Effects of Ionic Liquid and Biomass Concentration to Partial Vapour Pressure Change in Hydrothermal Carbonization

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Abstract. This study aims to investigate the effects of ionic salt liquid and biomass concentration to partial vapour pressure change in hydrothermal carbonization system. The durability of reactor and safety aspect are crucial point for constant volume system which pressure is independence and important in scaling up hydrothermal process. The ionic salt including calcium propionate with the molality of 0.33, 0.43 and 0.65 and sodium chloride with the molality of 0.86, 1.14 and 1.71 were used. The suspension of corncob biomass and deionized water with the ratio 1:20 and 1:10 also were evaluated. The partial vapour pressure of the solution of sodium chloride with the molality of 1.71 decrease for 12.5 %. The partial vapour pressure of corncob biomass concentration with 1:20 decrease for 2.8%. The hydrochar produced from the 240 °C of reaction temperature and 100 minutes reaction time demonstrated the gradually decrease of hemicellulose constituent corresponding with higher biomass concentration.

Keywords: Hydrothermal carbonization, Hydrochar, Partial Vapour pressure, Pressure reduction.

1. Introduction
Among the biomass conversion technology as physical, chemical, biochemical and thermochemical conversion, the thermochemical conversion converts biomass to energy categories including combustion, pyrolysis, torrefaction and hydrothermal process. The combustion, pyrolysis and torrefaction are the technology for dry process which the wet biomass required or supplied some energy before actual process. Consequently, the utilization of wet condition without supplied energy is more attractive. Hydrothermal technology which water as the medium retained in the liquid phase is classified as the wet process. Biomass slurry with the different ratio is investigated the potential to change or convert into energy as solid, liquid and gas fuel. The hydrothermal conversion divide into three process as carbonization, liquefaction and gasification demonstrated in Figure 1. Products distribution including hydrochar, bio-oil and gas depends on the hydrothermal condition. The conversion process or production process plays important role in controlling the specific properties of the required products while quality of incoming feedstock should be related.
As general, in fixed vessel or constant volume reactor, pressure is independence. The durability of reactor is very important and significant. Especially, the hydrothermal that requires the gas main products operate at high temperature. The question of operating at high pressure for the safety and reactor cost aspects still doubted. The reduction of pressure at the interested reaction temperature is the challenge pathway. In variety constant-volume batch experiment, the pressure was always approximately the vapour pressure of saturated steam at the reaction temperature chosen [1]. Reduction the vapour pressure at the reaction temperature by means of partial vapour pressure, one of colligative properties is the possible way. For reactions at hydrothermal conditions, pressure must be higher than the vapour pressure of water to keep the reaction in the liquid phase because gaseous water loses one of the most important properties for a reaction medium [2].

The specific characteristics of water in subcritical region is predominant and advantage for hydrothermal technique. The water in subcritical condition penetrate the boundary and constraint of dry process technology. The boundless of wide range of feedstock wet-to-dry and deal with the hydrothermal technology to produce various valued product. Due to unique properties of water at elevated temperature versatile chemicals and fuels in gaseous, liquid, or solid state can be produced. In these process water may act as solvent, reactant or a catalyst [3]. The properties of water at ambient temperature contrary to high temperature. Water at ambient conditions is a polar solvent of polar molecule. It is good solvent for polar compounds and salts and weak solvent for non-polar compounds including gases like hydrogen or nitrogen [4]. The dramatic decrease in solvent viscosity, increase in substrate solubility, and enhance sensitivity of solvating properties of subcritical fluid with respect to temperature and pressure make it attractive as a potential solvent [5]. The thermodynamic properties of water (at both ambient and subcritical conditions) are typically described in terms of hydrogen bonding strength and hydrogen bonding structure [6].

Ionic salt is the one ionic compound which occurring ionization process when dissolve in the water. The hydronium ion (H$_3$O$^+$) or hydroxyl ion (OH$^-$) from hydrolysis of salt (reaction of salt and water) result in the acid base properties. Sodium chloride is the common ionic salt and electrolyte compound which solution is neutral. The subcritical approach has the advantage that salts are mostly solved and therefore plugging by salt precipitation is less [7].

The vapour pressure of pure substance depend on the reaction temperature, $P_{sat}(T)$. For example, the vapour pressure of water is 0.6117 kPa at 0.01 °C, 101.42 kPa at 100 °C, 1,554.9 kPa at 200 °C, 2,319.6 kPa at 220 °C, 3,347.0 kPa at 240 °C, 8,587.9 kPa at 300 °C and 22,064 kPa at 373.95 °C [8]. For ideal liquid, the pressure ($P$) influenced by component in gas phase which proportional to vapour pressure of pure liquid. The vapour liquid equilibrium (VLE) of mixture which compose of ideal liquid mixture and ideal gas where Raoult’s Law states that for any component $i$, the partial pressure ($P_i = y_i P$) equals to the vapour pressure of pure component $i$, multiplied by its mole fraction $x_i$ in the liquid phase as the equation (1). Therefore, the partial pressure ($P_i = y_i P$) is reduced from $P_{i,sat}(T)$ (pure component) to $x_i P_{i,sat}(T)$ (ideal mixture) [9].

