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Thermodynamic Evaluation of the Intermediate Liquid Compounds (ILC) from Biomass Fast Pyrolysis

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Abstract. Biomass fast pyrolysis process is a technology that converts renewable solids into a dense liquid. This study aims to apprehend the thermodynamic behaviour of the Intermediate Liquid Compounds (ILCs) observed during the biomass fast pyrolysis. The system studied was a closed system (20 mL) with air and a mixture solution of five components (Acetic acid (AA), hydroxyacetone (HX), phenol; furfural (FF) and methanol) at 90°C and under atmospheric pressure. The flash calculation was conducted at a given temperature and pressure. The vapor-liquid equilibrium compositions were determined combining equation of state and activity coefficient models, the Soave-Redlich-Kwong (SRK) equation of state coupled with Modified Huron-Vidal (MHV2) mixing rules incorporating the UNIversal Functionnal Activity Coefficient (UNIFAC) model. Theoretical calculations of vapor-liquid equilibrium compositions were experimentally validated by using a Head-Space GC-MS system. A quantitative agreement between simulated and measured concentrations in the liquid phase was achieved with this combined state-predictive model of SRK-MHV2-UNIFAC model; thus, confirming that it accounts well for the nonidealities.

1. Introduction

To respond to global concerns linked to climate changes caused in a large part by the increasing energy demand and fossil fuels use, alternative and renewable energy solutions such as biomass-based conversion technologies have received considerable attention. Conversion of biomass into liquid fuel, namely bio-oil, using a thermochemical process, most specifically the fast pyrolysis, has received great interest [1]. Fast pyrolysis is the rapid thermal decomposition of organic compounds in the absence of oxygen, which can be considered as the superposition of three degradation processes respectively for the three main components that are cellulose, hemicelluloses and lignin [2]. In fact, a melting phenomenon can be observed in the experiment of pyrolyzing biomass, which is called Intermediate Liquid Compound (ILC). The short state-of-the-art on pyrolysis mechanisms suggests that the formation

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of ILC is a common stage to all lignocellulosic polymer pyrolysis. Some of the existing research has focused on the formation of ILC during the fast pyrolysis of cellulose. They often called this type of ILC as "active" cellulose or melt cellulose [3-5]. Some essential physical properties of ILC are shown in Table 1.

The formation of ILC occurs at early stages of fast pyrolysis. As a result, the ILC is considered to have a lower degree of polymerization (DP) and crystallinity [6]. However, the exact structure and chemical composition of ILC is still unknown. Experimental and kinetic studies could be evidently interesting aspect for the study of ILC. However, due to the extremely short life of ILC, it is impossible to obtain ILC samples directly. Therefore, it is an attractive approach to explore the thermodynamic behavior of ILC through model compounds.

Table 1. Main thermophysical characteristics of ILC

Fraction	Formation Temperature (°C)	Life Time(s)	Liquid Density (kg/m^3)	Surface Tension (N/m)	Viscosity (kg/m*s)
Cellulose ILC	300-350 [3]		1000 [5]	10^{-6}-10^{-5} [3]	10^{-6}-10^{-5} [3]
Hemicellulose ILC	200-275 [3]	0.02-0.1[5]	---	---	---
Lignin ILC	200-350 [3]		---	---	---

Figure 1 proposed a degradation model for lignocellulose pyrolysis. The objective of this study is to apprehend the thermodynamic behavior of ILC model solutions. Acids, phenols, aldehydes and ketones, furans, and alcohols are the five major chemical families that compose bio-oil. Therefore, five compounds from those five major chemical families will be used to formulate the ILC solution: Acetic acid (AA), hydroxyacetone (HX), phenol, furfural (FF) and methanol. We are interested in predicting the vapor-liquid equilibrium of this model mixture. Simulis thermodynamics software will be used to determine the thermophysical properties and the vapor-liquid equilibrium composition of the mixture. Different models such as Soave-Redlich-Kwong (SRK) equation-of-state combined modified Huron-Vidal (MHV) mixing rule and UNIFAC (SRK-MHV2-UNIFAC) will be tested for simulation. The experimental validation will be done using the Head-Space system coupled with a gas chromatography/mass spectrometry.

