

Catalytic pyrolysis of straw biomasses (wheat, flax, oat and barley straw) and the comparison of their product yields

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Abstract

Biomass can be converted through a biochemical and also thermochemical process. Pyrolysis is considered one of the thermochemical processes that can be used to breakdown biomass into a liquid product called bio-oil. Pyrolysis of Canadian straw biomasses was studied using a thermogravimetric analyzer (TGA) and a bench-scale horizontal fixed bed reactor, to understand the devolatilization process and, to obtain information about their product yields. In this work, the results of experimental studies on the pyrolysis of several Canadian biomasses are described. The pyrolysis of straw biomass was performed in a fixed-bed reactor at temperatures of 500°C, to study the influence of the feedstock on product distribution. The pyrolysis products were analyzed, and the effect of the catalyst on the product yield is also discussed. The yield of bio-oil and bio-char of the straw pyrolysis using zeolite catalysts was increased up to 46.44% and 38.77%, respectively; while the bio-gas yield was decreased to as low as 13.65%. The use of catalyst 2 (Zeolite YH2.2) had the most significant effect in increasing the yield of bio-oil about 2% and bio-char yield up to 8%. The use of catalyst number 2 also showed the most significant effect during pyrolysis of flax straw by increasing the bio-oil yield up to 46.44%. In the pyrolysis of oat straw, the use of catalyst consistently decreased the bio-gas yield; however, the bio-oil yield increased the most (43.32%) with the use of catalyst 1 (Zeolite YS2.2). The use of catalyst 1 also increased the bio-oil yield during the pyrolysis of barley straw (43.03%).

Keywords: biomass, biofuels, devolatilization process, kinetic of pyrolysis, proximate analysis, pyrolysis of biomass.



1 Introduction

Nowadays, biomass can be converted to various forms of energy through several different processes (chemical, biological, and thermochemical) as an alternative to fossil fuel such as gasoline and petrodiesel or into value added chemicals. Lignocellulosic straw biomass is considered one of the promising renewable feedstock for the production of chemicals and biofuels and they are widely available in prairie region of Canada. The use of biomass or waste biomass such as wheat straw, flax straw, barley straw, or sawdust for energy production will provides several advantages from environmental perspectives.

Biomass can be converted through chemical, biochemical and also thermochemical conversion. Pyrolysis is considered one of the thermochemical processes that can be used to breakdown some materials into a liquid product called bio-oil (Mahinpey *et al.* [1]). Although pyrolysis is an old technology, there has been a lot of progress in the past decade and is becoming more attractive than other thermochemical processes (Scott and Piskorz [2]; Mohan *et al.* [3]). During pyrolysis, the applied heat will decompose the materials into volatile compound (condensed and uncondensed material) that later will produce bio-char, bio-oil, and bio-gas.

Like wood, straws biomass (wheat, flax, barley, oat) are primarily composed of cellulose, lignin and hemicellulose (Bicho and Stumborg [4]). Each of straw biomass has different composition and suspected to have significant effects on the product yield and composition (Wang *et al.* [5]). Temperature of the reaction, heating rate, particle size, and residence time are parameters that significantly affect the properties of the product and its composition (Beis *et al.* [6]; Vamvuka [7]). For instance, Haykiri-Acma [8] suggested that increasing the heating rate to 50°C/min led to higher conversion rates due to the better mass and heat transfer inside the reactor (Biagini *et al.* [9]). In addition, the temperature of 500°C should be used to maximize the liquid oil yield (Mani *et al.* [10]). If these parameters are not used, secondary reactions may occur, thus decreasing the oil yield, which leads to higher yield of gas and char (Hosoya *et al.* [11]).

In this work, the results of experimental studies on the pyrolysis of several Canadian biomasses were described. The pyrolysis of straw biomasses (barley, flax, oat and wheat straw) was performed in a fixed-bed reactor at temperatures of 500°C to study the influence of the feedstock on product distribution. The pyrolysis products were analyzed, and the effect of the catalyst on the product yield was also discussed. To evaluate the effects of the zeolite catalyst on the straws, three forms of the zeolite catalysts were used (silica based solution, H-form of silica based solution, and silica sodium based solution). The results from the comparison of biomasses provide useful information about the suitability of biomass for particular end products such as bio-char, bio-oil, and bio-gas.