Raoult’s law
The pressure reduction of the system corresponding with equation (2),

\[ \Delta P = P_{i, sat}(T) - x_i P_{i, sat}(T) \]  

For the electrolyte system which obeyed Raoult’s Law, the partial vapour pressure is correlation with mole fraction of solvent in mixture solution (\(x_{solvent}\)). Therefore, the partial vapour pressure of mixture in liquid phase is lower than vapour pressure of pure solution. \(P_i\) is the partial pressure of specific solute such as ionic salt as equation (3). And partial vapour pressure change is equal the mole fraction of solute (\(x_{solute}\)) in the mixture solution as the equation (4).

\[ P = x_{solvent} P_{i, sat}(T) \]  
\[ \Delta P = x_{solute} P_{i, sat}(T) \]  

The relation of partial pressure for non-ideal mixture in subcritical at moderate pressure shown in equation (5). The activity coefficients, \(\gamma_i\), depends mainly on the liquid composition (\(x_i\)) and are usually computed from empirical equation such as the Wilson, NRTL, UNIQUAC and UNIFAC equation [9].

Non-ideal mixture at moderate pressure

\[ y_i P = \gamma_i x_i P_{i, sat}(T) \]  

A mixture in liquid phase, mole fraction of component or solute is the crucial role in the pressure reduction of hydrothermal system. The high pressure in hydrothermal system is the key factor in safety and reactor cost aspect. Therefore, the reduction of pressure is the critical point in scaling up hydrothermal process.

As the investigation of author, the study of the reduction pressure in hydrothermal system is a few. The salt of Calcium lactate, Calcium chloride, Lithium chloride, Calcium propionate, Calcium acetate, Calcium formate and Magnesium acetate are added in hydrothermal carbonization of loblolly pine. The ratio of salt to deionized water and salt to loblolly pine are 1:5 and 1:1 by weight respectively. The discussion involved the effect of salt addition on mass yield, energy densification, energy yield, pH and reduction pressure. Lithium chloride and Calcium chloride show markedly lower reduction pressure as 30% and 19% respectively. Magnesium and other calcium salt are 7-10% reduction pressure. However, the purpose of that study is for solid fuel utilization [10].

Beyond the effective reduction pressure in hydrothermal system, the properties of the wetting medium for biomass is the vast meaning. All the literature review, the effect of pressure reduction to the hydrothermal char never been studies especially the utilization for adsorption material.

For this study, hydrothermal liquid mixture having solute (ionic salt) in different concentration. The partial vapour pressure change correlated with mole fraction of solute in the mixture solution. This study aims to investigate the partial vapour pressure in hydrothermal system including the ionic salt and water able to reduce at concerned reaction temperature. And also investigate the biomass concentration effecting in the vapour pressure of hydrothermal system. The calcium propionate and common sodium chloride salt were studied. The pressure and temperature are recorded and plotted the vapour liquid equilibrium curve.

2. Methodology

2.1. Materials
2.1.1. Solution of ionic salts. Two types of ionic salt as calcium propionate or propionic acid calcium salt, \( \text{CaC}_2\text{H}_2\text{O}_4 \), (CAS RN. 4075-81-4, TCI Japan) and sodium chloride, \( \text{NaCl} \), (CAS RN. 7647-14-5, Merck KGaA, Germany) dissolved in deionized water (DI) (CAS No. 7732-18-5, RCI Labscan) were used to study as shown in Figure 2. The ratio of ionic salt and DI as 1:10 and 1:20 \( \% \text{w/w} \) are tested.

![Figure 2](image)

(a) Calcium propionate; (b) Sodium chloride

2.1.2. Corncob feedstock. Corncob is the selected feedstock in this research. The corncob feedstock as shown in Figure 3 was shortened and sieved with size 10-20 mesh (2-0.841 mm). The sieved corncob sample were dispersed in deionize water for hydrothermal conversion.

![Figure 3](image)

Figure 3. Corncob feedstock.

2.2. Experiment

The experiments performed in 10 liters hydrothermal carbonization reactor as demonstrated in Figure 4. The temperature of the reactor system was controlled using a Proportional-Integral-Derivative (PID) temperature controller. The pressure of the system was measured by pressure transmitter.

![Figure 4](image)

Figure 4. Hydrothermal carbonization reactor (HTC reactor) (Supported by Energy Research and Development Institute-Nakornping, Chiang Mai University).
2.2.1. Measuring temperature and pressure of deionized water in HTC reactor. The 6 kg deionized water filled in 10 liters pressurized vessel reactor. The reactor was heated with heating rate of 5°C/minute. The pressure and temperature were recorded simultaneously from ambient temperature until 240 °C. The VLE curve was plotted.

