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# Supercritical reactors for the production of advanced bio-fuels: A review

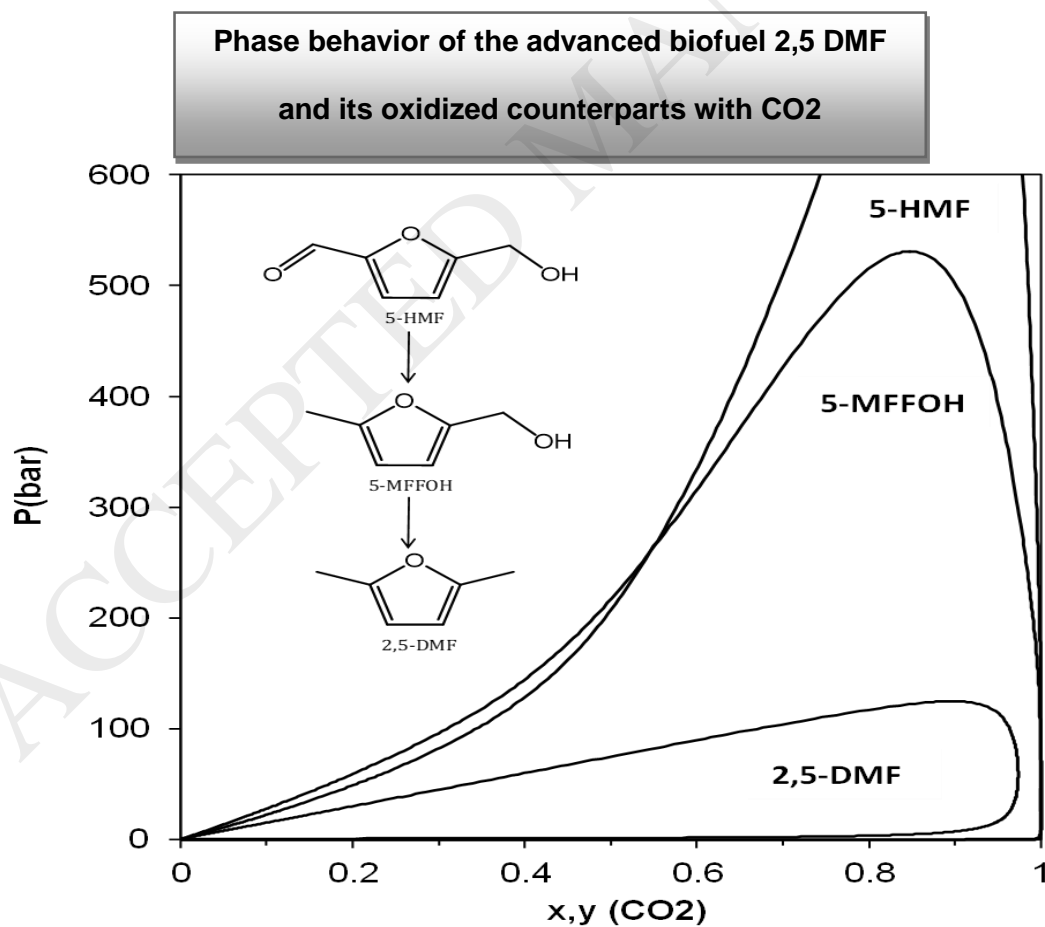
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## Graphical Abstract



## Highlights

- Advanced biofuels allow highly efficient and clean propulsion systems
- Several gas-liquid catalyzed reactions are involved in biofuel production
- Supercritical reactors offer opportunities to enhance yield by removing diffusional limitations
- Phase equilibrium and modeling tools available/needed are discussed

## Abstract

Advanced biofuels, when used as components in fuels, offer advantages over fossil-based hydrocarbons and conventional biofuels to realize highly efficient and clean propulsion systems.

Among the several chemical routes to produce biofuels, special attention is given to gas-liquid heterogeneous catalyzed reactions to reduce carbohydrate derived platform building blocks.

Supercritical reactors offer opportunities to enhance yield of these type of reactions. In this review, we present studies that take advantage of supercritical technologies to reduce platform biobased molecules. In addition, we discuss related high-pressure phase equilibrium experimental data and modeling tools available, as well as the gaps and needs, for engineering supercritical reactors to produce advanced biofuels. Due to the possibility of tuning solubility with density, opportunities arise in the use of supercritical fluids in combined reaction and separation processes. In this regard, the design of less energy intensive processes is needed to boost the production of advanced biofuels.