2 Experimental section

2.1 Materials

The straw biomass samples (barley, flax, oat and wheat straw) used in this study were obtained from a farm in Saskatchewan, Canada. Straws biomasses were ground and sieved to obtain an average particle size less than 1 mm. The chemical composition of the samples is given in Table 1.

Table 1: Chemical composition of wheat, flax, oat and barley straw samples.

	Wheat straw	Oat straw	Flax straw	Barley straw
Cellulose	34.2 ^a	37.6 ^a	53.0 ^b	33.8 ^c
Hemicellulose	23.7 ^a	23.3 ^a	13.0 ^b	21.9 ^c
Lignin	13.9 ^a	12.9 ^a	24.0 ^b	13.8 ^c

^aAdapa *et al.* [12]; ^bBuranov and Mazza [13]; ^cMussatto and Teixeira [14].

2.2 Proximate and ultimate analysis

Proximate analysis of straw has been performed using a thermogravimetric analyzer (NETZSCH TG 209 F1 Libra). All experiments consist of three different steps: drying, devolatilization in a nitrogen inert atmosphere, and combustion with air (Figure 1). About 10 mg of the sample with a particle size of 1 mm was used for this experiment. Initially, the biomass sample was kept at 25°C for 4 min in a nitrogen atmosphere. The moisture content was determined from the weight loss when the sample was heated at 85°C/min up to 110°C and held constant for 5 min. Devolatilization began once the temperature was at 110°C, and the heating rate of 80°C/min was maintained to 900°C. The final temperature was held constant for 7 min in an air atmosphere to allow for complete combustion. The flow rate of the nitrogen and air was maintained at 45 mL/min. An ultimate analysis was performed using a 2400 CHNS/O analyzer (2400 elemental analyzer, Perkin-Elmer). The results of proximate and ultimate analyses of the biomasses are given in Table 2.

Table 2: Proximate analyses of biomasses.

	Wheat straw	Oat straw	Flax straw	Barley straw
Moisture	5.3	4.38	4.75	2.69
Volatile	75.88	74.04	74.8	75.64
Fixed Carbon	14.12	18.37	19.32	17.28
Ash	4.69	3.21	1.12	4.38

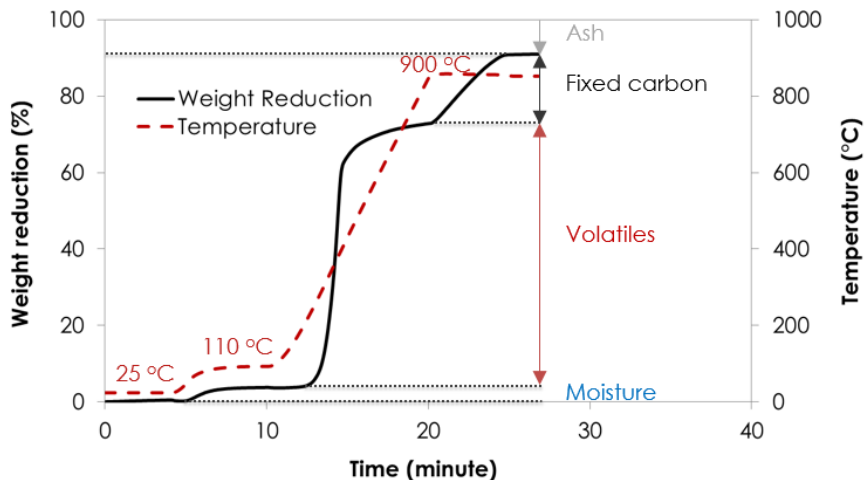


Figure 1: Typical TGA profile for proximate analysis using TGA.

Table 3: Elemental analysis of raw biomasses.

