**H2 Solubility in Gamma-Lactones for Hydrodeoxygenation to Biofuel Components**

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**Highlights**

* Gamma-Lactones are derivatives and model compounds of biorefinery platform compounds.
* H2 solubility is important in liquid-phase Hydrodeoxygenation for biofuel production.
* In γ-nonalactone, solubility increased more from 200 to 250 °C than from 250 to 300 °C.
* The solubility of H2 was greater in γ-nonalactone than in γ-heptalactone.

**1. Introduction**

Levulinic acid (LA) dimers are a potential platform stream in lignocellulose biorefineries [1]. LA dimers are slightly branched C10 molecules, containing lactone, carbonyl, and carboxyl moieties, which cannot be blended in fuel. However, valorization could be possible by heterogeneously catalyzed hydrodeoxygenation (HDO). Recently, the HDO of LA dimers has been assessed through the study of a relevant model compound, γ-Nonalactone (GNL), at 6 MPa H2 and at 200-280 °C [2]. Because HDO is performed in three phases, H2 can only reach the catalyst after its dissolution from the gas phase into the liquid reaction mixture. Due to lack of empirical data on the solubility of H2 in GNL, it is difficult to clarify the effect of hydrogen on the reaction. Thus, in the present work, the solubility of gaseous H2 in liquid lactones was studied at temperatures and pressures relevant to HDO. The length of the aliphatic side chain was thought to improve the solubility. Hence, both γ-heptalactone (GHL) and GNL were studied.

**2. Methods**

The lactones were purified by vacuum distillation at 60 mbar before use. The solubility measurements were performed in a continuous flow apparatus with temperature and pressure control. The saturation point was identified by the appearance of gas bubbles in the liquid flow, which was monitored in an optical cell. Saajanlehto et al. [3] described the apparatus and the procedure in detail. For each lactone, H2 solubility was measured at 200, 250, and 300 °C and for pressures in the range of 3 to 10 MPa. The isotherms (H2 mole fraction vs. pressure at selected constant temperatures) are expected to intercept the y axis at a value equal to the vapor pressure of the pure lactone at the given temperature. Thus, the vapor pressures were calculated based on literature [4] and added to the isotherms. The 6 MPa measurements of GNL at 200 and 250 °C were repeated at different residence times in order to verify that the system was operated at steady state.

**3. Results and discussion**

The measured saturation points are presented in Figure 1 with regression lines. The standard deviations of the repeated measurements at different residence times were 4.43·10-4 on average, i.e. two orders of magnitude lower than the values of the measurements. The saturation mole fractions in GNL were 10% to 41% higher than in GHL. However, when accounting for molecular mass, the differences were only 4% to 16% and in some cases, the solubility per lactone mass was greater in GHL. It is worth noting that the solubility of H2 at 250 °C for GHL had an intermediate position between the solubilities at 200 and 300 °C, whereas for GNL, the H2 solubility at 250 °C was closer to the solubility at 300 °C than to the solubility at 200 °C. At 6 MPa, the solubility in GNL went from 0.049 at 200 °C to 0.058 at 250 °C and to 0.064 at 300 °C. That is, it increased by ~20% from 200 to 250 °C and by ~10% from 250 to 300 °C. In order to provide a rough picture of the solubility, Henry’s law solubility constants can be estimated from the reciprocals of the regression slopes (Table 1).



**Figure 1.** Solubility of H2 in A) γ-heptalactone and B) γ-nonalactone at pressures and temperatures relevant to hydrodeoxygenation. The isotherms present the saturation pressures at given H2 mole fractions.

**Table 1**. Slopes of regression lines.

|  |  |  |
| --- | --- | --- |
|  | **GHL slopes (MPa)** | **GNL slopes (MPa)** |
| **200 °C** | 149.3 | 130.7 |
| **250 °C** | 125.5 | 100.4 |
| **300 °C** | 107.4 | 89.2 |

**4. Conclusions**

The H2 mole fractions in GNL at the HDO conditions studied in [2] were between 0.049 and 0.058. There was a strong dependence on temperature and pressure and, in the case of GNL, the solubility increase was more marked from 200 to 250 °C than from 250 to 300 °C. This observation might be significant for HDO kinetics. On the other hand, H2 was more soluble in GNL than in GHL.

**References**

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