**Keywords:** supercritical reactors, advanced biofuels, hydrogenation, biobased platforms

## 1. Introduction

Sustainability issues have driven the industry to renewable sources for energy and chemical production. As biomass is the only source of renewable carbon, its potential to replace fossil-oil derived chemicals, solvents, or even fuels, is permanently assessed. In particular, non-edible lignocellulosic biomass is the most abundant renewable source in the nature[1]. However, nowadays, only first generation biorefineries, based on edible crops, are well established commercial enterprise. These industries have the advantage of dealing with uniform raw materials (either vegetable oils or sugars from cane, corn or wheat) and require relatively simple processes to produce ethanol or biodiesel. In addition to the unappealing fact of using edible materials for biofuel production, their usage was shown to increase CO<sub>2</sub> emissions up to 20% compared to oil-based fuel when effects of indirect land use are considered[2]. In contrast, biofuels made from waste biomass (lignocellulosic biomass or side streams of agroindustrial processes) incur little or no carbon debt and can contribute to mitigate GHG emissions[3]. Nevertheless, unlike first generation, biorefineries based on residual biomass are unfeasible if devoted to a single feedstock/product, due to the many operational steps and high costs of complicated conversion and separation steps. Therefore, the design trend has been directed towards processing plants of multiple biomass feedstocks and multiple products[4]. In general, three main processing steps are found in a second generation biorefinery: pretreatment, conversion and upgrading/separation technologies. The multi-feedstock alternatives by excellence are thermochemical conversions, which offer low-cost products through mature technologies like biomass pyrolysis or gasification. On the other hand, hydrothermal (HT) reforming appears today as a sustainable alternative to the traditional pyrolysis, thermochemical conversion, digestion, etc[5]. Independently of the conversion technology, in all cases biomass depolymerization through different routes is conducted, leading to the formation of bio-oils that require further upgrading. Bio-oils are a complex mixture of organo-oxygenated compounds, with high content of oxygen, that need to be reduced in order to produce drop-in biofuels.

Supercritical fluid science and technology was already widely applied for conversion of biomass to useful fuels and chemicals. For example, supercritical or subcritical water [6] treatment can decompose lignocellulosic materials to lignin-derived products (aromatic chemicals) and carbohydrate-derived products. If the treatment is prolonged, lignocellulose can also be converted to organic acids [7]. On the other hand, catalyst-free vegetable oil transesterification has been extensively studied with supercritical methanol or ethanol to produce biodiesel [8–11]. Dahmen et al. [12] discuss high pressure in synthetic biofuels, using gasification technology to convert biomass. In this work, we review the use of supercritical reactors in the synthesis of new advanced biofuel candidates derived from carbohydrates. Special attention is given to gas-liquid heterogeneous catalyzed reactions carried out to reduce biobased platform building blocks. We first summarize the studies that take advantage of supercritical technologies to reduce platform biobased molecules. In addition, we discuss the high-pressure phase equilibrium experimental data and modeling tools available, as well as gaps, for engineering supercritical reactors to produce advanced biofuels.

## **2. Current State**

Gas-liquid catalyzed reactions are diffusion controlled, not only because of the low solubility of permanent gases in liquids, but also because of the poor transport properties of liquid phases. The use of supercritical fluids as reaction medium allows reducing this controlling step by eliminating the gas-liquid interface, if homogenous operation is achieved, and increasing the diffusivity of reactants to the favorable values of near critical or supercritical fluids. Reaction rates are greatly increased and better selectivities can be achieved due to the possibility of uncoupling process variables. For instance, while gas-liquid hydrogenation reactions require high temperatures to increase hydrogen solubility, the temperature of the supercritical process can be modified with no effects in compositions. This allows the selection of an operating tempera-

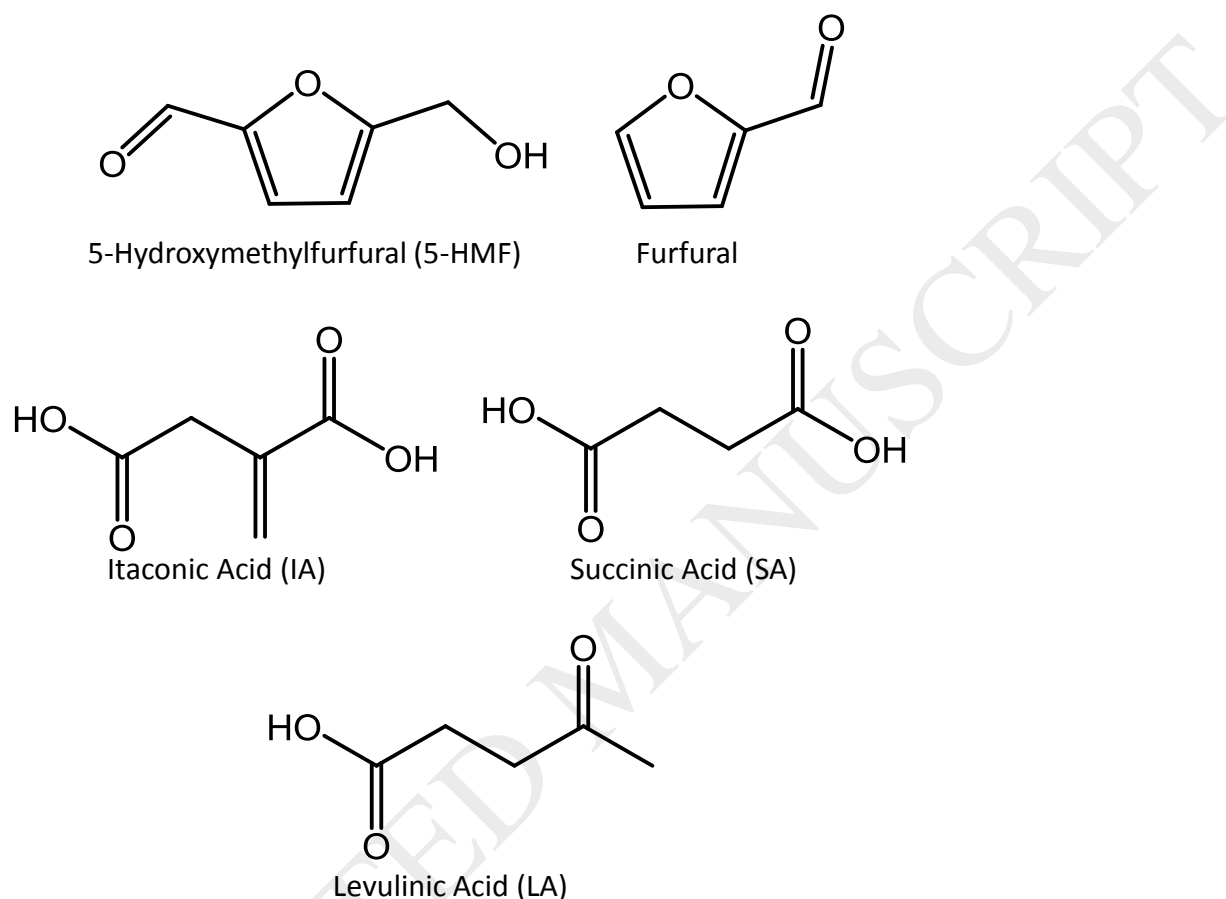
ture that improves selectivity without reducing conversion. Moreover, isomerization reactions favored by the lack of hydrogen at the catalyst surface can also be avoided[13,14]. In biomass processing, several organo-oxygenated substrates are difficult to dissolve in scCO<sub>2</sub>, so an alternative operation mode propose the use of gas-expanded liquids (GXL), i.e. using polar liquid solvents expanded with scCO<sub>2</sub>[15]. In GXLs technology, the reactive system stays heterogeneous but with more favorable transport properties, relative to the use of conventional liquid solvents[16].