2.2.2. Measuring temperature and pressure of solution of ionic salt in HTC reactor. The solution of ionic salt (Ca Propionate and Sodium chloride) with the ratio of ionic salt and DI water were 1:10 and 1:20 w/w. The solubility data of Ca Propionate (100°C) and molecular weight are 48.44 g/100 g of water, 186.22 g/mole respectively. The solubility data of NaCl (100°C up) and molecular weight are 384 mg/mL, 58.44 g/mole respectively. The pressure and temperature were recorded simultaneously from ambient temperature until 240 °C. The VLE curve was plotted.

2.2.3. Measuring temperature and pressure of system including suspension of corncob in HTC reactor. Preparation the suspension of corncob and DI water with 1:1 ratio of ionic salt in the 2.2.2 The pressure and temperature were record simultaneously from ambient temperature until 240 °C. The VLE curve was plotted.

2.2.4. Fibre composition analysis of corncob and hydrochar in 2.2.3 of 240 °C reaction temperature with 100 minutes reaction time

3. Results and Discussion
This study, the relation of vapour pressure (MPa) and temperature (°C) relation of deionized-water in HTC reactor shown in Figure 5, the relation of pressure and temperature of ionic salt solution deionized with different concentration of ionic salt solution and the relation of pressure and temperature of suspension solution deionized with different concentration corncob biomass are demonstrated in Table 1.

![Figure 5](image)

**Figure 5.** The pressure and temperature relation of deionized water in HTC reactor

| Table 1. The molality of ionic solution, pressure & temperature relation and vapour pressure change |
|-----------------------------------------------|------------------------|------------------|------------------|------------------|
| Items                          | Molality (mole/kg) | Pressure & Temperature relation | R²   | Vapour Pressure (MPa) at 180, 240 °C | ΔP (%) |
| DI                            | -                    | $P = 0.0207e^{0.021T}$          | 0.9983 | 0.940, 3.355   | -               |
| CaPro : DI (1:20)            | 0.33                  | $P = 0.0202e^{0.021T}$          | 0.9981 | 0.934, 3.353   | -0.06          |
| CaPro : DI (1:15)            | 0.43                  | $P = 0.0201e^{0.021T}$          | 0.9973 | 0.930, 3.337   | -0.54          |
CaPro : DI (1:10) 0.65 \[ P = 0.0199e^{0.0213T} \] 0.9981 0.920 , 3.303 -1.55
NaCl : DI (1:20) 0.86 \[ P = 0.0196e^{0.0213T} \] 0.9979 0.906 , 3.254 -3.01
NaCl : DI (1:15) 1.14 \[ P = 0.0239e^{0.0203T} \] 0.9973 0.923 , 3.121 -6.98
NaCl : DI (1:10) 1.71 \[ P = 0.0348e^{5.4169T} \] 0.9946 0.847 , 2.935 -12.52
CC : DI (1:20) - \[ P = 0.0238e^{0.0205T} \] 0.9985 0.953 , 3.261 -2.80
CC : DI (1:10) - \[ P = 0.0230e^{0.0207T} \] 0.9986 0.955 , 3.306 -1.46

Remark:
The fitting equations were fitted by using data range of 180-240 °C
Deionized water (DI), Calcium Propionate (CaPro), Sodium Chloride (NaCl), Corncob (CC)

The decrease of partial vapour pressure of ionic solution in hydrothermal system corresponding with the molality of liquid. For 1.71 molality of sodium chloride solution shown the tremendous decrease with 12.15 %. The clear results show that the liquid concentration effects to the reduction of partial vapour pressure and the lowering of pressure is not relate to ionic salt. In case of the pressure reduction of corncob suspension in HTC reactor, the lower concentration of biomass without ionic salt tend to more reduce the partial pressure. By considering the fibre composition of hydrochar produced from the 240 °C reaction temperature with 100 minutes reaction time, hemicellulose obviously gradually decrease corresponding with higher biomass concentration as shown in Table 2.

The lowering vapour pressure is the important factor for safety and durability in HTC, however the degradation of biomass feedstock with the suitable liquid concentration for success properties will be optimized.

Table 2. Fibre composition of corncob and hydrochar

| Sample | Cellulose (%) | Hemicellulose (%) | Lignin (%) |
|--------|---------------|-------------------|------------|
| Corncob | 39.02 | 36.68 | 9.02 |
| Hydrochar, CC : DI (1:20) | - | 33.94 | - |
| Hydrochar, CC : DI (1:10) | - | 26.85 | - |

4. Conclusion
This study aims to evaluate the partial vapour pressure change in HTC system using ionic salt solution as the liquid medium and the suspension of biomass in different concentration. The reduction of the partial vapour pressure, one of colligative properties, at the interested hydrothermal reaction temperature is the expected purpose. Based on the results obtained from this study, the ionic salt liquid can reduce the vapour pressure in the hydrothermal system at interested reaction temperature. And biomass concentration also effected to the vapour pressure of HTC system. Nevertheless, the degradation of biomass for the specific application of hydrochar with the maximized pressure reduction are the ultimate expectation. Therefore, the crucial of next work is the investigation of the properties of hydrochar using the ionic salt liquid for reduction of partial vapour pressure.

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