Co-hydrogasification of lignocellulosic biomass and swelling coal

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Abstract. The hydrogasification of pine wood (PW) and rice husk (RH) was carried out in a two-stage fixed-bed reactor to investigate the effects of hydrogen pressure and hydrocracking temperature on the yields of gas and tar compositions. The elevation in hydrogen pressure promoted the conversion of two biomasses, leading to the improvement in gaseous hydrocarbons but resulted in a decrease in the yield of BTX (benzene, toluene and xylene). The increased severity of hydrocracking boosted the yield of methane, ethane and BTX mainly at the expense of heavy compounds in tar for PW under 1 MPa. The co-hydrogasification of biomass and DWG swelling coal chiefly showed a synergistic effect on the yields of BTX and PCX (phenol, cresol and xylene) at 500 °C hydrocracking temperature under 5 MPa.

1. Introduction

Lignocellulosic biomass, as a relatively abundant and renewable carbon source alternative to the traditional fossil resources, has recently received great interest to produce bio-fuels and bio-chemicals. The hydrogasification of biomass may be an effective way to produce energy-dense oil enriched with light aromatics as well as methane rich gases [1]. Pindoria et al. [2] used sugarcane bagasse for pyrolysis under different atmosphere of hydrogen and helium, and found that the existence of hydrogen inhibited the repolymerization of tar. Pütün et al. [3] conducted pyrolysis and hydropyrolysis of sunflower bagasse at different temperatures, heating rates and pressures, and observed that pressurized hydrogen (> 50 bar) increased the oil yields by up to about 10 wt.%.

The availability of biomass largely relies on seasons and geographical environment. During the last few years, the co-pyrolysis of coal and biomass has become a technique that can manage seasonal fluctuations in biomass availability and increase energy density of the feedstock [4]. Collot et al. [5] used coal and biomass samples for co-pyrolysis and co-gasification with the final temperature of 850 °C or 1000 °C and pressure up to 25 bar, but the gas and liquid compositions were not determined. However, so far, there are seldom any literature reports referring to the effect of hydrogen atmosphere on product distribution and bio-oil composition, nor the co-hydrogasification of biomass and coal.

The aim of this work is to investigate the formation of gaseous and oil products from a pinewood (PW) and a rice husk (RH) under pressurized hydrogen atmosphere. The co-hydrogasification of RH
and DWG subbituminous swelling coal was also checked to provide insights into the mutual effects between biomass and coal.

2. Experimental
The proximate and ultimate analyses of two biomass samples (pine wood and rice husk) and a subbituminous coal featured in strong swelling are shown in Table 1. The process flow diagram of the pressurized reactor had been shown elsewhere [6]. In this case, the vertical tubular reactor was heated by the electric furnace by two separate temperature controllers. The upper zone of reactor was preheated at a heating rate of 20 °C min⁻¹ and held at 500 °C or 700 °C, and the sample (2.5 or 4 g) or the mixture of biomass and coal (mass ratio=1:1) at the bottom of reactor was then heated from ambient temperature to 700 °C at a heating rate of 15 °C min⁻¹. The temperature in upper zone is called the hydrocracking temperature, and the temperature in lower zone is referred to the devolatilization temperature. The hydrogen gas flowed from the inlet at the bottom of the reactor to the outlet at the top. The gas flow rate was controlled at 100 ml min⁻¹ under 1.0 MPa and 500 ml min⁻¹ under 5.0 MPa to ensure the same residence time. To prevent the unexpected condensation of volatile matter and preheat the hydrogen flow, the heating tape twined around the tubular lines which were connected to the inlet and outlet of reactor and was kept at the temperature of 260 °C. A series of stainless steel traps were dipped into the cooled salt water (−12 to 6 °C) to collect the liquid product and expect that the last section was cooled by liquid nitrogen (~−196 °C) to condensate liquid products as much as possible. The yield of liquid product was determined by analytical balance. Char product was collected after the experiment. The incondensable gases were gathered in the gas bags for compositional analysis. The analytical method of these products can be seen elsewhere [6].

Table 1. Proximate and ultimate analyses of the biomass and coal samples.

|                  | Proximate analysis (wt.%, ad basis) | Ultimate analysis (wt.%, daf basis) |
|------------------|------------------------------------|-----------------------------------|
|                  | Moisture  | Ash      | Volatile | Fixed carbon | C  | H  | N  | S  | O  |
| Pine wood        | 14.14     | 0.52     | 72.32    | 13.0         | 49.96 | 5.78 | 0.10 | 0.00 | 44.16 |
| Rice husk        | 1.55      | 9.86     | 72.58    | 16.0         | 51.20 | 6.17 | 0.36 | 0.10 | 42.17 |
| DWG              | 0.43      | 15.97    | 28.88    | 54.72        | 85.29 | 5.19 | 1.50 | 2.76 | 5.26  |

* by difference.