### 2.1. *From platform bio-based molecules to advanced biofuels*

Advanced biofuels, when used as components in fuels, offer advantages over fossil-based hydrocarbons to realize highly efficient and clean propulsion systems that require less complex engine control and exhaust gas aftertreatment[17]. The comprehensive review by Leitner et al.[17] assesses the whole process chain of a biofuel production and consumption, considering aspects related, not only to propulsion and emissions, but also to their synthesis route. The authors proposed an interesting fuel design process, considering propulsion and production aspects simultaneously to find out the best chemical structure candidates.

All the major components of biomass should be used in a lignocellulosic biorefinery. This is, the carbohydrates composing cellulose and hemicellulose (pentoses and hexoses) and the lignin fraction. Synthesis of bio-based chemical building blocks have been intensively investigated and their wide range of applications are reviewed elsewhere[18,19]. Among them, furfurals and carboxylic acids have gain special attention as carbohydrate derivatives. In addition, the furfurals can be produced exclusively by thermochemical conversion routes[20]; in contrast to dicarboxylic acids and other chemical building blocks, which can also be products of biochemical conversions. Dehydration and decarboxylation are the predominant transformation in

the acid-catalyzed or fermentative processes of cellulosic or hemicellulosic carbohydrates. Consequently, platform chemicals are C5 or C6 compounds (as derivatives of pentoses and hexoses) containing carbonyl, hydroxy and olefin functionalities. Figure 1 shows the platform chemicals that are reviewed in this manuscript as raw material for advanced biofuel production.



**Figure 1:** Platform chemicals that are reviewed in this manuscript as raw material for advanced biofuel production.

Furfural and 5-HMF are produced by dehydration of pentose (xylose) and hexoses (fructose) in the presence of an acid catalyst, respectively. Levulinic acid is not formed directly from sugars, but rather through the rehydration of 5-HMF[20]. In the case of succinic and itaconic acids, the more promising renewable routes are biological fermentation of carbohydrates, using mainly glucose[17].

The starting materials shown in Figure 1 need further processing towards less oxidized products, in order to be used as biofuels. Moreover, compression ignition engines also need higher molecular weight compounds. Tables 1 and 2 summarize the transformations that furfural and carboxylic acids, respectively, should undergo in order to produce molecules suitable for biofuel candidates, besides other high-added value chemical products. The tables also report the normal boiling point and pure component density at 25°C of reactants and products, as well as the source of chemical reduction routes (studies in supercritical reactors are highlighted in bold). As can be seen, in general, gas-liquid catalyzed reactions are involved in the chemical routes, predominantly hydrogenation reactions. It is worth noting that platform molecules are low volatile substrate (except for furfural) due to the typical molecular association of alcohols and carboxylic acids (see normal boiling points in Tables 1 and 2).



**Table 1:** Advanced biofuel candidates derived from furfural derivative platform chemicals and their chemical reduction routes. Bold references indicate studies in supercritical reactors

Platform Chem./ Biofuel Candidates	NBP <sup>a</sup> /°C	$\rho^b$ / gcm <sup>-3</sup>	Source	Chemical routes
5-hydroxymethylfurfural (5-HMF), NBP = 266°C[21], 1.243 gcm <sup>-3</sup> at 25°C[22]				
2,5-dimethylfuran (2,5-DMF)	92	0.89	[23][24] [25] <b>[26] [27]</b>	
2-furfuryl alcohol (2-FFOH)	170	1.128	[28]	
2-butoxymethylfuran (2-BMF) <sup>c</sup>	190	0.958	[17]	
1-nonanol (1-NoOH)	214	0.83	[29]	
C8/C9 alkanes	126/ 151	0.703/ 0.718	<b>[30]</b>	
5-ethoxymethylfurfural (5-EMF)	235	1.099	[31][32] [33]	
furfural, NBP =161.5 °C, $\rho$ =1.160 gcm <sup>-3</sup> [34]				
2-methylfuran (2-MF)	63	0.91	[35] [26][36]	
furfuryl alcohol (2-FFOH)	170	1.128	[37][38] <b>[36] [39]</b>	
furan (F)	31.3	0.936	[40] <b>[36]</b>	
2-butyltetrahydrofuran (2-BTHF) <sup>c</sup>	160	0.86	[41][42] [29]	
tetrahydrofuran (THF) <sup>c</sup>	66	0.8892	[43][44]	
2-butylfuran (2-BF)	154	0.89	[45] [17]	
1-octanol (OcOH)	195	0.82	[46]	

