

Carbon Dioxide and Hydrogen Solubility in Furfural, a Potential Bio-Based Chemical, at various Temperature and Pressure Conditions

Ljudmila Fele Žilnik*, Blaž Likozar

Department of Catalysis and Chemical Reaction Engineering, National Institute of Chemistry, Hajdrihova 19, 1001 Ljubljana, Slovenia
 ljudmila.fele@ki.si

In this work, carbon dioxide and hydrogen solubility in furfural, a potential bio-based chemical, is investigated at temperatures 313–323.8 K and pressures up to 12 MPa. The measured data are compared to the literature data. Good agreement between the measured data in this work and the data available in the literature was achieved for carbon dioxide solubility in furfural, but disagreement was found between one datum available in the literature and our measured hydrogen solubility data.

1. Introduction

Nowadays much of research is focused on the valorisation and production of the second generation of the biofuels and chemicals from bio-oils, originating from biomass resources. To avoid the competition with food, the processing routes for the non-feed biomass residue conversion to fuels and chemicals are being proposed. Biomass consists of three key building blocks: cellulose, hemicellulose and lignin, which are thermally and chemically unstable. Bio-oils, produced by thermochemical methods, are a complex mixture of the compounds with very high oxygen content, which is the main cause for their low LHV (lower heating value), high viscosity or chemical instability. Therefore, hydrogenation and/or hydro-deoxygenation are applied either to improve their properties for their further use in the co-processing in traditional refineries or as a valuable source for the production of the bio-based chemicals by catalytic hydrogenation reactions. The latter usually take place in a slurry reactor with the three phases present, namely liquid (reactants, solvent and products), solid (catalyst) and gas (hydrogen). The solubility of hydrogen in solvent and in oxygenated components that act as a precursor towards the desired bio-chemicals is of great importance, since it affects selectivity, reaction rates and catalyst activity. Reactions are therefore limited by a poor solubility of gas (hydrogen).

Cellulose and the hexoses from hemicellulose can be transformed to various bio-based chemicals, such as 5-hydroxymethylfurfural (HMF) and levulinic acid (LA), by acidic hydrolysis or dissolution, and further de-formylation to levulinic acid (LA) (Grilc et al., 2017). Both have received meaningful attention as the platform chemicals for the further synthesis of a wide range of chemicals and bio-based fuels. The C₅ sugars from hemicellulose can also be converted either by the acidic hydrolysis or dissolution to furfural, which is also recognized as a platform chemical for the further production of bio-based fuels and bio-chemicals. Lignin, as the third biomass building block can also be seen as a source of a large amount of bio-based chemicals to replace those derived from oil.

The main goal of this work was to study the solubility of hydrogen and CO₂ in a few selected model compounds evolving along the principal transformation paths of the main biomass building blocks through the intermediates towards value-added bio-based chemicals. At present, very limited data, or even none, is available in the literature. Very recently, the hydrogen solubility in furfural at three temperatures and pressures up to 12.47 MPa was considered (Jaatinen et al., 2017), as well as the hydrogen solubility in eugenol at two temperatures and pressures up to 15.59 MPa (Qureshi et al., 2016). A review on the available solubility data of hydrogen in oxygenated molecules and water was also presented (Trinh et al., 2016).

Neat furfural and eugenol compounds were planned to be examined as the potential bio-based chemicals of interest, while some others were planned to be examined with diluting solvent addition (different mixing ratios), at various thermodynamics conditions. Unfortunately, up till now only part of the planned task was accomplished, which means that only CO₂ solubility and few measurements of H₂ solubility in furfural was realized. The work is still in progress.

2. Experimental section

2.1 Experimental setup and methods used

The apparatus consisted of a high pressure view cell that enables precise phase equilibrium measurements, described in details elsewhere (Fele Zilnik et al., 2016), and was used in this work. The cell is constructed of a high quality alloy cast steel Hastelloy C4, of a cylindrical form with an inner diameter of 50 mm, closed on one side with a sapphire window enabling a high visibility into the cell and a membrane bellows on the other side. The temperature in the cell was controlled by a thermostat Julabo Presto LH46 by pumping the heating/cooling media through the double jacket of the cell. The temperature in the cell was measured by a platinum resistance thermometer Pt-100, calibrated by the accredited metrology laboratory LMK according to the international temperature standard ITS-90, with extended uncertainty of the measured value of ± 0.1 K (0.95 level of confidence). A calibrated pressure transducer Omegadyne PX1004 was used for the pressure measurements in the cell in the range between 0.1 and 17.2 MPa, with determined extended uncertainty of the measurement of 0.003 MPa (0.95 level of confidence). Mixing in the cell was established by a magnetic stir bar placed in the cell and a rotary electromagnetic field around the cell.