3. Results and discussions

3.1. Overall distribution of products

Figure 1. Yields of gas, tar, water and char products from hydrogasification at the different hydrocracking temperature of 500 °C and 700 °C under 1 MPa and 5 MPa for PW and RH biomass. * cracking temperature: 700 °C and in all other cases, 500 °C.
Figure 1 shows the gross distributions of gaseous, tar, water and char products from two biomass samples at 1 MPa and 5 MPa where all yields are counted in mass percent on a dry biomass basis. The yield of gas contains the yields of seven gases (CH$_4$, CO$_2$, CO, C$_2$H$_6$, C$_2$H$_4$, C$_3$H$_8$ and C$_3$H$_6$) regardless of other gaseous products, and the yield of water deducted the amount of moisture used in the air-dried sample.

With the increasing hydrogen pressure from 1 MPa to 5 MPa at the same hydrocracking temperature of 500 °C, the yield of gaseous products derived from PW increased at the expense of the char products. The vaporization of volatile matter may be retarded by high hydrogen pressure, and thus the secondary reaction of volatile matter was strengthened to produce more gases. The water yield remained almost constant at a level of 19.5%. The tar yield increased slightly from 27.4% to 28.12%. The hydrogasification behavior of RH was similar to that of PW.

With the increasing hydrocracking temperature from 500 °C to 700 °C under 1 MPa hydrogen pressure, the char yield and water yield obtained from PW almost remained unchanged. However, the tar yield decreased from 27.4% to 15.8% and this corresponded to the increase of gaseous products. It is because the secondary reaction of volatile matter was promoted by the increasing hydrocracking temperature to release more gases.

3.2. Yields of main liquid products

Figure 2. Quantitative analysis of 14 compounds in tar obtained from hydrogasification of two biomasses at two-stage reactor under 1 MPa and 5 MPa. 2-meth*, 2-methyl-naphthalene. Phenan*, Phenanthrene.

Figure 2 shows the yields of bio-oil products from two biomass samples at different hydrocracking temperatures under different pressures. With the hydrogen pressure increasing from 1 MPa to 5 MPa at the same hydrocracking temperature of 500 °C, the yield of BTX (benzene, toluene, m-xylene) derived from PW decreased slightly, but the yield of phenolic and polycyclic aromatics increased, of which phenol, p-cresol, 2, 4-xylene, naphthalene, 2-methyl-naphthalene, fluorene and phenanthrene.
increased obviously and o-cresol, indene and anthracene showed a minor increase. When comparing the yields of compounds obtained from PW by increasing hydrocracking temperature from 500 °C to 700 °C under 1 MPa, it was observed that the yield of BTX was soundly enhanced, especially for benzene and toluene. The yield of phenol and polycyclic aromatics also showed pronounced increase, while the o-cresol, p-cresol and 2,4-xylenol presented a decline trend, indicating that the high hydrocracking temperature facilitated the secondary reactions of volatile matter to produce more light aromatics such as BTX and phenol. The elevation off hydrogen pressure from 1 MPa to 5 MPa showed a similar impact on changes of main compounds yields from RH bio-oil in disregard of the decline in 2, 4-xylenol yield.

3.3. Yields of individual gas products

![Figure 3](image)

**Figure 3.** Quantitative analysis of main gases derived from hydrogasiification of two biomass at the hydrocracking temperatures of 500 °C and 700 °C under 1 MPa and 5 MPa.

Figure 3 shows the yield of gaseous products of PW and RH under hydrogen pressures of 1 MPa and 5 MPa at the hydrocracking temperatures of 500 °C and 700 °C. Firstly, the high hydrogen pressure led to the increase in yields of CO, CO\textsubscript{2}, CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, C\textsubscript{3}H\textsubscript{8} and C\textsubscript{3}H\textsubscript{6}. Meanwhile, the yield of C\textsubscript{2}H\textsubscript{4} remained almost constant. The yield of CO\textsubscript{2} decreased while the yield of CO increased with the increasing hydrocracking temperature. This was reasonable because the reversal water-gas shift reaction was promoted by the high hydrocracking temperature thermodynamically:

\[
CO_{2} + H_{2} \rightleftharpoons CO + H_{2}O \quad \Delta H = +41 \text{ KJ/mol}
\]  

The yield of CH\textsubscript{4} and C\textsubscript{2}H\textsubscript{6} increased substantially while the yield of C\textsubscript{3}H\textsubscript{4} merely changed at 700 °C hydrocracking temperature. However, C\textsubscript{3}H\textsubscript{8} disappeared due to its decomposition at high
hydrocracking temperature. The pressurized hydrogen facilitated the yields of CO, CH₄ and C2–C3 hydrocarbons for RH, but the change of CO₂ was unremarkable.

