

Mild Pretreatment and Liquefaction of Cypress in Ethanol for Bio-oil Production

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Abstract

Alkali pretreatment can decompose biomass and it is one of the most popular chemical agents because it is relatively inexpensive. In this study, cypress was pretreated with alkali and then was liquefied by sub/supercritical ethanol in a stainless steel reactor. The effect of temperature on the liquefaction of untreated and pretreated biomasses in sub- and supercritical ethanol was comparatively studied. The characteristics of pretreated and untreated cypresses were measured and compared to investigate the mechanism of the mild pretreatment and liquefaction cypress in ethanol by Thermo gravimetric analysis, Nitrogen Porosimetry, and Element analysis. Results showed that the pretreatment changed the main chemical components, physical structure and thermo-chemical character of cypress. The pretreated cypresses were less stable than the raw cypress. The mild alkali pretreatment increased surface area and pore volume of cypress, while it more effectively enhanced the bio-oil yield and decreased the temperature as compared to the untreated and stronger pretreated cypresses runs, in which the bio-oil yield increased from 15.5% to 23.5% and the optimum temperature decreased from 300 to 240 °C.

Keywords: Liquefaction, Lump, Cypress; FT-IR, GC-MS.

Introduction

Among thermo-chemical conversion methods, liquefaction is the most widely used approach due to its relatively lower reaction temperature as compared to pyrolysis method (Fan et al. 2011). This can prevent the formation of char compounds owing to the cross-linking hydrocarbon and aromatics compounds (Liu et al. 2008). While approaches of converting biomass into sources of fuels are constantly improving, and are advancing towards low environmental impact, the search for high-yielding biomass with economical feasibility is also ongoing (Kreuger et al. 2011).

The physical pretreatment method generally uses mechanical comminution (including chipping, milling and grinding) to make the biomass be exposed to high temperatures and this process is simple (Cadoche et al. 1989, Kumar et al. 2009). However, the higher energy consumption associated with it makes it not propitious to be implemented in a commercial scale production. Biological pretreatment method is associated with low hydrolysis rate which prolongs the pretreatment time of the process step (Harun et al. 2011). The chemicals commonly applied in the pretreatment process are either acid or alkali and the pretreatment has been successfully proven for biomass (Cheng et al. 2011, Rocha et al. 2011). The development of pretreatment approaches strong enough as to separate the cell wall arrangement and mild enough as to avoid a crucial chemical decomposing of biomass components is a challenge for today's chemical industry (Canettieri et al. 2007). For the novel pretreatment methods it is advisable to use cheap and easily recoverable chemicals and low-cost equipment. The use of environmentally friendly and low energy-intensive approaches is highly desired (Shuping et al. 2010). Alkali pretreatment can decompose biomass and it is one of the most popular chemical agents because it is relatively inexpensive.

In the previous papers (Liu et al. 2011a, Liu et al. 2011b), we first reported acid-chlorite pretreated and liquefied cornstalk in hot-compressed water and sub/supercritical ethanol for enhancing bio-oil production. The results showed that the shorter pretreatment times were more effective for enhancing the bio-oil yield and decreasing the optimum reaction temperature. In this work, the term 'mild pretreatment and liquefaction (MPL)' instead of 'liquefaction' was used to describe the thermo-chemical conversion of biomass, because the objective of this technology was to enhance the bio-oil yield and decrease the temperature in solvents liquefaction. However, the investigations can not evaluate systematically the chemical and physical characterization of biomass by pretreatment to study the mechanism of the MPL cypress in the present of ethanol.

In this study, cypress was pretreated with alkali and then was liquefied by sub/supercritical ethanol. The effect of temperature on the liquefaction of untreated and pretreated biomasses in ethanol was comparatively studied. The characteristics of pretreated and untreated cypresses were measured and compared to investigate the mechanism of the MPL cypress in ethanol by Thermo gravimetric analysis, Nitrogen Porosimetry, and Element analysis.

Materials and Methods

Materials. The cypress sample was collected from the city of Xuchang, Henan province in China. The feedstock was ground using a high-speed rotary cutting mill firstly, and then

sieved through 40 mesh. The cypress flour was extracted with water and ethanol to remove water-soluble compounds and polar organics, respectively, then dried at 105 °C for 24 h and kept in a desiccator at room temperature before used. The ash of cypress was determined by burning at 650 °C for 6 h.

