Characteristics of fast pyrolysis of corncob using $ZnCl_2$ for the production of furfural and acetic acid

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Abstract

Corncob was pyrolyzed using $ZnCl_2$ in a pyrolysis plant equipped with a fluidized bed reactor to produce furfural and acetic acid. The effects of reaction temperature and the $ZnCl_2$ content on the yields of furfural and acetic acid were investigated. The pyrolysis was performed within the temperature range between 310-410 °C, and the bio-oil yield were 30-58 wt% of the product. The furfural and acetic acid yields were 2 wt% and 13.1 wt%, respectively, when a corncob mechanically mixed with 20 wt% $ZnCl_2$ was pyrolyzed. Except water, these two compounds were the main compounds in the bio-oils. The high selectivity for furfural and acetic acid in the bio-oil obtained with $ZnCl_2$ would make the fast pyrolysis very economically attractive, because a high recovery efficiency of the two compounds from bio-oil can be expected.

Keywords: *Acetic acid, Furfural, Corncob, Pyrolysis, Fluidized bed, Bio-oil*

1. Introduction

Recently, the demand of fine chemicals has been increasing due to the rapid development of chemical industry. One of these fine chemicals is furfural which a platform chemical with a growing market. It has been widely used as a solvent, food additive and fungicide and also in the manufacture of pharmaceutical products, resins, and etc [1]. In contrast to most conventional fine chemicals which are generally petroleum-based, furfural is exclusively produced from renewable biomass resources. Industrial furfural production is presently conducted by acid catalytic dehydration of pentosan-containing lignocellulosic materials in a batch or continuous reactor [2]. Since this type of production method brings about tons of acid waste water, eco-friendly production methods have been passionately being researched. A promising alternative to the acid dehydration for the production of furfural is the pyrolysis of lignocellulosic biomasses consisting of cellulose, hemicelluloses, and lignin. For the furfural production by pyrolysis, corn residues such as corn stover and corncob, have been usually used. In particular, corncob is the widely used feedstock due to its rich contents of pentosans and cellulose among the common biomass materials. Meanwhile, acetic acid is an important chemical reagent and industrial chemical, mainly used in the production of cellulose acetate and polyvinyl acetate, as well as synthetic fibres and fabrics. Recently, about 75% of acetic acid made for use in the chemical industry is made by the carbonylation of methanol. Main aim of this study is to find the effects of reaction conditions, the $ZnCl_2$ content on the yields of furfural and acetic acid. The quantification of furfural and acetic acid in the bio-oil was performed with the GC external standard method.

2. Materials and Methods

Material. The feed material, corncob, was obtained from a farm in Korea. It was first ground using a grinder, and then sieved to obtain material with a diameter 0.425-1 mm. The material was then dried in an oven at 105 °C for 72 hr and was then used in each operation.

Pyrolysis plant and procedure. The fast pyrolysis plant was composed of a feeding system, fluidized bed reactor, char separation system, quenching system and product gas circulation system. A diagram of the plant is shown in Fig. 1.