<sup>a</sup> normal boiling point, <sup>b</sup> density at 25°C, <sup>c</sup> biofuel candidates not shown in the chemical routes (products of further hydrogenation of the furan ring towards a tetrahydrofuran ring). (\*) Value added products not suitable as biofuels: 2,5-DFF=2,5-diformylfuran, 2,5-FDCA=2,5-furandicarboxylic acid, FA=furoic acid, 2,5-BHFM=2,5-bis(hydroxymethyl)-furan[19].

**Table 2:** Advanced biofuel candidates derived from carboxylic acid platform chemicals and their reductive chemical route. Bold references indicate studies in supercritical reactors

Platform Chem./ Biofuel Candidates	NBP <sup>a</sup> /°C	$\rho^b$ /gcm <sup>-3</sup>	Source	Synthesis reactions
succinic acid (SA), NBP = 235.05 °C[47], $\rho$ = 1.050 gcm <sup>-3</sup> , at 190°C [48]				
tetrahydrofuran (THF)	66	0.8892	[49][50]	
levulinic acid (LA), NBP = 245.05 °C, $\rho$ = 1.134 gcm <sup>-3</sup> [51]				
2-methyltetrahydrofuran (2-MTHF)	80.21	0.854	[52]	
valeric esters (VE)	126	0.8947	[53]	
levulinic esters (LE)	206/ 237.5	0.9735/ 1.0111	[54][55]	
$\gamma$ -valerolactone (GVL)	219	1.0794	[52][56]	
itaconic acid (IA), NBP = 327.85 °C, $\rho$ = 1.275 gcm <sup>-3</sup> at 166 °C [34]				
3-methyltetrahydrofuran (3-MTHF)	89	0.87	[52]	

<sup>a</sup> normal boiling point, <sup>b</sup> density at 25°C. (\*) Value added products not suitable as biofuels: GBL =  $\gamma$ -butyrolactone, 2-PY=2-pyrrolidone, 1,4-BDO = 1,4-butanediol, 1,4-PDO = 1,4-pentanediol, 2-MBDO = 2 methyl-1,4-butanediol, 3-MGBL=3-methyl- $\gamma$ -butyrolactone.

## 2.2. Supercritical reactors in advanced biofuels synthesis

As already mentioned, supercritical reactors can operate under homogeneous or heterogeneous regime. Also, as reviewed by Pereda et al.[57], the SCF may act only as a solvent or can be involved in the reaction, like in methanolysis/ethanolysis, amination or acylation reactions.

On the other hand,  $\text{scCO}_2$  is a highly effective medium for continuous catalytic reactions. It has been very successful in terms of process intensification and scale-up. However, the relatively poor solvent power of  $\text{scCO}_2$  implies that it is often necessary to use a co-solvent, which may need to be separated from the product later on, increasing the energy costs. Nevertheless, its poor miscibility may create opportunities in homogenous reactions running in an organic/aqueous mixture with a water-soluble catalyst[58]. Supercritical reactions are more energy intensive than many conventional processes. If separation can be integrated into a supercritical reactor, the high-pressure process can consume considerably less energy. Tables 1 and 2 highlights in bold fonts the references of the only reactions that have been carried out under supercritical medium, up to our knowledge.

In a discussion of batch vs. continuous reactors for fine chemistry, the group of Poliakoff[36] published an interesting study of hydrogenation of furfural in  $\text{scCO}_2$  with “real-time” switching between different products. As the authors highlighted, this operation mode would allow chemical industries to respond more rapidly to changing market demand for products, enhancing profitability and reducing reactor downtime. As shown in Table 1, hydrogenation of furfural could potentially end up in a number of compounds: furfuryl alcohol (FFOH), 2-methylfuran, tetrahydrofurfuryl alcohol (THFA), methyltetrahydrofuran and furan. In order to produce multiple furan derivatives, the authors used two reactors in tandem with different heterogeneous catalytic bed and temperatures. In this case,  $\text{scCO}_2$  was an effective medium because furfural shows high solubility in this solvent, allowing  $\text{H}_2$  and furfural to be in an homogeneous phase[59]. The authors compared the performance of several catalysts, operating temperatures, reactants loading and residence time in each reactor. The optimum results were achieved when copper chromite catalyst was used in combination with 5 wt.% Pd on activated carbon. All five compounds were produced in high yield, over 80% for all products, but even over 95% for three of them (furan, FFOH and THFA), simply by changing the temperature of the reactors (between 120 and 300°C) and the amount of hydrogen dosed into the system. Later, Chatterjee et al.[26] carried out the full hydrogenation of furfural towards 2-methylhydrofuran using the same reac-

tion medium. They achieved full conversion in 2 hours and claimed that, under the same condition, 100% selectivity towards 2-methylfuran (21% conversion) was attained within a short reaction time of 10 min.