Analysis. The element composition of solid residue was analyzed by CHNO Elemental Analyzer Vario EL (ELEMENTAR, Germany). The composition of oxygen (O) was estimated by difference. The higher heating values were obtained from calculation by Dulong's formula.

$$HHV(MJ / Kg) = 0.3383 \times C + 1.442 \times (H - O / 8) \quad (1)$$

Where *C*, *H* and *O* are the weight percentages of carbon, hydrogen and oxygen, respectively.

Thermal analysis of the untreated and pretreated cypresses were carried out by thermo-gravimetric (TG) and differential thermo-gravimetric (DTG) analysis on a simultaneous thermal analyzer (SDT Q600, TA Instrument, Selb, Germany). The samples were weighed between 4 and 8 mg and the scans were carried out from room temperature to 600 °C at a rate of 10 °C per minute under nitrogen flow. Nitrogen Porosimetry (Micromeritics ASAP 2010, USA) was used to measure the surface area and pore volume of the cypress before and after pretreatment. The surface area was calculated using the Brunauer-Emmett-Teller (BET) model, and the pore volume was calculated using the Barrett-Joyner-Halenda (BJH) method.

Apparatus and experimental procedure. For the alkaline pretreatment, cypress (150.0 g) was incubated with 5% (w/v) NaOH at a solid-to-liquid ratio of 1: 6 (w/v) at 90 °C for 0.5 h, 1 h and 2 h, respectively. The pretreated materials were filtered through double layered muslin cloth and then washed extensively with water until neutral pH. To calculate its dried weight, the pretreated cypresses were dried at 105 °C for 24 h. The liquefaction experiments were carried out in a 1000 ml stainless steel reactor (Parr, USA) and the reactor can be worked at a maximum temperature of 350 °C and maximum pressure of 13 MPa. In a typical run, 10 g cypress powder and 100 ml ethanol were charged into the reactor. The air inside the autoclave was purged by nitrogen gas. Agitation was set at 150 rpm and kept constant for all tests. When the reactor was heated up to the setting temperature, the reactor was cooled down to room temperature by means of cooling coils, which was installed inside of the reactor. Briefly, the gas was removed from the autoclave after the reactor was cooled to room temperature and then the autoclave was opened. The solid and liquid mixture was removed from the autoclave for separation. After that, water and acetone were removed in a rotary evaporator and the corresponding fraction was weighed and designated as water-soluble oil (WSO) and heavy oil (HO). Solid residue was defined as the acetone insoluble fraction. All the experimental data were calculated on a dry-ash-free basis. Each test was performed twice and the reproducibility of the experimental data was shown to be within ± 6%.

Results and discussion

Elemental analysis of untreated and pretreated cypresses. The elemental composition of biomass is a key factor affecting efficiency of bio-oil production during conversion processes. Table 1 shows the elemental analysis of the untreated and pretreated cypresses. After alkali pretreatment, the C content of the cypress decreased, and the O content increased. The higher heating value (HHV) of the raw cypress was higher than that of the pretreated cypresses

because of the removal of the C content and the increasing of O content. In fact, the HHV of biomass represented the HHV mainly from lignin and partially from cellulose and hemicelluloses (Shi and He 2008). As reported in the paper that holocellulose (cellulose and hemicelluloses) had a HHV of 18.6 MJ/Kg, whereas lignin had the HHV of 23.26-26.58 MJ/Kg. Therefore, for production higher HHV of bio-oil, mild pretreatment would be favorable for liquefaction of cypress.

Table 1 Elemental analysis of untreated and pretreated cypresses.