The cell was evacuated by a chemistry hybrid vacuum pump Vacuumbrand RC6, through the isolated cold trap with a double jacket and the vacuum was measured by a Pirani vacuum gauge VAP 5 with the measuring range $1000\text{-}10^{-3}$ mbar (uncertainty of the measurement ± 10 % of the indicated value).

The gas from the cylinder was introduced into the cell through the HP capillary tube (1/4") and the desired high pressure in the cell was achieved by a pneumatic compressor Maximator DLE 75. The degassed liquid component was fed into the cell using a screw pump (SITEC), through a manifold enabling the evacuation of the capillary line leading to the pump.

National Instruments CompactDAQ system was employed for data acquisition of temperature, pressure, bellows distance and flow of gas, while data logging and further treatment of the data, pictures was realized by LabVIEW 2010 software. For the observation of the cell a digital camera (National Instruments) was connected through FireWire with a data acquisition system.

For all experiments, liquid component of high purity was used. The purchased liquid component was first distilled on a Normag batch rectification column of diameter 25 mm under vacuum to achieve colourless liquid of desired purity. Distillation was carried out at 2.7 mbar, with bottom temperature from 41 °C to 43 °C and top temperature of 29.5 °C. The distillate was cooled down by using a cryostat keeping the temperature of the cooling media at around -25 °C. Around 80 % of the initial bottom amount was collected as a distillate. The distillate purity was checked by GC chromatography.

A FOCUS Thermo Scientific GC Instrument equipped with a flame ionization detector and AS 3000 was used for the analysis, while an identification of the components in the samples was carried out by gas chromatography coupled to a mass spectrometer (Agilent GC/MS-FID). Thermo-Scientific TR-5 capillary column of the length 30 m, 0.32 mm ID with 0.25 μm film thickness was used to achieve the separation. The column was 5 % phenyl methyl poly-siloxane, non-polar low bleed column with a slight increase in polarity according to phenyl groups. Oven initial temperature was 50 °C and it was held for 1 min, then a temperature was increased with a rate of 30 °C/min up to 240 °C and kept at this temperature for 5 min. The injector and detector temperatures were 300 °C and 300 °C, respectively. Helium was used as a carrier gas and its flowrate was 1 ml/min. Split mode with the ratio of 1:10 was applied. The samples were diluted in acetone.

The collected furfural from distillation was then degassed under vacuum at total reflux ratio for approx. 2 h at 1.56 mbar for further use on the equilibrium high-pressure view cell that can be seen on Figure 1.

A synthetic method was applied in all the experiments. Synthetic-visual and partly nonvisual (PV) methods were used in our experimental work. The synthetic method was carried out to measure the bubble point pressure from the homogeneous liquid phase. After extensive and thorough cleaning of the cell and evacuation, the gas (CO₂ or H₂) was introduced to the cell up to desired pressure and let the system to equilibrate and reach the desired temperature. The pressure in the cell should be above the estimated boiling-point pressure to start the experiment in the one-phase region. After equilibration, the degassed liquid component was fed into the cell using a screw pump (SITEC), through a manifold enabling the evacuation of the capillary line leading to the pump. The measurements were carried out at a variable volume of the cell, at pressures up to 12 MPa and temperatures up to 323.8 °C.