Composition	Wheat straw	Oat straw	Flax straw	Barley straw
C	43.64	43.26	46.76	44.83
H	5.82	6.12	6.34	6.25
N	0.68	0.88	1.11	0.93
S	1.08	1.14	1.14	1.18

2.3 Pyrolysis experiment

Pyrolysis experiments were carried out using a thermogravimetric analyzer (NETZSCH TG 209 F1 Libra) and a batch-type horizontal reactor enclosed by a horizontal split tubular furnace. The reactor consists of a stainless-steel tube with a length of 535 mm and inside diameter of 22.5 mm. Thermocouples were placed within the reactor system to measure the furnace temperature, pyrolysis reactor temperature, and outlet temperatures. Nitrogen was used as the inert gas with a constant flow rate of 50 mL/min throughout the process. During the experiments, the sample was heated at a rate of 100°C/min to a final temperature of 500°C at atmospheric pressure. At the end of the reactor, volatile products (gas and liquid) were separated using a separator that was submerged in a 0°C of liquid water-ice. The liquid products were collected and measured using a scale. The non-condensable gases were passed into an online gas chromatograph for gas analysis. For each experiment, 10 g of the straw biomass was loaded into the stainless-steel reactor. Each experiment was performed with the same amount of

straw under temperature of 500°C for about 1 hour. The product yield was determined by weighing the char and liquid amount and subtracting them from the initial biomass weight. All of the experiments were performed twice. The error associated with the data was within 5%.

3 Results and discussion

The result of proximate and ultimate analysis of all four biomass samples is presented on Table 2 and Table 3, respectively. The results demonstrate that the moisture content of the biomasses is in the range of 3–5%, volatile content is about 74–76%, fixed carbon is in the range of 14–19%, and ash content is below 5%. The volatile data from this analysis can be used to predict pyrolysis products. This volatile consist of condensable (bio-oil) and non-condensable material (bio-gas) that are produced during pyrolysis. The elemental analysis proved that the sulphur content of biomass is very small (~1%), while the oxygen content were about 45% (calculated by difference).

Table 4: Products comparison of pyrolysis of wheat, flax, oat and barley straw.

Yield	Wheat straw	Oat straw	Flax straw	Barley straw
Bio-char	36.21	32.65	32.14	33.51
Bio-oil	40.48	40.04	40.18	35.83
Bio-Gas	23.31	27.31	27.68	30.66

A comparison can be made between the volatile content produced and the yield of bio-oil and bio-gas altogether from each sample (Table 4). It was shown that the yield of both products during pyrolysis was close to the volatile content data of each sample with discrepancy about 7–9%. The total of bio-oil and bio-gas yield were always below the volatile content produced in proximate analysis. This discrepancy can be explained by the analysis of bio-char product from pyrolysis as shown on Table 5. The elemental analysis of bio-char produced during pyrolysis still contained about 3% of hydrogen and about as high as 26% oxygen. The availability of hydrogen, oxygen, and carbon in the char can be used to produce more volatiles (bio-oil and bio-gas) with the use of catalyst, faster heating rate, or perhaps different pyrolysis temperature.

A lower value of sulphur content on the bio-char (Table 5) compared to the value in the raw biomass sample (Table 3) suggested that half of the sulphur might be converted to SO₂ by oxidation, H₂S by reduction, and COS. Shao *et al.* [15] concluded that SO₂, H₂S, and COS gases can be produced under pyrolysis condition (200–500°C).

Table 5: Elemental analysis of bio-char produced from each biomass samples.

Composition	WS char	OS char	FS char	BS char
C	67.87	66.42	71.73	72.61
H	2.97	2.34	2.8	3.09
N	3.02	1.26	2.32	1.73
S	0.55	0.49	0.61	0.62

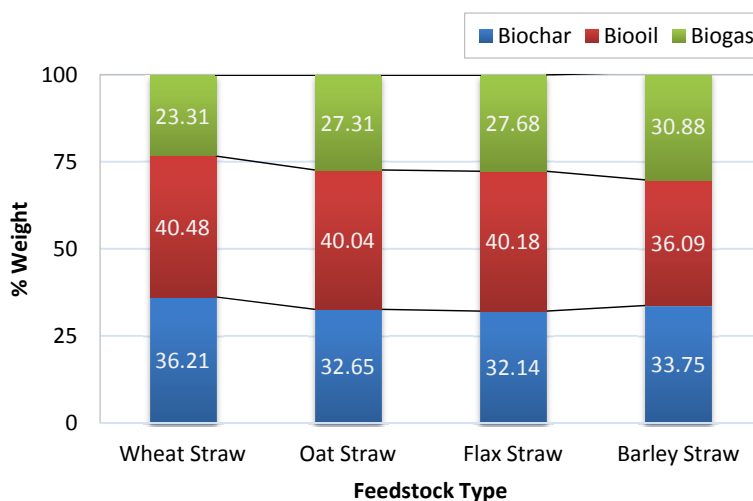


Figure 2: Product yields of biomasses pyrolysis.