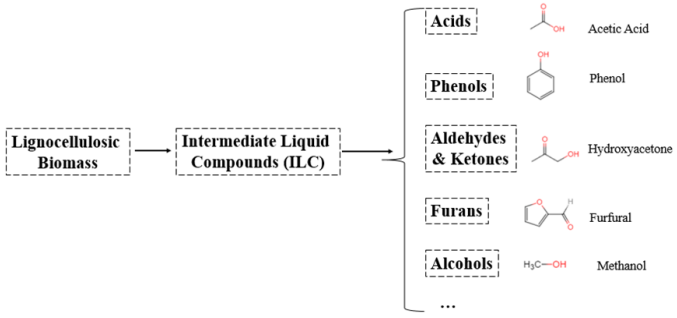


Figure 1. Proposed degradation model for lignocellulose pyrolysis

2. Materials and Methods

Standard solutions for calibrations and model intermediate compounds were prepared adding primary standards together: Acetic acid (AA, 99.9%, Sigma-Aldrich), hydroxyacetone (HX, 95%, Alfa Aesar), phenol (99.9%, Sigma-Aldrich), furfural (99%, Acros Organics), methanol (99.9%, Sigma-Aldrich). Acetone (99.9%, Suprasolv®) and fluoranthene (98%, Sigma-Aldrich) were used respectively as solvent and internal standard for preparing the standard solutions. The acetone was selected as solvent because it is a polar solution, in which the model pure compounds were miscible. The selection of main compounds was made according to the chemical composition of bio-oils produced from a wide range of

feedstocks and systems found in the literature [7]. The ILC model mixture was composed of 33.3 wt% acetic acid, 33.3 wt% hydroxyacetone, 13.3 wt% phenol, 13.3 wt% furfural, and 6.8 wt% methanol.

2.1. Chromatographic methods

The samples were analyzed using a Head-Space system coupled with a GC-MS system (Shimadzu GCMS-TQ8030). The chromatographic conditions were based on Moore et al. [8]. The headspace system (Shimadzu AOC-5000 Plus) is an injection unit of the gas chromatograph using the gas-tight syringe technique. The incubation setting temperature of the Head-Space system should be lower than 180°C, which is a technical parameter of the equipment and represents an operating limitation to reach for pyrolysis conditions. An amount of sample was placed into an incubation oven at a given temperature until the sample reaches the thermodynamic equilibrium. Then, an aliquot of volatile components was taken by the heated syringe and injected into the GC-MS. It is a sensitive technique for testing volatile organic compounds. The column was operated in a constant flow mode, 1.26 mL/min, using Helium (Scientific grade 6.0, Linde France) as the carrier gas with a solvent delay of 1.5 min. The heating program settings were initially maintained at 50 °C for 4 min before to be increased to 250 °C at a heating rate of 10 °C/min, and thereafter held for 5 min. The mass spectrometer was operated in an electron ionization mode at 70 eV. The ion fragments were separated via a quadrupole and the detection range set as 30-600 Da. The selected ion monitoring (SIM) mode was used to quantify the specific analytes. Compounds were identified according to the NIST Standard Reference database (NIST SRD 69).

The incubation temperature needs to be lower than the bubble point of the solution to ensure that the air pressure in the glass vial of 20 mL (Restek) does not change during the incubation process. This precaution prevents damage to the syringe caused by high air pressure in the glass vial. A thermodynamic calculation using Simulis Thermodynamics® was performed to determine the bubble point of each mixed solution to select the incubation temperature. The temperature of the syringe should be higher than that of the incubator to prevent condensation on the surface of the syringe when taking samples. The direct injection mode was used for analysing liquids and the Headspace injection mode was used for gas analysis. Duplicate measurements were made to determine the reproducibility. The methanol was not quantified as its retention time was lower than that of the solvent.

2.2. Modelling approach

The system studied is a closed system with air and liquid mixtures under the ambient temperature and atmospheric pressure. Input and output information were collated in an Excel spreadsheet in which was inserted a Simulis Calculator object. The Simulis calculator allows the selection of compounds and models. The initial default temperature was 25°C and pressure was 1 atm. Using pressure and temperature as input values of this system, the pressure was kept at 1 atm and the temperature was determined by the boiling point of liquid phase. The thermodynamic properties such as vaporization rate, density, bubble point, and dew point were determined using TP-Flash Simulis Calculator. The vapor-liquid equilibrium of the system could be predicted by using SRK-MHV2-UNIFAC predictive model at giving temperature and pressure. Then, the concentration of each component in gas and liquid phases could be obtained.

3. Results and Discussion

3.1. Properties of mixtures

The calculated physical properties of the ILC mixture were found to be: 110°C for the bubble point, 151°C for the dew point and 1.048 g/mL for the density. As a result, the incubation temperature of the Head-Space system was set at 90°C, an incubation temperature lower than the bubble point of 110°C. Those experimental conditions allowed the investigation of vapor-liquid equilibrium, which is also a very necessary part of the thermodynamic evaluation process.