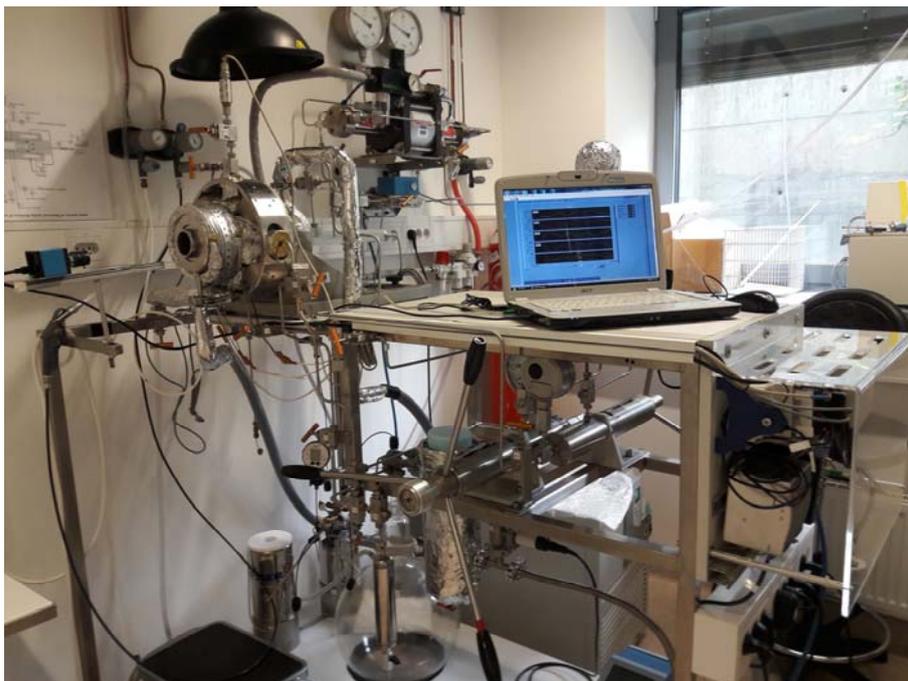


Figure 1: View on the apparatus consisted of a high-pressure view cell, surrounded by auxiliary equipment for transferring the components into the cell, evacuating and stripping of the cell, sampling and data acquisition systems

An amount of CO₂ in the cell was calculated using the equation of state (Span and Wagner, 1996), while for the H₂ NIST Chemistry Webbook, SRD 69 was used to calculate an amount of H₂ from the density data at certain (P,T) conditions and known volume of the cell. The density of furfural was calculated using the empirical models (Guerrero et al., 2011 and Lomba et al., 2011).

The nonvisual synthetic method is not based on the observation of the mixture in the cell, but rather on recording of equilibrium pressure attained at different volumes of the cell at constant temperature and composition. Normally, the equilibrium pressure is achieved by mixing the content in the cell in approx. 15 min at very small volume change of the cell, at constant temperature and composition.

The measurements were performed at following temperatures (CO₂ + furfural: 313.3 K ± 0.1 K and 323.3 K ± 0.1 K; H₂ + furfural: 323.8 K ± 0.1 K).

The purity of furfural before and after the experiments when using H₂ as gas was checked by gas chromatography and it was revealed that no thermal reactions (no other GC peak except furfural) of furfural during the measurements occurred.

2.2 Chemicals used

Specification of chemicals used during experimental work is given in Table 1.

Furfural purchased from Sigma-Aldrich was dark colored (coffee brown); therefore distillation under vacuum described above was necessary to prepare fresh furfural without color.

Table 1: Chemicals used

Chemical name	Source	Initial purity (wt. fraction)	Purification method	Final purity (wt. fraction)	Analysis method
CO ₂	Messer Griesheim	0.999995	-	-	-
N ₂	Messer Griesheim	0.99999	-	-	-
Furfural	Sigma-Aldrich	0.99	Distillation	0.999	GC
Acetone	Merck	0.999	-	-	-

3. Results and Discussion

Boiling points have been measured for the CO₂ + furfural and H₂ + furfural systems, applying the synthetic-visual method at two temperatures, namely at 313.3 K and 323.3 K for the first system and only few points were measured till now for H₂ + furfural system at 323.8 K. It was observed during the experiments that CO₂ dissolves much faster in furfural compared to H₂. At small volume change of the cell and at constant temperature and composition, an equilibrium pressure of CO₂ was reached in approx. 10-15 min. Much longer (up to 3 fold) time was required when H₂ was used as gas, because of a quite slow dissolution dynamics observed during the experiments.

The measured solubility data are listed in Tables 2 and 3 and shown in Figures 2 and 3 for both systems; however in Figures 2 and 3 the available literature data are also shown.

Table 2: Measured CO₂ solubility (X₁) data points in furfural at 323.3 K and 313.3 K and pressure P

T/K	P/MPa	X ₁
323.3	8.408	0.5863
323.2	7.991	0.5581
313.3	8.309	0.9642
313.3	8.063	0.8275
313.2	7.988	0.7902
313.3	7.822	0.7561
313.3	5.908	0.5212
313.4	5.798	0.5114
313.2	5.598	0.4903
313.2	5.267	0.4600
313.4	5.133	0.4460
313.4	4.921	0.4330

Table 3: Measured H₂ solubility (X₁) data points in furfural at 323.8 K and pressure P

