and fats using supercritical methanol is a good example where phase equilibrium engineering tools can help to understand the process and to select optimum operating conditions. In these reacting systems the reactants, methanol and vegetable oil, are only partially miscible at ambient temperature. High temperatures, close to 180 °C, are required to have complete miscibility of methanol and oil. The reaction products, glycerin and fatty esters, are also immiscible. Saka and Kusdiana [65], in their pioneering work, carried out this reaction in a 5-mL closed vessel at very high temperatures and pressures, around 350 °C and up to 650 bar. In this way they obtained a very high conversion in a short time. Cao et al. [66] also attained high conversions in reasonable short times, using co-solvents like CO<sub>2</sub> or propane. Cao and co-workers claimed that cosolvents reduce the critical point of the mixtures, allowing the transesterification to be carried out in a supercritical phase under milder conditions. The methanol–sunflower oil global phase diagram shown in Fig. 3 compares the operating conditions applied in Saka and Kusdiana and Cao et al. experimental works. It is clear from this figure that the extreme conditions applied by Saka and Kusdiana are not justified on the basis of achieving homogenous operation, and that it is possible to use milder conditions.

Hegel et al. [67] studied the phase transitions during the transesterification reaction, in a windowed cylindrical reactor. In this study, the global density inside the reactor was carefully controlled, and a clear relation between phase behavior, final pressure and global density was established. Fig. 4 shows the trajectory of transesterification experiments carried out at different global densities (0.8 g/cm<sup>3</sup> in Fig. 4a and 0.5 g/cm<sup>3</sup> in Fig. 4b). It is clear that at high

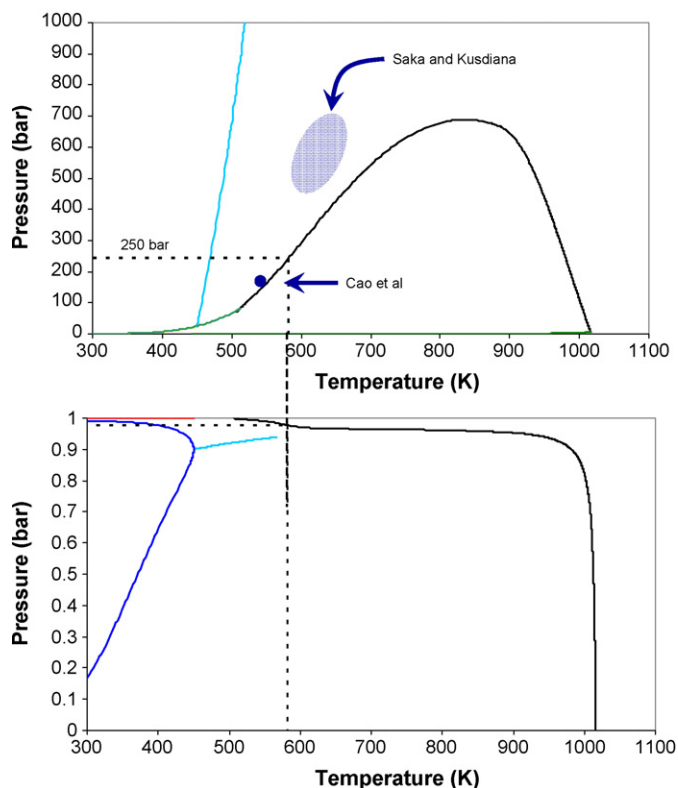


Fig. 3. Methanol + sunflower oil global phase diagram. Comparison between operating conditions selected by Saka and Kusdiana [65] and Cao et al. [66] (dashed line corresponds to methanol:oil molar ratio = 40).

densities the reaction takes place in the liquid phase. Under these conditions the pressure increases drastically with temperature.

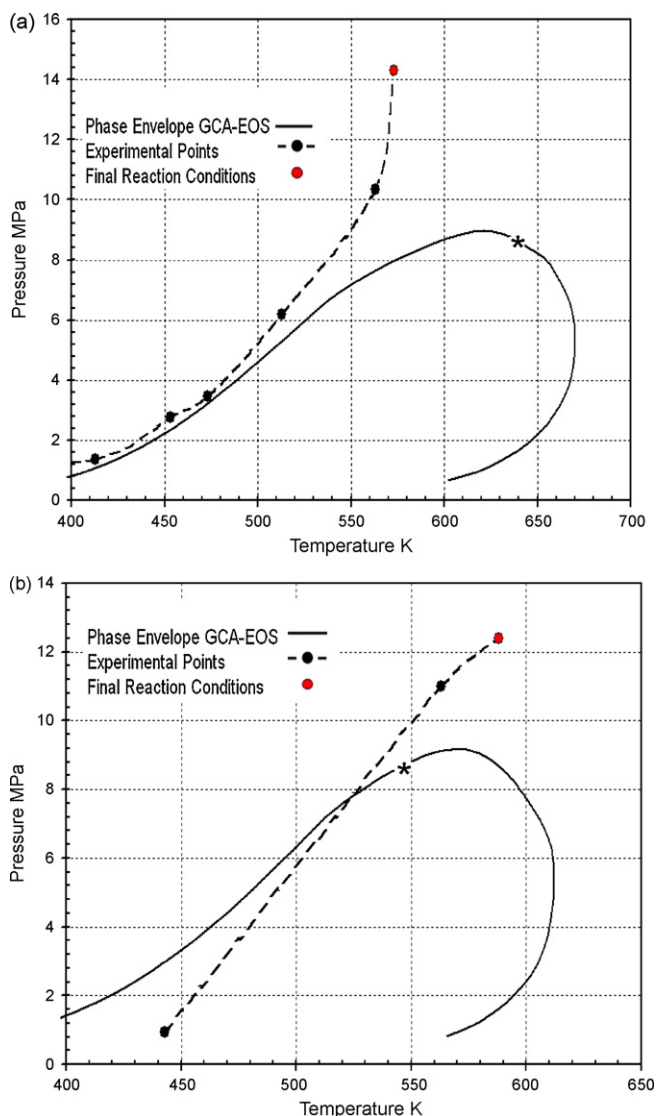
Bogdan et al. [68] studied the isomerization of *n*-butane over solid acid catalysts, and found that operating close to the *n*-butane critical density increased markedly the lifetime of the catalysts. In another work, Bogdan and Kazanskii [69] studied the alkylation of isobutene and the oligomerization of butanes under supercritical and ordinary gas–liquid conditions. The main effects of going from gas–liquid to supercritical conditions were a dramatic increase in the rate of reaction and the in situ regeneration of the deactivated catalyst.