Bourne et al. [56] addressed the conversion of levulinic acid (LA) to  $\gamma$ -valerolactone (GVL) in  $scCO_2$  (see Table 2). They combined the use of water as a co-solvent with phase manipulation using  $scCO_2$  to integrate reaction and separation[58] into a single process with reduced energy requirements, when compared to conventional distillation. LA conversion to GVL involves a hydrogenation followed by intramolecular cyclization, with the loss of water. Bourne et al. [56] carried out the reaction in aqueous phase, expanded with  $scCO_2$ , at about 10 MPa with 5% Ru on  $SiO_2$ , high concentration of LA (LA :  $CO_2$  ca. 1 : 10) and an excess of  $H_2$  ( $H_2$  : LA = 3 : 1). At 200°C they achieved a 99% yield towards the desired product. Since GVL is miscible with  $H_2O$ , following the approach proposed by Lazzaroni et al.[58], the authors demixed the GVL by further pressurizing the system with  $scCO_2$ .

Chatterjee et al.[26] and Hansen et al.[27] proposed two different approaches to hydrogenate 5-HMF towards DMF using SCF. The first, likewise Bourne et al.[56], carried out the reaction using  $scCO_2$ +water as solvent because of the poor solubility of 5-HMF in  $scCO_2$ . By tuning the  $CO_2$  pressure, the authors achieved various intermediate compounds, such as tetrahydro-5-methyl-2-furanmethanol (MTHFM) (<10 MPa), 2,5-dimethylfuran (2,5-DMF) (10 MPa) and 2,5-dimethyltetrahydrofuran (2,5-DMTHF) (>10 MPa) with very high selectivity. In an extensive experimental work, the authors evaluated several catalysts, the effect of  $CO_2$  and  $H_2$  partial pressure, residence time, temperature and water content on the selectivity. Regarding phase behavior, they showed that the system is heterogenous in presence of water. However, the partition between phases and the molar concentration of gaseous compounds (inferred from their partial pressure) were not assessed, key information to comprehend outcomes of the reactive experiments[13]. On the other hand, Hansen et al. [27] used supercritical methanol ( $scMeOH$ ) as catalytic transfer hydrogenation (CTH) for the conversion of HMF to DMF or even more extensive

reduction to 2,5-DMTHF. Over a Cu-doped porous metal oxide catalyst and in scMeOH, the hydrogen equivalents needed for the reductive deoxygenation of 5-HMF was originated from the solvent itself, upon its reforming. In less than one hour, full conversion of 5-HMF was achieved and the maximum yield of 2,5-DMF is 40%, in reactions carried out between 240°C and 320°C. Furthermore, the authors did not detect the formation of higher boiling side products and undesired char from 5-HMF under the milder reaction conditions. Finally, Chatterjee et al.[30] accomplished the formation of linear alkane in supercritical carbon dioxide through a two-step reaction (1-hydrogenation and 2-dehydration/hydrogenation) of 4-5-(5-(hydroxymethyl) furan-2-butyl-3-en-2-one, which is an aldol condensation product of 5-HMF and acetone, instead of directly starting from 5-HMF. Using a similar structure model compound (only differs in a hydroxymethyl moiety of the furan ring), the authors were able to control the process selectivity, by means of CO<sub>2</sub> partial pressure, towards the half-hydrogenated product of the first step or full hydrogenation to alkanes, under mild conditions (80°C). Several catalysts were tested, showing Pd/Al-MCM-41 the best outcomes. At 14 MPa they achieved 99% selectivity towards alkanes with full conversion after 20hs. In a final run, they achieved a similar yield using the aldol condensation compound derived from 5-HMF (99% selectivity to alkanes). The authors discussed the system phase behavior based on previous studies performed with the model compound. In that case the increase of the CO<sub>2</sub> pressure resulted in the transition from the two-phase medium (>10 MPa) to a single-phase medium, visually observed in an equilibrium cell. It is worth noting that the hydroxymethyl moiety, that differentiates the aldol condensation derivative of 5-HMF from the commercial model compound, should greatly impact on the phase behavior, since alcohols are difficult to dissolve in scCO<sub>2</sub>[60]. The alternative route is interesting to reduce the high immiscibility of the original platform molecule (5-HMF); however, more phase equilibrium studies are needed to set the optimum operating window [13,61].

### 3. Challenges and Knowledge Gaps / Needs

From previous section, it is clear that most of the gas-liquid heterogeneous catalyzed reactions of Tables 1 and 2 have not been studied in supercritical reactors. This gap leaves an important room for new challenges in biomass valorization in intensified reactors. Moreover, the poor solvent power of  $scCO_2$  calls for assessing alternative supercritical solvents to enhance reaction yields. However, among the several existing options, attention is drawn to the fact that many SCF are not suitable for conversion processes due to their reactivity in reductive atmospheres, which is, unfortunately, the case of dimethyl ether (DME) that has recently been classified as a green solvent[62] and the FDA published a report concluding DME is a Generally Recognized as Safe (GRAS) solvent[63]. Light hydrocarbons, like propane or butane, show better solvent power than  $CO_2$  for relatively larger organic molecules. However, like DME, these alternative SCFs are flammable, Mixed SCFs, combining the alternative SCF with  $scCO_2$ , help to reduce the flammability hazard of the solvent [64].