T/K	P/MPa	X ₁
323.8	10.144	0.0541
323.8	10.895	0.0572
323.8	12.132	0.0611

Good agreement between measured carbon dioxide solubility in furfural with literature data (Sako et al., 1995) at temperature 323.3 K can be seen in Figure 2. There is no data available in the literature at 313.3 K; therefore the comparison was made with the data at lower temperature 303 K. Carbon dioxide solubility measurement data at 313.3 K is well in line with the data of Sako et al. (1995) at lower temperature of 303 K. However, we cannot say the same in the case of hydrogen solubility measurements. In Figure 3 experimental hydrogen solubility data in furfural at temperature of 323.8 K is presented. It can be noticed that hydrogen solubility in furfural is quite low at measured temperature and pressure conditions compared to the carbon dioxide solubility. But, our measured data show higher equilibrium solubility of hydrogen in furfural compared to one literature datum at approx. the same temperature and pressure. One reason for such disagreement could lie in the method used for the solubility measurements. As already pointed out, the dissolution dynamics of hydrogen in furfural was observed to be quite slow compared to CO₂. Not only the absorption of H₂ in furfural, but also desorption of H₂ out of furfural is very slow. It might be that the authors (Jaatinen et al., 2017) might not have achieved the equilibrium solubility conditions by the method used. At the moment we cannot see any other reason, since no major difference between the furfural before and after experiments by GC-MS was noticed.