The synthesis of propylene carbonate directly from supercritical CO<sub>2</sub> and propylene oxide using basic heterogeneous catalysts (ion exchange resins) is a neat process which requires no additional solvent and offers a very simple separation of the reaction products [70]. Ballivet-Tkatchenko et al. [71] studied the direct synthesis of dimethyl carbonate from supercritical CO<sub>2</sub> and methanol. The supercritical reaction conditions were established by phase equilibrium calculations and the highest yield was obtained at 20 MPa, under single-phase homogeneous operation.

The use of supercritical ammonia as a reactant in amination processes gives better selectivity and reaction rates as reported by Martin et al. [31] and Fischer et al. [72].

## 8. Use of near-critical solvents to modify the solubility of solids

In general, reactions that involve solid reactants are very slow when carried out in the absence of solvents. Similarly, reactions that form solid products are difficult to perform when they come close to completion. In both cases, the addition of a near-critical inert gas can improve reaction rate and yield.



**Fig. 4.** Product phase envelopes (full lines) and reaction trajectories (dotted lines) for different global density in the transesterification reactor: (a) 0.8051 g/cm<sup>3</sup> and (b) 0.513 g/cm<sup>3</sup>. \*Critical point.

Glebov et al. [73] reported a sharp increase in the apparent rate constant of the reaction between maleic anhydride and isoprene under scCO<sub>2</sub>, due to the increase of maleic anhydride solubility in the supercritical solvent. This phenomenon was confirmed by visual observation of the phase behavior. Also supercritical CO<sub>2</sub> is used for the zeolite-catalyzed alkylation of naphthalene with methanol and 2-propanol as reported by Glaser and Weitkamp [74].

Jessop et al. [75] found that the catalyzed hydrogenation of solid vinyl naphthalene was greatly accelerated by the addition of gaseous CO<sub>2</sub> at 306 K and 52 bar. On the other hand, at 307 K and 60 bar CO<sub>2</sub> pressure, the hydrogenation of liquid oleic acid to solid stearic acid reaches 97% conversion after only 1 h [76]. Jessop et al. [76] attribute this rate and yield enhancement to the melting-point lowering effect of the near-critical gas. These results are qualitatively explained by the phase diagram of a binary mixture between a subcritical gas and an organic solid having a triple point temperature higher than the critical temperature of the gas.

On the other hand, the possibility of tuning the solvent power of supercritical fluids by changing their density makes it possible to precipitate products out of the reaction media. Supercritical poly-

merizations, for example, can be run until the polymer chain is sufficiently large to become insoluble and drop out of the reaction solution [77].

## 9. Conclusions and challenges

Experimental and modeling studies reported in recent literature on the phase behavior of reacting systems at near-critical conditions have been reviewed, and the effect of phase conditions on the performance of heterogeneous-catalyzed and non-catalytic supercritical reactions was discussed. Compared to previous decades, the amount of papers published in the literature on this matter has increased substantially in the last period. This gives an indication of the central role that phase-equilibrium engineering plays in understanding and controlling the output of supercritical reaction processes.

Opportunities arise in the use of supercritical fluids in combined reaction and separation processes, due to the possibility of tuning solubility with density. The concept of miscibility switch [78] highlights the capacity of supercritical fluids to induce miscibility/immiscibility in a reaction mixture, through a change in temperature and/or pressure. In this respect, the combined use of ionic liquids (ILs) and supercritical fluids (in particular carbon dioxide) appears promising [79]. Supercritical CO<sub>2</sub> is soluble in ILs, while ILs have a negligible solubility in scCO<sub>2</sub>. Hence, the products of a chemical reaction can in principle be recovered from the supercritical phase, free of ILs. Again, experimental data and modeling tools are required to be able to represent the phase scenario of these mixtures in order to select adequate operating conditions to induce miscibility or phase split, as required by the process. Knowledge about the effect of supercritical solvents on liquid–liquid equilibria is required. Substrate-diluted systems should receive special attention, since most reactions are carried out under these highly non-ideal conditions. Moreover, the working region in simultaneous reaction and separation processes can be located around the system's plait point, an area that presents special experimental and modeling difficulties. The thermodynamic models should be able to correctly predict distribution coefficients and binodal curves in this region.

Besides phase equilibria, volumetric properties play an important role in the design of continuous supercritical reactors, since the density of the reacting mixture determines the residence time in the reactor. This type of information is seldom available in the literature. Experimental data and upgraded thermodynamic models for the prediction of densities under reaction conditions are badly needed.

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