Samples	Elemental components (wt %)				O/C	H/C	HHV (MJ/Kg)
	C	H	N	O			
Cypress	48.9	6.0	0.3	44.8	0.92	0.12	17.1
0.5 h	47.7	5.8	< 0.3	46.2	0.97	0.12	16.2
1 h	46.6	6.0	< 0.3	47.1	1.0	0.13	15.9
2 h	45.3	6.1	< 0.3	48.3	1.1	0.13	15.4

Thermo gravimetric analysis of untreated and pretreated cypresses. Thermogravimetric tests in inert nitrogen were achieved to evaluate the effect of alkali pretreatment on the pyrolytic behaviour of the cypress. The results obtained from the typical thermogravimetry and differential thermogravimetric curves of the untreated and pretreated cypresses are shown in Figure 1. The TG of the untreated and pretreated cypresses shows a two-step weight loss curve. The first one occurred between 50 °C and 100 °C and corresponded to the loss of water naturally trapped into the samples structure. This water represented about 3% of the samples initial weight, and the mainly weight loss of the samples occurred in the range 200 °C to 360 °C. Above 360 °C, an abrupt change in the slope of the TGA occurred leading to a slower weight loss in the temperature range 360 °C to 600 °C. In addition, as can be observed, the weight loss was 50.0% when the temperatures reached 345 °C (raw cypress), 335 °C (0.5 h), 338 °C (1 h) and 336 °C (2 h) for untreated cypress and pretreated cypresses. In the DTG curves, the exothermic peaks of the untreated and pretreated cypresses occurred around 354 °C (raw cypress), 339 °C (0.5 h), 342 °C (1 h), and 344 °C (2 h), respectively. These results indicated that the pretreated cypresses were less stable than the raw cypress. Therefore, the alkali pretreatment favored the thermal decomposition of cypress.

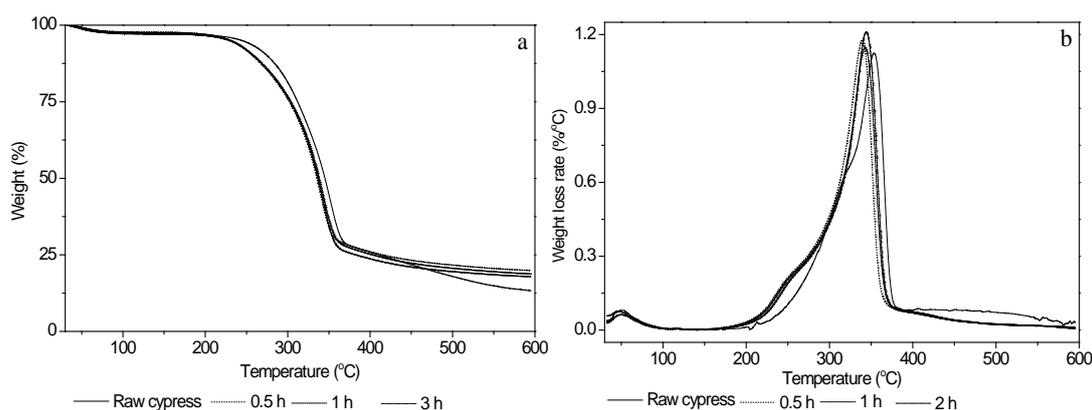


Figure 1. TG and DTG curves of the untreated and pretreated cypresses at 10 °C/min in nitrogen atmosphere.

Surface area and pore volume of cypresses before and after pretreatment. Nitrogen

porosimetry has been employed for the skin porous structure of cypresses before and after pretreatment. Figure 2 shows the adsorption isotherms for cypresses at three pretreatment times with untreated sample. The difference among the untreated cypress and the cypresses treated at 0.5 and 1 h is dramatic noticeable. Figure 2 shows a significant increase in the quantity of gas absorbed for the cypresses treated at 0.5 and 1 h, indicating a greater pore volume and a higher specific surface area. The results of surface area and pore volume are shown in Figure 2. Clearly, the shorter pretreatment times (0.5 and 1 h) resulted in bigger surface area and pore volume of cypress. For example, the surface area and pore volume of the pretreated cypress at 1 h increased by about 24.3% and 38.5%, respectively, as compared to the untreated sample. In addition, a reduction in surface area and pore volume of the pretreated cypress at 2 h also observed in Figure 2. This was mainly due to the degradation of micropores during the longer time alkali pretreatment process. Bigger surface area and pore volume could enhance the reaction rate of liquefaction process; therefore, the shorter pretreatment time was more favorable.