3.4. Co-hydrogasification of RH and DWG

**Figure 4.** Yields of gas, water, tar and char products produced by hydrogasification at 700 °C for individual sample or mixture of RH and DWG. Hydrocracking temperature, 500 °C; heating rate, 15 °C min⁻¹. Holding time, 0h.

**Figure 5.** Yields of 11 light aromatics obtained under 5 MPa without holding time at the final temperature of 700 °C for the hydrogasification of individual sample or mixture of RH and DWG.
The co-hydrogasification of RH and swelling DWG coal was investigated to check whether the mutual effects existed by adding fossil fuel into renewable sources under H₂ atmosphere. Figure 4 shows the distributions of gas, water, tar and char products obtained by the hydrogasification of RH/DWG or co-hydrogasification of RH and DWG mixture. Compared with the distribution of RH products, the hydrogasification of DWG produced exhibited much higher char yield as well as lower water and gas yield. This is reasonable because RH contained higher organic oxygen content (Table 1) to produce water and carbon oxides. The co-hydrogasification of RH and DWG mixture showed lower char yield than calculated char yield assuming no mutual effect. It indicated that the co-hydrogasification of RH and DWG can promote the total conversion of mixture. The gas and tar yield almost stayed constant, despite a slight increase in water yield.

Table 2 shows the yields of CO, CH₄, CO₂ and C₂–C₃ hydrocarbons obtained by hydrogasification or co-hydrogasification process. It can be seen that methane mainly derived from DWG coal and carbon oxides chiefly produced by RH during hydrogasification. But those two sample showed similar patterns in gas yields of C₂–C₃. The co-hydrogasification of RH and DWG merely showed mutual effect on alterations of final gas compositions. It demonstrated that no synthetic effect existed in gas phase.

Figure 5 presents the yields of 11 main light aromatics quantitatively determined under 5 MPa at the final temperature of 700 °C for hydrogasification or co-hydrogasification process. DWG produced higher yield of BTX while RH harvested more PCX. It is interesting to found that the co-hydrogasification significantly enhanced the yield of both BTX and PCX, but showed minor influences on other aromatics. The strengthened yields of BTX and PCX could be probably due to the addition of biomass into coal. It destroyed the swelling behaviour of DWG during heating-up period, which benefit the escaping of volatile matter from coal particles. On the other hand, the biomass contained appreciable amount of potassium (0.42wt.%, dry sample basis) which has been widely regarded as a catalyst during thermal conversion of coal. It is possible that this kind of potassium would act as active sites which promote the hydrocracking of primary tar compositions into monocyclic enriched aromatics during co-hydrogasification.

Table 2. Yields of CO, CH₄, CO₂ and C₂–C₃ hydrocarbons (wt. % daf.) at 700 °C hydrogasification temperature for individual sample or mixture of RH and DWG. Hydrocracking temperature, 500 °C.

| Sample       | CO  | CH₄ | CO₂ | C₂H₆ | C₂H₄ | C₃H₈ | C₃H₆ |
|--------------|-----|-----|-----|------|------|------|------|
| RH           | 4.3 | 5.9 | 12.5| 2.4  | 0.1  | 0.5  | 0.1  |
| DWG          | 1.1 | 10.8| 0.7 | 2.3  | 0.0  | 0.4  | 0.0  |
| 1RH1DWGᵃ     | 2.7 | 8.3 | 6.6 | 2.4  | 0.1  | 0.5  | 0.1  |
| 1RH1DWGb     | 3.0 | 8.4 | 6.8 | 2.3  | 0.1  | 0.5  | 0.0  |

ᵃ calculated value.
b experimental value.

4. Conclusions
At a lower cracking temperature of 500 °C, the production of phenolic and polycyclic aromatics was enhanced with increasing hydrogen pressure, and BTX decreased slightly for hydrogasification of lignocellulosic biomass. Increasing the cracking temperature up to 700 °C significantly promoted the formation of BTX. Co-hydrogasification significantly enhanced the yield of both BTX and PCX. More studies are needed to investigate the co-effect of temperature and hydrogen pressure.
A. 1 Nomenclature

| Symbol | Definition |
|--------|------------|
| PW     | Pine wood  |
| RH     | Rice husk  |
| BTX    | Benzene, toluene and xylene |
| PCX    | Phenol, cresol and xylenol |
| DGW    | The subbituminous coal from the place of origin named DWG |
| FID    | Flame ionization detector |
| TCD    | Thermal conduct detector |
| H₂     | Hydrogen gas |
| CH₄    | Methane |
| CO     | Carbon monoxide |
| CO₂    | Carbon dioxide |
| C₂H₆   | Ethane |
| C₂H₄   | Ethylene |
| C₃H₈   | Propane |
| C₃H₆   | Propylene |
| C₂     | Ethane and Ethylene |
| C₃     | Propylene and Propane |

Acknowledgements
This work is funded by the National “863” Scientific Research Program (2011AA05A201) and the National Natural Science Foundation of China (Grand No. 21376080).

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