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# HYDROTHERMAL CONVERSION OF CATTLE MANURE TO BIOOIL: BIOOIL DEFINITIONS

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## ABSTRACT

A number of researchers have reported that biooil was produced through hydrothermal conversion of different types of biomass. However, it is difficult to evaluate and compare these biooils in terms of yields and chemical properties. They applied different organic solvents to extract biooil from products after hydrothermal conversion of biomass. The purpose of this study is to assess the impact of extraction solvents on the quantity and chemical structure of biooil. Cattle manure was used as one type of biomass feedstock for biooil production. And dichloromethane ($CH_2Cl_2$), chloroform ($CHCl_3$) and diethyl ether ($C_4H_{10}O$) were used for biooil extraction. Results showed that extraction solvents influenced biooil yields. The highest biooil yield of 48.78 wt% of volatile content of cattle manure was obtained when using $CH_2Cl_2$ solvent. The main components of biooil extracted by $CH_2Cl_2$ and $CHCl_3$ were ketones and carboxylic acids, while those extracted by $C_4H_{10}O$ were aromatic chemicals. In terms of elemental compositions and high heating values of biooil, no statistically apparent differences were caused by different solvents. The mean elemental compositions (by weight) of biooils were carbon of 73.79%, hydrogen of 8.18%, nitrogen of 4.38% and oxygen of 13.65%. And the mean high heating value of biooil was 36.74 MJ/kg.

## INTRODUCTION

Hydrothermal conversion (HTC) is a promising technology of producing biooil from biomass and is attracting world wide interests. Literature has showed that HTC converted different biomass to biooil, including dry biomass of wood chips[1], straw[2], sawdust and stalk[3], and wet biomass of swine manure[4], domestic garbage[5] and sewage waste[6].

Compared with biological production of bio-ethanol from biomass, HTC process is faster and applicable to various biomass feedstocks. Conversion time of HTC is usually in the range of 5 to 120 min [1-6], which is much less than 48 h of bio-ethanol production from fermentation of glucose using enzymes[7]. In addition, enzymes can not directly access cellulose, hemicellulose and lignin, expect for glucose, so pretreatments of hydrolysis of real biomass (mainly consisting of cellulose, hemicellulose and lignin) to glucose are required for bio-ethanol production. A recent review showed that pretreatment accounts for the main cost for bio-ethanol process [7]. Futhermore, current pretreatment technologies can not completely hydrolyze lignin to simple sugar unit like glucose, so biomass containing high lignin content is not suitable for bio-ethanol production. Naturally, bio-ethanol production chooses food crop like corn as feedstock, because food crop contain less lignin content. However, the food crop for bio-ethanol production is limited, since food crop is also important to humane being. According to a recent World Bank report, bio-ethanol based on food crop caused the world food prices to increase [8]. Therefore, stable feedstock supply is a problem in bio-ethanol production. In contrast, HTC is applicable for all of cellulose, hemicellulose and lignin without pretreatments. As mentioned at the beginning, HTC technology converted different lignin-containing real biomass to biooil.

HTC is also different from pyrolysis of biomass to biooil, for examples, in terms of feedstocks and conversion temperatures. So far, nearly 100 types of biomass has been converted to biofuel by pyrolysis, ranging from agriculture wastes such as straw, olive pits, and nut shells to energy crops such as miscanthus and sorghum[9]. However, pyloysis is better suitable for dry biomass than wet biomass, because water content in biomass does not contribute to biofuel formation during pyrolysis. In contrast, high water content wastes more input energy when it is also heated to 600~650 °C. Generally, biomass as received has the moisture content in the range 50~60% (wet basis) [10]. Thus, a predying unit is required for biomass pyrolysis process and presents a high capital, maintaining and energy input cost [11]. In addition, high conversion temperatures of 600~650 °C result in high energy input/consumption for pyrolysis. For HTC, not only dry but wet biomass feedstocks are suitable since water is the reaction media, and then the predying of biomass is not required. Meanwhile, conversion temperature of HTC is in the range of 200~400°C much lower than 600~650°C of pyrolysis. Therefore, besides pyrolysis and bio-ethanol processes, HTC is also being widely investigated for biooil production.

However, we find that it is difficult to compare biooil data in literature, because there is a shortage of consistent definition for biooil in HTC process. Research groups used different organic solvents, such as $CH_2Cl_2$[6], $CHCl_3$[12] and diethyl ether [13], to extract biooil after HTC of biomass. In order to help understand effects of organic solvents (biooil definitions) on yield and chemical structure of biooil, we applied above 3 organic solvents to extract the identical liquid product of HTC of cattle manure. Research results, particularly, are useful to future HTC biooil separation and standard development.