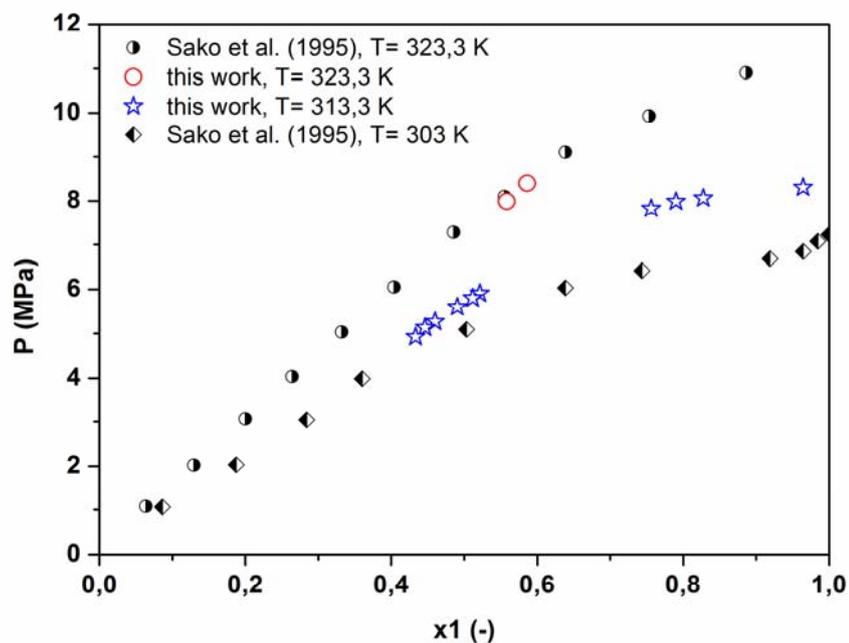


Figure 2: Carbon dioxide solubility in furfural at 313.3 K and 323.3

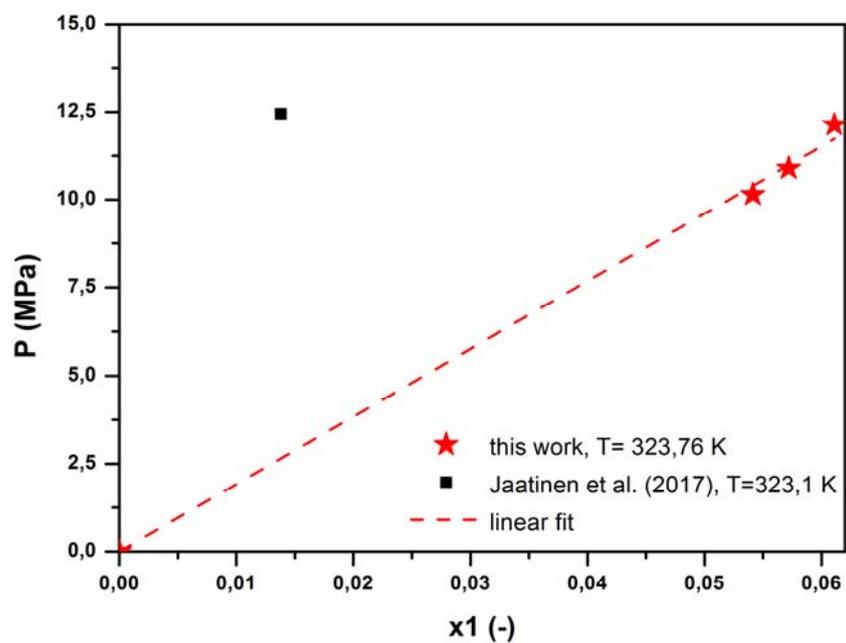


Figure 3: Hydrogen solubility in furfural at 323.8 K. The vapour pressure of furfural at $X_1=0$ is calculated by PSRK method

4. Conclusions

The study is a part of a broader investigation on hydrogen and carbon dioxide solubility in model potential bio-based chemicals, starting with the neat furfural. The measurements performed and presented here for carbon dioxide solubility in furfural were carried out at temperatures 313.3 K - 323.3 K and pressures up to 8.4 MPa, while hydrogen solubility in furfural was investigated at the moment only at 323.8 K and pressures up to 12 MPa. Good agreement between existing literature data on carbon dioxide solubility in furfural was observed and new data at 313.3 K were measured. Unfortunately, it turned out that measured hydrogen solubility in furfural is not in very good agreement with one existing literature datum. We have obtained approx. four times higher hydrogen solubility in furfural compared to the value given in the literature. Further work is planned for the near future to examine hydrogen solubility in furfural at some other temperatures and solubility of both gases in other potential bio-based chemicals of interest, some of them with diluting solvents at various thermodynamics conditions.

Acknowledgments

Financial support from ARRS, the Slovenian Research Agency, under P2-0152-0104 is gratefully acknowledged.

References

- Fele Zilnik, L., Grilc, M., Levec, J., Peper, S., Dohrn, R., 2016, Phase-equilibrium measurements with a novel multi- purpose high pressure view cell: CO₂ + n-decane and CO₂ + toluene, *Fluid Phase Equilibria*, 419, 31-38.
- Grilc, M., Likožar B., 2017, Levulinic acid hydrodeoxygenation, decarboxylation and oligomerization over NiMo/Al₂O₃ catalyst to bio-based value-added chemicals: Modelling of mass transfer, thermodynamics and micro-kinetics, *Chem. Eng. J.*, 330, 383–397.
- Guerrero, H., Lafuente, C., Royo, F., Lomba, L., Giner, B., 2011, PpT behavior of several chemicals from biomass, *Energy Fuels*, 7, 3009–3013.
- Jaatinen, S., Touronen, J., Karinen, R., Uusi-Kyyny, P., Alopaeus, V., 2017, Hydrogen solubility in furfural and 2-propanol: Experiments and modelling, *J. Chem. Thermodyn.*, 112, 1–6.
- Lemmon, E.W., McLinden, M.O. Friend, D.G. "Thermophysical Properties of Fluid Systems" in NIST Chemistry WebBook, NIST Standard Reference Database Number 69, Eds. P.J. Linstrom and W.G. Mallard, National Institute of Standards and Technology, Gaithersburg MD, 20899, doi:10.18434/T4D303, retrieved November 30, 2017.
- Lomba, L., Giner, B., Bandres, I., Lafuente, C., Rosa Pino, M., 2011, Physicochemical properties of green solvents derived from biomass, *Green Chem.*, 8, 2062–2070.
- Qureshi, M. S., Touronen, J., Uusi-Kyyny, P., Richon, D., Alopaeus, V., 2016, Solubility of hydrogen in bio-oil compounds, *J. Chem. Thermodyn.*, 102, 406–412.
- Sako, T., Sugeta, T., Nkazawa, N., Otake, K., Sato, M., Ishihara, K., Kato, M., 1995, High pressure vapour-liquid and vapour-liquid-liquid equilibria for systems containing supercritical carbon dioxide, water and furfural, *Fluid Phase Equilibria*, 108, 293-303.
- Span, R., Wagner, W., 1996, A new equation of state for carbon dioxide covering the fluid region from the triple-point temperature to 1100 K at pressures up to 800 MPa, *J. Phys. Chem. Ref. Data*, 25, 1509-1596.
- Trinh, T.K.H., de Hemptinne, J.C., Lugo, R.; Ferrando, N., Passarello, J.P., 2016, Hydrogen solubility in hydrocarbon and oxygenated organic compounds, *J. Chem. Eng. Data*, 61 19–34.