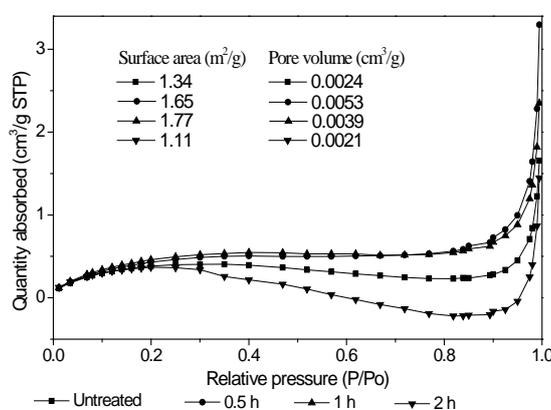


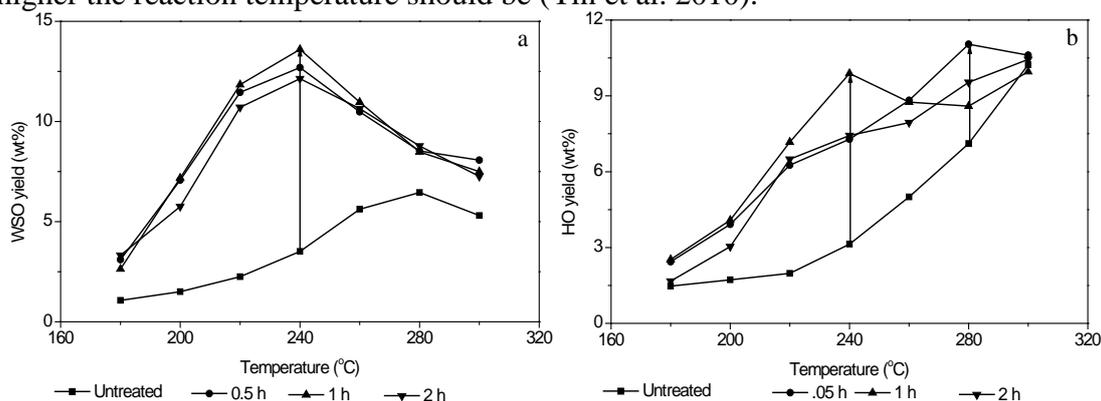
Figure 2. Nitrogen sorption isotherms for cypresses before and after pretreatment.

Liquefaction yields. The bio-oil yields from the liquefaction of the four samples at different final temperatures are shown in Figure 3. Obviously, as the temperature increased from 180 °C to 300 °C, the total conversion rate (100% - yield of solid residue) increased continually regardless of the untreated and pretreated cypresses liquefaction runs. It was worthy noting that all pretreatments increased the total conversion rate over the whole range of the temperatures tested as compared to the liquefaction of the untreated cypress. This might be due to the changes of the structure and chemical components, which made it easy for the liquefaction reagent to enter into the cypress. The increased in the total conversion rate with increasing temperature could either be owing to greater primarily decomposition of the cypresses at higher temperatures or via secondary decomposition of the solid residue.

As can be seen in Figure 3 (c), when the liquefaction temperature was increased from 180 °C to 300 °C the bio-oil obtained from raw cypress liquefaction showed an increase in the range 2.5% to 15.5 %. Comparatively, the pretreated cypresses conversion showed higher bio-oil yields and lower conversion temperatures as compared to that of the untreated cypress liquefaction run. The higher bio-oil yields obtained from the pretreated cypresses liquefaction were 20.0% (0.5 h), 23.4% (1 h) and 19.6% (2 h) at the reaction temperature of 240 °C, respectively. However, as the temperature was increased further, the bio-oil yields were decreased with the increase in temperature. Higher temperature was not usually suitable for production of liquid bio-oil. In general, there were two reasons for this result. Firstly the

secondary degradations reaction became active at higher temperatures, which led to the formation of gases (El-Rub et al. 2004). Secondly, the recombination of free radical reactions led to the tar formation due to their high amounts (Akhtar et al. 2011). These two mechanisms became dominant at higher temperatures, which reduced the production of bio-oil from cypress. As compared to the stronger pretreatment, the mild pretreatment were sufficient for the cypress form oily compounds, giving the higher bio-oil yields (23.4% and 20.0%). The higher temperature and stronger pretreatment resulted in a lower bio-oil yield and pretreatment yield, lower reaction temperature and mild pretreatment were more favorable. Therefore, operation the reactor system at the lower temperature and mild pretreatment were preferred because the bio-oil yield and pretreatment yield would be higher, and heat loss per unit mass of bio-oil produced was significantly lower, making the process more economical feasibility.