Figure 2 shows experimental records of the ageing test for the ILC model mixture. The results indicate that ILC model mixture was stable during its preparation and use, and that the substances did not react with each other at 25°C. Indeed, there were no by-products separated by the GC column and detected by the MS detector, which further suggests that no chemical reaction could occur between those model components.

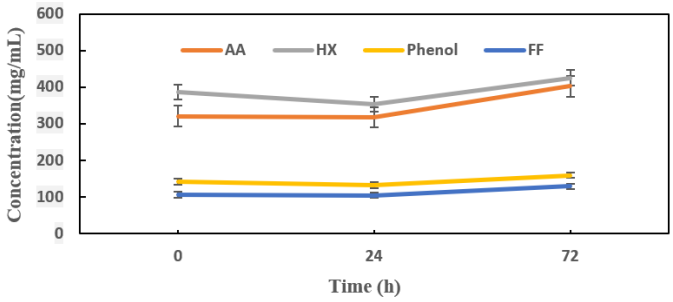


Figure 2. Concentrations measured in liquid mixture at 25°C before heating.

3.2. Optimization of chromatographic conditions

By using the internal standard method for calibration to determine the concentration of analytes in unknow sample, the GC conditions were optimized to avoid the electronic saturation of the MS detector. To do this, different split ratios were used to control the detector response. When the response was too weak the Selective Ion Monitoring (SIM) mode was used to detect the specific analytes. The selection and tracking of specific mass fragments can increase the detector sensitivity relative to full scan mode. The main parameter to be optimized is the split ratio according to the analyte's concentration. It was found that there is a non-linear correlation coefficient between different split ratios when analysing the same analyte. The relative Split Ratio Factor (A/B) (equation 1) was used to describe this phenomenon.

$$\text{Relative Split Ratio Factor}\left(\frac{A}{B}\right) = \text{RSRF}\left(\frac{A}{B}\right) = \frac{[X]A}{[X]B} \quad (1)$$

Where $[X]_A$ is the calculated concentration of X for a split ratio A; $[X]_B$ is the calculated concentration of X for a split ratio B.

By using this factor that describes the effect of split ratio value on concentration, it is possible to relate two measured concentrations for a same component determined at different split ratios. Those relationships depend on the factor used to draw the calibration curves: when using Concentration (X-axis) and Area ratio (Y-axis), the RSRF (50/10) is equal to 0.95±0.00008 and the RSRF (200/10) corresponds to 0.385±0.005; when using Concentration (X-axis) and Area of Analyte (Y-axis), the RSRF (200/10) is 18.9±2.18.

Table 2 shows all the equations of calibration curve used to determine the analytes concentration in the ILC model mixture. It can be seen, all the regression coefficients are above 0.99, indicating that the calibration curve equation fits well the experimental values.

Table 2. Equations of calibration curves associated with regression coefficient (R2) for ILC mixtures according to the chromatographic conditions.

	Liquid phase				Gas phase			
Injection mode	Direct				Headspace			
Concentration range (mg/mL)	70-354				0.0061-0.3550			
Product	AA	HX	FF	Phenol	AA	HX	FF	Phenol
Scan or SIM mode	Scan	Scan	Scan	Scan	Scan	Scan	Scan	Scan
Slope	14.74	15.758	126.79	111.43	30,000,000	30,000,000	4000,000	4000,000
y-intercept	-0.871	-0.204	-16.69	-15.08	-2000,000	-720998	-598856	-512122
R^2	0.9958	0.9976	0.9999	0.9941	0.9968	0.9995	0.9988	0.9926

After optimizing the chromatographic conditions, each component in the ILC model mixture could be detected (Figure 3) and quantified by GC/MS.

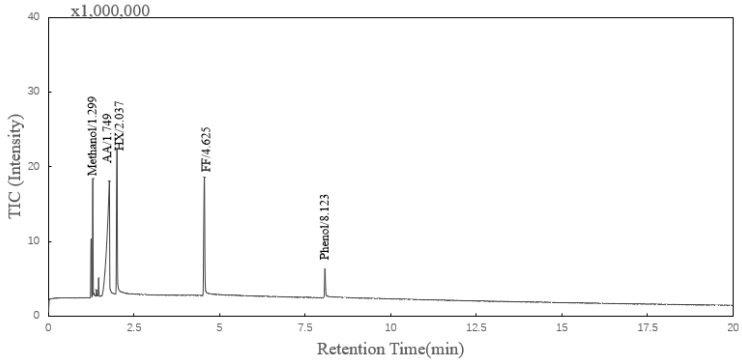


Figure 3. Chromatogram indicating the separation of each ILC model compound after incubation of 15 min at 90°C.