## EXPERIMENTAL

### CATTLE MANURE

Fresh cattle manure from Western Feedlots, Strathmore, AB, were characterized and used for this study. Fresh cattle manure was first ground without extra water using a blender. Then 3 samples were analyzed in terms of contents of water, solid, volatile solid and ash by following methods of 2540 B and 2540 E of Standard Methods for Examination of Water and Wastewater[14]. Elemental compositions of carbon, hydrogen and nitrogen were determined using an elemental analyzer (Perkin Elmer Model 2400 series II). Oxygen content was calculated by mass difference.

Results in Table 1 show that the properties of cattle manure samples used in this research were consistent, since the corresponding standard deviation was small. It is noted that fresh cattle manure had high water content of 76.37 wt%, and it justified the application of hydrothermal conversion since HTC uses water as reaction media and wet biomass like cattle manure can be directly converted to biooil without the need of drying.

Table 1. Properties of fresh cattle manure

| | Average | Standard derivation |
|---|---|---|
| Water content (wt %) | 76.37 | 1.73 |
| Solid content (wt %) | 23.63 | 1.73 |
| Volatile content (wt %) | 16.21 | 1.14 |
| Ash content (wt %) | 7.16 | 0.66 |
| Elemental analysis (wt %) | | |
| C | 35.38 | 0.40 |
| H | 4.73 | 0.11 |
| N | 2.38 | 0.11 |
| O | 57.51 | 1.4 |

### PROCEDURE OF HYDROTHERMAL CONVERSION OF CATTLE MANURE TO BIOOIL

Hydrothermal conversion of cattle manure was carried out in a bath HTC system (HT/HP 4500, Parr Co. IL), which mainly consisted of a 1.8-liter stainless steel reactor and a control system (Figure 1). The 1.8-liter reactor was equipped with a stirrer, a pressure gage, a thermocouple, an inner cooling water loop, and gas inlet and outlet. The controller was used to turn on/off the heating system, and to control the reaction temperature, stirring speed, and to monitor the temperature of the liquid phase and the pressure of the gas phase in the reactor. When the reactor temperature was higher than the desired value, the controller will open a water valve to cool this reactor through the inner cooling water loop. In this HTC system, the pressure and pressure limits of HTC reactor were 500 °C and 5000 Psig, respectively.

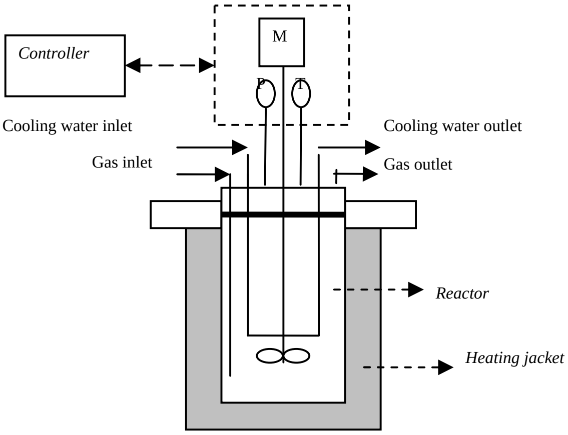

Figure 1. Illustration of 1.8L batch reactor system (M: magnetic agitator; P: pressure meter; T: thermocouple;)

In each test, 125 g of cattle manure, 500mL of water, and 6 g of NaOH were loaded to the 1.8L reactor. Head space of the reactor was purged by CO through gas inlet and outlet. And then reaction temperature of 310 °C was set up by the controller, and the heating switch was turned on to heat this reactor. As the temperature researched the desired temperature, this condition was maintained 15 min. Then the reactor was cooled down to room temperature. The solids in the mixture were removed by filter paper (Whatman NO.1), and biooil was separated from the liquid products using the organic solvents.

### BIOOIL DEFINITION / SEPARATION

Three organic solvents of $CH_2Cl_2$, $CHCl_3$, and diethyl ether were used to separate /extract biooil. First, liquid products were extracted by an organic solvent with the volume ratio of 1:1 in a separation funnel for 3 hours. Then organic extracts were treated by a rotary evaporator (BUCHI RE-121 Rotavpaor with BUCHI 461 water bath) to remove the organic solvent. The evaporation temperatures were determined, according to the boiling points of organic solvents. After the organic solvents were evaporated, the remaining liquid in the round flask was herein defined as biooil. By measuring the mass of the biooil using an electronic scale with resolution of 1 mg (A&D HR-120), the biooil yield was determined by Equation 1.

$$Biooil\ \% = \frac{W_{BO}}{VC} \times 100\ \% \qquad (1)$$

where $W_{BO}$ is the mass of biooil (g); $VC$ refers to the total volatile content (g) of the input cattle manure in HTC reactor.