WSO mainly consisted of simple organic acids, furfural, sugars, etc., which are primarily formed from the conversion of holocelluloses through hydrolysis and de-polymerization reactions (Behreddt 2008, Xu et al. 2008). However, the HO primarily composed of phenolic compounds and phenols, results from the decomposition of lignin or from the dehydration of intermediate products derived from cellulose and hemicelluloses (Behreddt 2008, Xu et al. 2008). In addition, owing to various bio-oil formation temperatures for the different chemical components of biomass (i.e., cellulose, hemicelluloses and lignin), the optimum temperature for WSO and HO yields may depend on the relative abundance of chemical components in the raw material. Figure 3 (a) and (b) showed the effect of temperature on the WSO and HO yields obtained from untreated and pretreated cypresses liquefaction. Regardless of all the pretreated cypresses liquefaction runs, the WSO yields showed an identical trend, increasing after 180 °C, with a peak at 240 °C before decreasing. Possible reason to account for the level-off of the WSO yields at the higher temperatures would be cracking of the WSO products to HO. At the reaction temperature of 300 °C the HO yields obtained from raw cypress and stronger pretreated cypress liquefaction reached maximum of 10.2% and 10.4%, respectively. As compared with the untreated and stronger pretreated cypresses, the mild pretreated cypress liquefaction produced more HOs at the lower temperatures. For example, the maximum HO yields were 9.8% and 11.1% when the reaction temperature reached to 240 °C and 280 °C, respectively. This might be due to that the more lignin a biomass contains, the higher the reaction temperature should be (Yin et al. 2010).



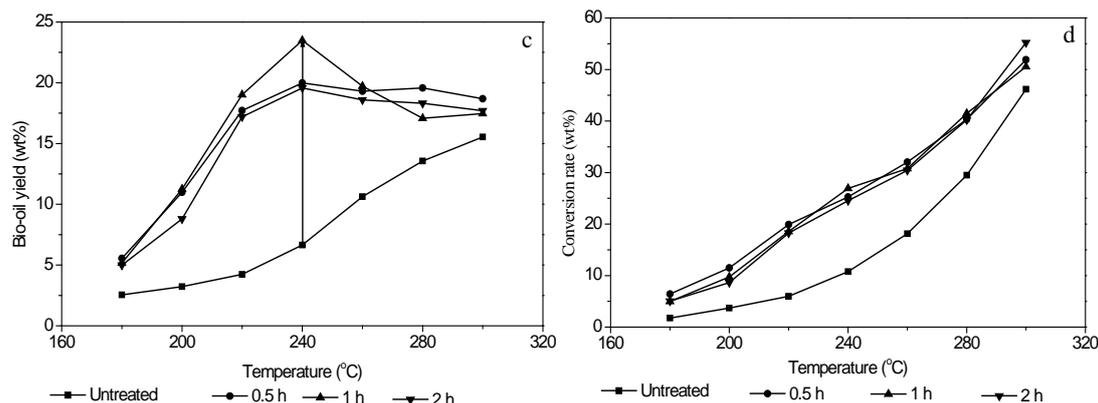


Figure 3. Effect of temperature on bio-oil yield, (a) WSO yield; (b) HO yield; (c) bio-oil yield; (d) conversion rate. (Conditions: 100 ml of ethanol, residence time of 0 min and 10 g of untreated or pretreated cypresses).

Conclusions

In this study, the cypress was subjected to alkali pretreatment and then liquefied in ethanol at different temperatures under a nitrogen atmosphere. The results showed that the pretreatment changed the main chemical components, physical structure and thermo-chemical character of cypress. The pretreated cypresses were less stable than the raw cypress. The mild alkali pretreatment increased surface area and pore volume of cypress, while it more effectively enhanced the bio-oil yield and decreased the temperature as compared to the untreated and stronger pretreated cypresses runs, in which the bio-oil yield increased from 15.5% to 23.5% and the optimum temperature decreased from 300 to 240 °C.

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