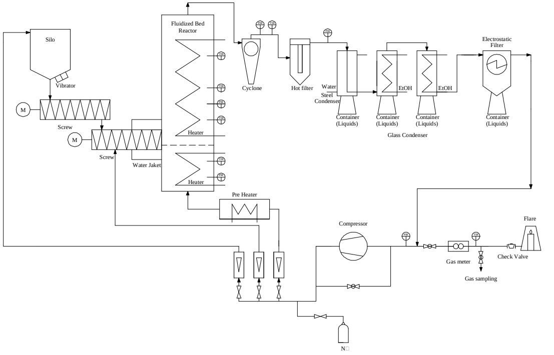

Fig. 1 Pyrolysis plant

The key part of the plant is the fluidized bed with a height of 390 mm and an inner diameter of 110 mm, which is made of a 316 SS tube. To monitor the reaction temperature and fluidization behavior during pyrolysis, three thermocouples are installed inside the reactor. The pyrolysis reaction temperature is determined by the average value of the three thermocouples. The fluidized bed reactor is heated indirectly in an electric heater. The feeding system is comprised of two screw feeders which help load material uniformly and directly into sand in the fluidized bed. To avoid a reflow of pyrolysis vapor into the feed system, part of the product gas is introduced into the silo and feeder during experiment. The char separation system is composed of a cyclone and ceramic hot filter designed to capture particle bigger than 10 and 2 µm, respectively. The quenching system consists of one water-cooled steel condenser and two ethanol-cooled glass condensers, which operate at 20 and -25 °C, respectively. To capture aerosols, an electrostatic precipitator behind the condensers is used. Part of the product gas is either burned in a stack to regulate the pressure in the plant or is used for gas sampling. Much of the product gas is circulated into the fluidized bed reactor through a pre-heater using a compressor for fluidization. **Reaction condition.** In each experiment, the input of the feed material was 100 g, and 2.6 kg quartz sand with a mean diameter of 0.4 mm was used as the fluidized bed material. The feed rate was about 2 g/min, and the product gas was used for the fluidizing medium. To maintain a constant residence time of pyrolysis vapor in the reactor, the flow rate of product gas was corrected with respect to the reaction temperature. Main reaction conditions are shown in Table 1.

Table 1. Reaction conditions

Parameters	Run				
	1	2	3	4	5
Reaction temperature (°C)	311	357	411	356	358
Feed rate (g/min)			2		
Flow rate (NL/min)	38	36	33	36	36
Feed size (mm)			0.425-1		
ZnCl2 content (wt%)		0		10	20

Main reaction parameter was reaction temperature (Effects of other parameters will also be presented in conference). Also, the effect of the $ZnCl_2$ content on the yields of furfural and acetic acid were investigated. To see the influence of reaction temperature on the product spectrum, Runs 1 to 3 were conducted; to find the influence of the $ZnCl_2$ content in the mechanical mixing, Runs 4 and 5 were carried out for comparison with Run 2. **Analysis of products.** Pyrolysis products were divided into three fractions: bio-oil, gas and char. The water content of each bio-oil was measured using a Karl Fischer titrator. Bio-oil was qualitatively and quantitatively analyzed by comparing the peaks obtained by a GC-FID and a GC-MS. For the quantification of furfural and acetic acid in bio-oil, a calibration curve for each compound was established using standard solutions. The concentration of each compound in a bio-oil sample could be graphically determined. The pyrolysis gases were analyzed offline using GC-TCD and GC-FID, with argon as the carrier gas

3. Results and Discussion

Product distribution. In all experiments, mass balances were established. Table 2 shows product mass balances of the experiments. In the case of the bio-oils obtained without $ZnCl_2$, the bio-oil yield was between 48-58 wt% with the water content of about 57 wt%. With increasing the amount of $ZnCl_2$, the bio-oil yield strongly was reduced.

Table 2. Mass balance

Products (wt%)	Run				
	1	2	3	4	5
Oil	48.2	52.7	58.3	46.3	29.8
(water)	(57)	(57)	(56.9)	(62.4)	(68.1)
Gas	17.7	21.5	24.3	16.8	14.9
Char	34.1	25.8	17.5	36.9	55.3

Effects of reaction parameters on the furfural and acetic acid yields. Table 3 shows the influences of reaction temperature and the $ZnCl_2$ content on the furfural and acetic acid yields. In the absence $ZnCl_2$, the furfural yield increased, then maximized and finally decreased with increasing reaction temperature from 311 to 411 °C; whereas the acetic acid concentration was gradually increased. With increasing the $ZnCl_2$ content, the furfural and acetic acid yields gradually was increased.

Table 3. Yields of furfural and acetic aicd

Yield (wt%)	Run				
	1	2	3	4	5
Furfural	0.2	0.8	0.6	1.4	2
Acetic acid	4.6	6.2	9.9	10.4	13.1

4. Conclusions

In this study, a bench scale fast pyrolysis of corncob was conducted to co-produce furfural and acetic acid, and the effects of reaction temperature and the $ZnCl_2$ content on the yields of furfural and acetic acid were investigated. The pyrolysis was performed within the temperature range between 310-410 °C. The bio-oil yield was 30-58 wt% of product. The main compounds of bio-oil obtained were acetic acid, hydroxyacetic acid, furfural and hydroxyacetone. The furfural yield was positively influenced by the increasing $ZnCl_2$ content, and its maximum yield was 2 wt% of the product. Under the same conditions, the maximum acetic acid yield (13.1 wt% of the product) was achieved

References

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