3.3. Vapour-Liquid Equilibrium Analysis of ILC model mixture

Figure 4 presents the concentration of components in ILC model mixture after 15 minutes of incubation at 90°C. The vapor-liquid flash was calculated at the 90°C and under atmospheric pressure. The simulated values (L-sim, G-sim) and the measured values (L-exp, G-exp) obtained under the same initial conditions and associated relative deviations were compared. The results indicated that the calculated data were well correlated with the experimental values measured in liquid phase (Figure 4A) for the hydroxyacetone and phenol, the relative deviation (RD) were respectively 7.7% and 5.3%, less than 10%, which was not the case for the acetic acid (RD = 20.4%) and the furfural (RD = 38.3%). With respect to gas phase simulations, only an appropriate relative deviation of 3.6% was confirmed for phenol, while RD of 21.4%, 26.8% and 53.7%, respectively, for furfural, hydroxyacetone and acetic acid were found (Figure 4B). Those large deviations obtained for gaseous concentrations can be explained by the fact that the heated flask containing the liquid mixture was not sealed. As a result, further model investigations and a more appropriate experimental set-up are required to appropriately describe the thermodynamic properties of the liquid and therefore offers a better response to predict quantitative information in both liquid and gaseous phases.

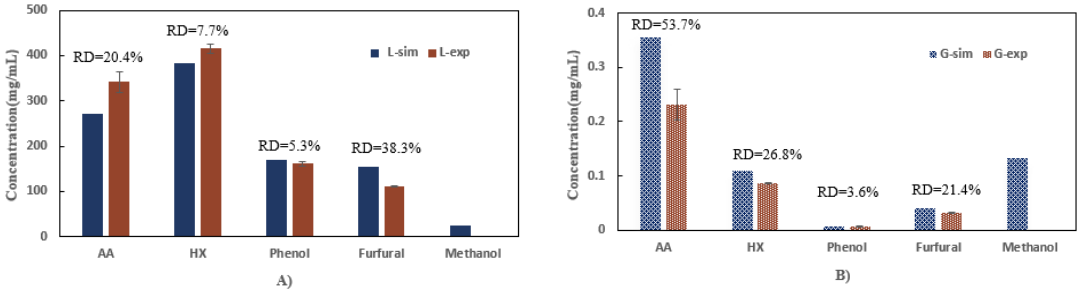


Figure 4. Concentrations of each component in ILC model mixture: A) in liquid phase and B) in vapour phase after an incubation period of 15 min at 90°C.

The overall mass balance is also displayed in Figure 5. It is important to note that experimental concentrations were employed while the total produced liquid and gas volumes were computed. Despite of the large standard deviation found in the case of acetic acid, both chromatographic quantification developments and use of the SRK-MHV2-UNIFAC model appear to be a suitable approach for studying liquid equilibrium.

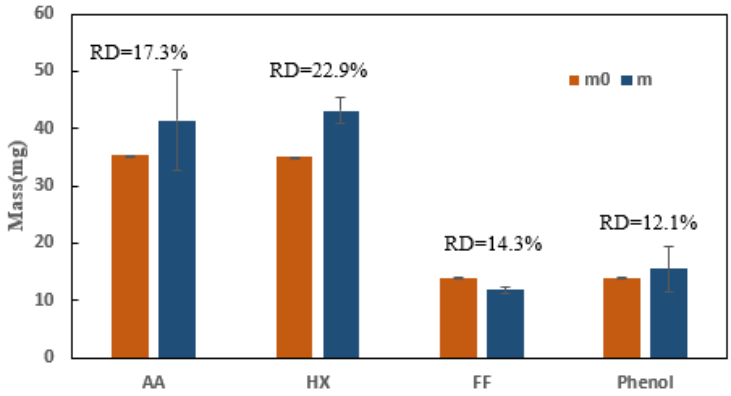


Figure 5. Mass balance for each analyte before (m0) and after (m) incubation at 90°C.

4. Conclusion and Perspectives

Both TP flash thermodynamic model and head-space gas chromatographic methods were developed and used to predict the vapor-liquid equilibrium for the ILC model mixture. The system studied was a closed Air-Mixture solution system at 90°C and under atmospheric pressure. The chemical composition of the ILC model mixture was successfully assessed. The comparative study between simulated and measured values indicates that further investigations are required to confirm the encouraging results provided by the use of SRK-MHV2-UNIFAC model. Meanwhile, a chemical kinetic model should be developed for studying the system under dynamic conditions.

Acknowledgments

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