### BIOOIL ANALYSIS

After extraction by different organic solvents, biooil was analyzed in terms of elemental compositions of CHNO and high heating value. CHNO contents of biooil were determined by an elemental analyzer (Perkin Elmer Model 2400 series II). The heating value of biooil was calculated using Equation 2 which was developed by Fridl et al. based on data of 154 biomass samples [15].

$$\text{HHV (kJ/kg)} = 3.55[C]^2 - 232[C]-2{,}230[H] + 51.2[C]\times[H] + 131[N] + 20{,}600 \qquad (2)$$

where HHV is the high heating value, and [C], [H] and [N] are mass percentages of carbon, hydrogen and nitrogen, respectively.

In addition, chemical structures of bioooil were analyzed by UV-VIS. UV spectroscopy can determine whether unsatisfied chemical bonds existed in biooil. In the UV spectroscopy analysis, the solubilisation product was scanned with a light of wave lengths from 200 nm to 500 nm using a spectrophotometer (Genesis 20, Thermo Scientific).

## RESULTS AND DISCUSSION

### EFFECTS OF EXTRACTION SOLVENTS ON BIOOIL YIELDS

Results (Figure 2) showed that extraction solvents did affect biooil yield. For the same HTC product, $CH_2Cl_2$ extracted a biooil yield of 48.78%, followed by $CHCl_3$ (38.52%) and $C_4H_{10}O$ (28.85%). By applying ANOVA one-way analysis, the calculated P value was 0.002< 0.05, which meant that with 95% confidence, there was a significant difference between biooil yields caused by different organic solvents.

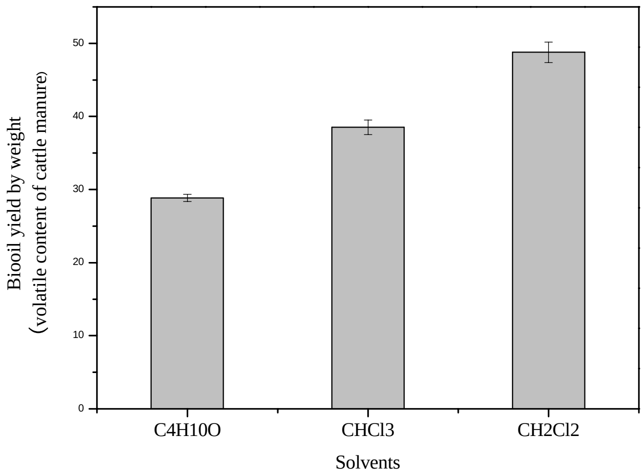

Figure 2. Effect of organic solvents on biooil yields (Conditions: temperature of 310 $^{o}$C, 125g of cattle manure, 500mL of water, 6g of NaOH, process gas of 0 psig of CO, and residence time of 15 min)

Effect of organic solvents on biooil yield can be attributed to the polarity of biooil from HTC. According to literature [16], biooil of HTC was more chemically polar than petroleum, so relatively high biooil yields could be obtained when using polar organic solvents for biooil extraction. In this study, the highest biooil yield was obtained by $CH_2Cl_2$, whose chemical polarity was larger than $CHCl_3$ and $C_4H_{10}O$.

The above result revealed that the choice of organic solvents for biooil extraction influenced reported biooil yields. Furthermore, it implies that it is incorrect to directly compare biooil yield results in literature where different organic solvents were used to extract biooil.

### EFFECTS OF EXTRACTION SOLVENTS ON ELEMENTAL COMPOSITIONS AND HEATING VALUES OF BIOOIL

As presented in Figure 3, elemental compositions (CHNO) of biooil were not obviously influenced by different organic solvents ($C_4H_{10}O$, $CHCl_3$ and $CH_2Cl_2$). ANOVA one-way analysis confirmed that with 95% confidence, there was no significant difference (P value >0.05). The average elemental compositions of biooil in this study were carbon of 73.79%, hydrogen of 8.18%, nitrogen of 4.38% and oxygen of 13.65%. But, when compared with cattle manure, biooil contained more carbon, hydrogen, nitrogen, but less oxygen.