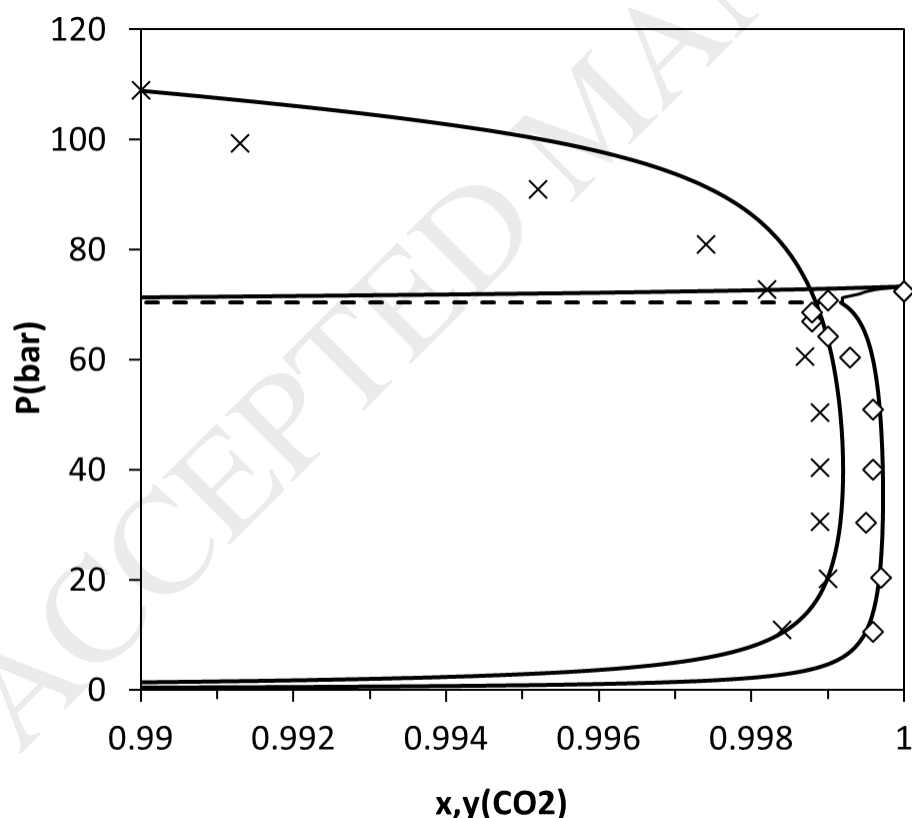
Due to the high oxygen content of the platform molecules, GXLs reactors have potential to carry out the redox routes efficiently in shorter reaction times, smaller reactors and milder pressures than in homogenous supercritical reactors, if  $sCO_2$  is used as solvent. However, controlling the outcome of the reactive process is more difficult in GXLs, since operating variables are not independent. This stresses even more the importance of controlling the phase scenario that fulfills the process needs, taking into account compounds distribution between phases. It is worth noting that phase equilibrium engineering provides a number of principles that guides the design process of adequate phase scenarios [14,61]. A poor phase design might cause improvements in the reaction yields, since the transport properties of the reactive system are enhanced in the presence of SCF. However, the possibility to greatly intensify the process and controlling yields require a good knowledge of the phase behavior as the reaction proceeds[13,65]. In the search for  $scCO_2$  partial pressures that guarantee homogenous condition or to confirm the heterogeneous state, most of the works discussed in the previous section included phase behav-

ior visualization of the reactive mixture with addition of CO<sub>2</sub>. However, little is known regarding the evolution of the distribution of compounds between phases, with the change of composition in the reactive mixture, which is also important to control the reaction kinetics.

In that regard, a literature review on high-pressure phase behavior of platform molecules, as well as their derivatives, shows little or no data available, even in scCO<sub>2</sub>, the most widely used solvent. Up to our knowledge, solubility studies in scCO<sub>2</sub> are published only for furfural[66,67], 5-HMF[68] and levulinic acid (LA) [69]. Except for that of the LA, the investigations were all focused in recovering the biomass derivatives from their synthesis broth. The furfural study also included water, and its aim was to use scCO<sub>2</sub> as extracting agent. The authors, not only measured solubility of furfural in scCO<sub>2</sub> up to ca. 20 MPa[66], but also evaluate VLE and LLE, in aqueous media for designing a miscibility switch process to separate furfural by liquid split instead of extracting it. The equilibrium data was modeled with Peng-Robinson EOS combined with an asymmetric mixing rule. Gamse et al.[59], also interested in the recovery of furfural, measured the solubility in scCO<sub>2</sub> up to 30 MPa and assessed the effect of acetic acid (also present in the aqueous production of furfural) on the furfural extraction yields. In the case of 5-HMF[68], since its solubility in scCO<sub>2</sub> is extremely low, ethanol was tested as cosolvent. Solubility measurements were carried out using a synthetic method up to 20 MPa and with 0, 2.5 and 5% (molar basis) of ethanol. For similar reasons, the ethanol enhancement of the LA solubility in scCO<sub>2</sub> was also tested (up to 20MPa and 5% ethanol) [69]. Lastly, several authors measured [70–72] high-pressure vapor liquid equilibria of the cyclic ether THF with scCO<sub>2</sub>. In contrast with 5-HMF, THF is more soluble, so the system becomes completely miscible at relatively low pressure.