The yield of pyrolysis products, such as liquid, gas, and char from all biomasses were presented in Figure 2. The bio-oil yield was maximized at 40.18% from wheat straw biomass, while the maximum gas yield of 30.88% was obtained from barley straw. In terms of bio-char product, the yield is in the range of 32.14% to 36.21%. The difference between the product yields between biomasses may be influenced by the composition of the raw biomasses (Table 1); however, there is no clear trend between the structural composition of biomasses and the yield of the product. Nonetheless, the ash composition data from proximate analysis suggest that the higher the ash content of the biomasses the lesser bio-gas can be produced during pyrolysis.

Three different catalysts have been used in the experiment in order to see their effect on the product yield. As seen in Table 6 and Figure 3, the use of catalyst 2 (Zeolite YH2.2) had the most significant effect in increasing the yield of bio-oil about 2% and bio-char yield up to 8%. Also, the use of catalyst number 2 confirmed the most significant effect during pyrolysis of flax straw by increasing

Table 6: Product comparison of pyrolysis of wheat straw using catalyst.

	Wheat straw	+ Catalyst 1	+ Catalyst 2	+ Catalyst 3
Bio-char	36.21	38.17	44.54	38.77
Bio-oil	40.48	40.81	41.81	41.51
Bio-gas	23.31	21.02	13.65	19.72

the bio-oil yield up to 46.44%. In the pyrolysis of oat straw, the use of catalyst decreased the bio-gas yield; however, the yield of bio-oil increased the most (43.32%) with the use of catalyst 1 (Zeolite YS2.2). The use of catalyst 1 also increased the bio-oil yield during the pyrolysis of barley straw (43.03%).

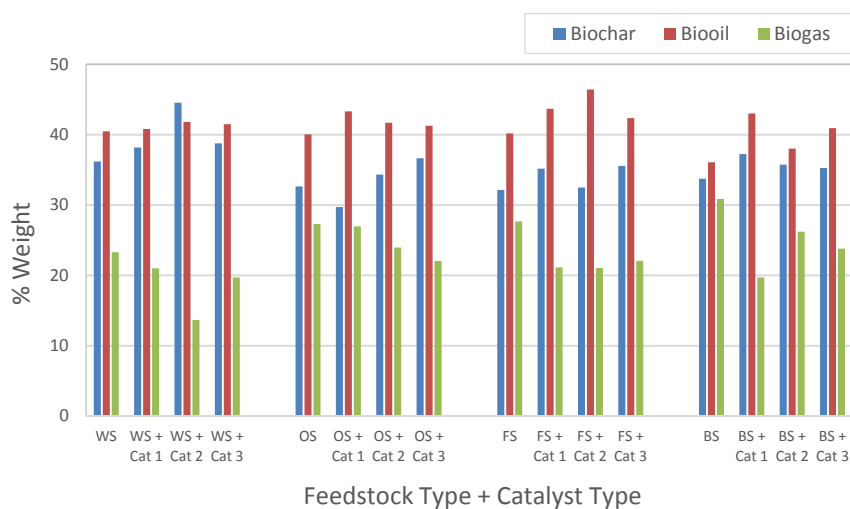


Figure 3: Comparison of the product yield among the biomasses.

4 Conclusions

The result of proximate analysis on raw biomasses can be used to predict the product yield produced during pyrolysis. The total yield of bio-oil and bio-gas were consistently lower than the volatile content produced in proximate analysis. The ash composition value from proximate analysis suggested that higher ash content suppressed the production of bio-gas. The pyrolysis of four different biomasses was performed with and without use of three different catalysts. It was observed that the bio-oil yield during the pyrolysis increased with the use of zeolite based catalyst. The use of Zeolite YH2.2 catalyst showed the most significant effect in increasing the bio-oil yield during the pyrolysis of wheat

straw and flax straw, whereas the use of Zeolite YS2.2 showed the most significant effect during the pyrolysis of oat and barley straw.

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