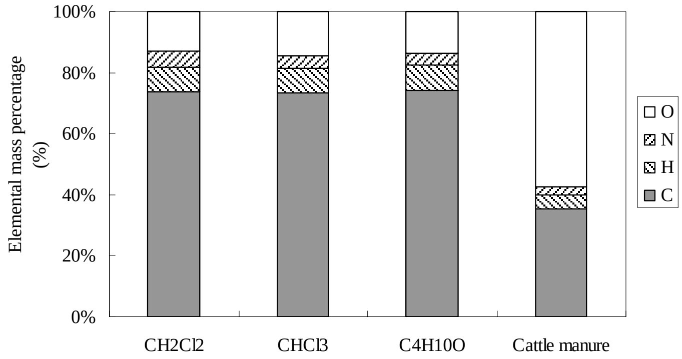

Figure 3. Elemental compositions of biooils extracted by different organic solvents and cattle manure.

(Conditions: temperature of 310 °C, 125g of cattle manure, 500mL of water, 6g of NaOH, process gas of 0 psig of CO, and residence time of 15 min)

Because biooil extracted using different organic solvents had similar elemental compositions, high heating values of biooil were not affected by extraction solvents either (Table 2). The mean high heating value of the biooil was 36.74 MJ/kg higher than 15.2 MJ/kg of cattle manure.

Table 2. High Heating values of biooil and cattle manure

| Biooil | Heating value( MJ/kg) | Standard derivation |
|---|---|---|
| Biooil(extracted by $CH_2Cl_2$) | 36.08 | 2.06 |
| Biooil(extracted by $CHCl_3$) | 35.55 | 0.99 |
| Biooil(extracted by $C_4H_{10}O$) | 36.56 | 0.18 |
| Cattle manure | 15.2 | 0.73 |

### EFFECTS OF EXTRACTION SOLVENTS ON CHEMICAL STRUCTURES OF BIOOIL

Result (Figure 4) showed that biooil spectra against wavelength were different from each other. Detail analysis showed that main components of biooil extracted by $CH_2Cl_2$ and $CHCl_3$ were ketones and carboxylic acids (205~300 nm), while those of biooil extracted by $C_4H_{10}O$ were aromatic chemicals (200~205 nm) [17].

As mentioned before, HTC biooil was more polar than petroleum, so organic solvents with higher polarity extracted more biooil. Now, spectra analysis did show that biooil extracted by relatively more polar organic solvents ($CH_2Cl_2$ and $CHCl_3$) contained more polar chemicals like ketones and carboxylic acids. In contrast, main components of the biooil extracted by the organic solvent with lower polar ($C_4H_{10}O$) contained less polar chemicals such as aromatic chemicals, as revealed by UV-VIS.

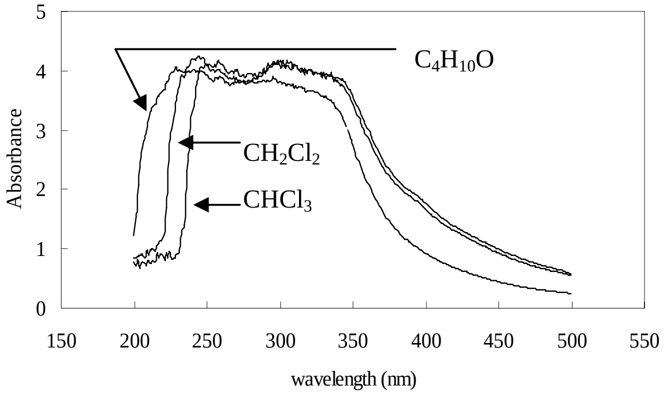

Figure 4. UV-VIS analysis spectra of biooil extracted by $C_4H_{10}O$, $CH_2Cl_2$ and $CHCl_3$.

(Conditions: 125g of cattle manure, 500mL of water, 6g of NaOH, process gas of 0 psig of CO, and residence time of 15 min)

## CONCLUSIONS

This paper studied effects of extraction solvents on biooil yields and chemical structures. There following conclusions can be drawn based on the tests.

(1) Extraction solvents affected the measured biooil yields. In this study, three organic solvents ($C_4H_{10}O$, $CHCl_3$ and $CH_2Cl_2$) were investigated and results showed that the highest biooil yield of 48.78% was obtained when using $CH_2Cl_2$.

(2) Extraction solvents did not influence the elemental compositions and corresponding high heating values of the biooil. The elemental compositions of biooil in this study were carbon of 73.79%, hydrogen of 8.18%, nitrogen of 4.38% and oxygen of 13.65%. And the mean high heating value of biooil was 36.74 MJ/kg.

(3) Extraction solvents influenced the chemical structures of biooil. The main components of biooil extracted by $CH_2Cl_2$ and $CHCl_3$ were ketones and carboxylic acids, while main components of biooil extracted by $C_4H_{10}O$ were aromatic chemicals.

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