Thermodynamic models are also highly needed, not only for experimental design and data analysis, but also for optimizing operating windows. Related to the systems under review in this contribution, Gonzalez Prieto[21,73] extended the group contribution with association equation of state (GCA-EoS) to the five-membered aromatic heterocyclic family, including high

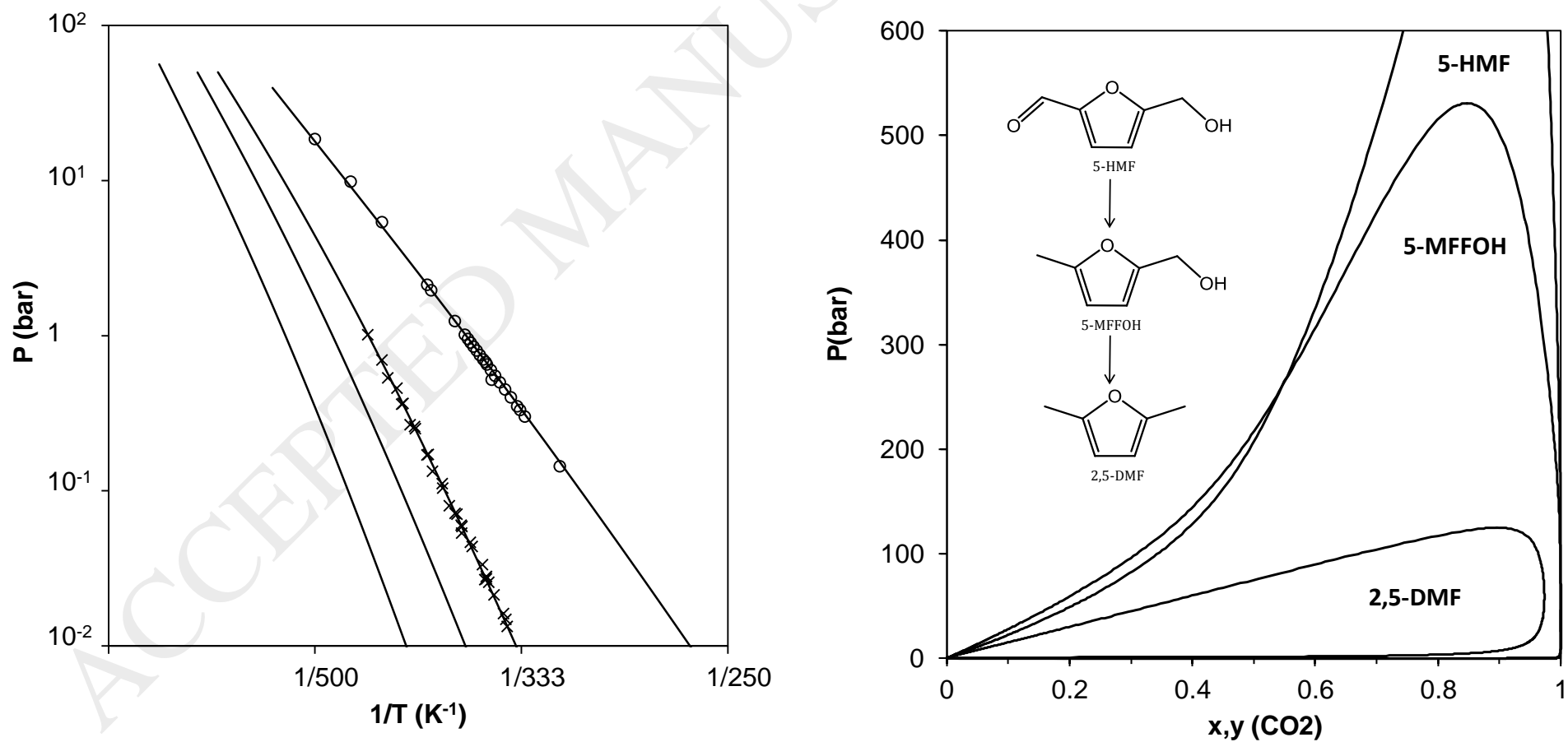
pressure data. The group contribution approach is very attractive for biomass derivatives because many compounds show similar chemical structure. The model can be trained with data of simple molecules that comprises the needed functional groups and more complex data, for which little or no data is available, can be predicted. Moreover, the high content of organo-oxygenated compounds makes that molecular association is always present. In that sense, GCA-EoS takes into account specific interactions, like hydrogen bonding, through a group contribution version of the SAFT association term[74]. Gonzalez Prieto[21] showed that the GCA-EoS is able to accurately predict the solubility data of 5HMF in scCO<sub>2</sub> [68] and its enhancement upon addition of ethanol. On the other hand, Figure 2 depicts GCA-EoS prediction of the solubility of furfural in scCO<sub>2</sub> at ambient temperature and up to ca. 10 MPa. The model correctly follows the phase behavior transformation with temperature, based on the GCA-EoS parameterization done in previous works[21,73].



**Figure 2:** High pressure phase equilibrium behavior of the binary CO<sub>2</sub>+furfural. Symbols: Experimental data at (◇)303K and (x)323K[67]. Lines: GCA-EoS predictions (solid lines: vapor liquid equilibria, dashed line: liquid-liquid-vapor equilibria)



As it was mentioned before, it is also important to have knowledge of phase behavior as the reaction proceeds. Based on the general behavior of organic families, it is known in advanced that a molecule being partially hydrogenated or reduced will become more soluble in  $\text{scCO}_2$  than its oxidized counterpart, if its molecular weight keeps more or less constant. Figure 3 illustrates this concept with GCA-EoS predictions of the binary systems of  $\text{CO}_2$  with 5-HMF, the partially hydrogenated 5-methylfurfuryl alcohol (5-MFFOH) and the full hydrogenated 2,5-DMF. Figure 3a shows GCA-EoS prediction of the vapor pressure of the three components together with experimental data, when available. Furfuryl alcohol (FFOH) is included to show that the model predicts well, by group contribution, the vapor pressure of a similar compound to the partially hydrogenated 5-MFFOH, since for the latter there is no data available. Even though the equilibrium data with  $\text{CO}_2$  is limited, it allows the parameterization of a model like GCA-EoS. Back to the reactive mixture, the behavior shown in Figure 3b means that, in general, the system will become more soluble in  $\text{scCO}_2$  as the reaction proceeds. Regarding hydrogenation reactions, also there is an important gap on phase equilibrium data of the ternary mixtures including hydrogen. Trinh et al.[75] review data of hydrogen solubility in 42 organo-oxygenated compounds, including alcohols, aldehydes, carboxylic acid, esters, ethers, alkanes, glycols, and water, and Pereda et al.[76–78] modeled with GCA-EoS all this families but ethers and glycols. Since THF is a widely used solvent, data of  $\text{H}_2$  solubility in THF is available elsewhere[79]. Also, there is data for furfural [80] and 2-MTHF [81] in the open literature.



**Figure 3:** Phase behavior of 5-hydroxymethyl furfural (5-HMF) and its reduced derivatives (5-methylfurfuryl alcohol and 2,5 dimethyl furan, 5-MFFOH and 2,5-DMF, respectively): a) GCA-EoS prediction of pure compound vapor pressure. Experimental data only available for ( $\times$ ) furfuryl alcohol (FFOH) and ( $\circ$ ) 2,5 DMF [82–85]. b) GCA-EoS prediction of binary high-pressure vapor liquid equilibrium of  $CO_2$  with 5-HMF, 5-MFFOH and 2,5 DMF at 353 K

Chemical equilibrium has received much less attention in this field, which clearly make sense in the case of hydrogenation reactions, since they are typically irreversible. However, also esterification and hydrolysis are also important transformations and often limited by the chemical equilibrium. Up to our knowledge, there are no recent studies in the open literature that specifically assessed chemical equilibrium, neither experimentally or theoretically, in this field. Regarding the solution of simultaneous phase and chemical equilibria, special emphasis has been given to the development of algorithms that solve the complex non-linear problem in the past [86]. Quite frequently, though, traditional cubic equations of state with classical mixing rules have been applied to highly non-ideal mixtures; this somehow invalidates the accurate numerical solutions obtained.

There is a plethora of publications discussing reaction mechanisms in the field of biobased platform molecules valorization. However, when comes down to supercritical reactors, little is said about kinetic models of the tandem reactions. In direct relation to this, it is worth noting the need of new PVT data of multicomponent reactive mixtures at the process conditions. It is well known the high sensitivity of the volumetric properties of near or supercritical fluids with temperature, pressure and composition. This physicochemical property directly impacts on reactants residence time, in continuous reactors, or on concentration, in batch reactors, affecting the quality of any derived kinetic model[8]. Due to the limited availability of PVT data of reactive systems, it is often assumed ideal solution behavior to estimate the density of the mixture. The synthetic isochoric method[87,88] provides a simple way to acquire high pressure/high temperature PVT data of reactive mixtures. Using this method, Hegel et al. [89] recently reported data for the typical mixtures found in the hydrogenation of vegetable oil with supercritical propane as solvent[89]. They also showed that applying a cubic equation of state to predict the mixture density, combined with the van der Waals mixing rule, is simple and substantially better than assuming ideal solution behavior. In particular, the authors selected the RK-PR equation of state[90,91] to predict (without binary interaction parameters) the PVT data of H<sub>2</sub>+propane+vegetable oil mixture[89].

#### 4. Future Perspectives

Biomass valorization is a relevant area of research which will continue attracting interest of the industrial sector as more and more consumers are increasingly concerned about the impact of derivatives of non-renewable fossil resources. Moreover, significant economic benefits are expected if low-cost residual biomass is processed, upon further technological development. The remarkable potential of biomass as an alternative source of chemicals, fuels and related commodities requires new knowledge for efficiently processing complex and diverse biomass feedstocks (e.g. lignocellulose, waste 'raw' materials). In view of these premises, platform molecules serve as an interesting starting point, giving rise to multiple biobased products venture, namely, biorefineries.

Several potential scenarios for biofuels can be foreseen in the future. In particular, nowadays, less pressure is seen on the willingness of replacing fossil fuels, since other renewable energies are growing rapidly. However, biomass is a source of interesting molecules to enhance the performance of today and future engines, advanced biofuels are under development and new candidates are appearing in the literature constantly.

Already two decades ago became evident the great potential of supercritical fluids to intensify gas-liquid heterogeneous catalyzed reactors. Most of the biofuel candidates are the product of single or multiple hydrogenation reactions in order to reduce the starting platform molecules. Today's knowledge allows designing reactive/separation systems which permits precipitating products instead of the energy intensive downstream conventional distillation recovery. Opportunities arise in the use of supercritical fluids in combined reaction and separation processes, due to the possibility of tuning solubility with density (miscibility switch). In this regard, the design of less energy intensive processes is needed to boost the production of advanced biofuels.

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