In-situ catalytic pyrolysis of lignin in a bench-scale fixed bed pyrolyzer

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A B S T R A C T

Thermal and in-situ catalytic pyrolysis of lignin were carried out in a bench-scale pyrolyzer. The yield and composition of the bio-oil produced were influenced largely by the type of lignin samples, pyrolysis temperature, and nitrogen carrier gas flow rate. The highest bio-oil yield of 35.95 wt.% was achieved using kraft lignin at 500 °C and a carrier gas flow rate of 600 ml/min. In-situ catalytic pyrolysis resulted in a decrease of the bio-oil yield, but the aromatic product distribution was altered greatly depending on the types of catalysts. In-situ catalytic pyrolysis also showed enhanced selectivity to valuable aromatic hydrocarbons.

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Introduction

Lignocellulosic biomass, consisting of cellulose, hemicellulose and lignin, is considered a major sustainable energy resource that might be a substitute for depleting fossil fuels [1–3]. In this regard, the thermochemical conversion of lignocellulosic biomass to biofuels or biobased chemicals/materials has attracted considerable interest [4–16]. Among the various thermochemical conversion processes, the fast pyrolysis of biomass can convert solid biomass directly to a liquid fuel, called pyrolysis oil or bio-oil [2,17]. Lignin constitutes 15–30% of the biomass weight and 40% of the biomass energy [18–20], and is an asymmetric macromolecule with a complex, amorphous cross-linked and highly branched structure. Lignin is composed mainly of the building blocks of p-coumaryl, coniferyl, and sinapyl alcohols [19–21]. The complex three dimensional structure of lignin includes polymerized phenyl propane units linked through C—O (ether) or C—C bonds [22–25]. Lignin is considered a high potential feedstock for the production of aromatic chemicals due the polyaromatic structure [19,22,26–34]. Monomeric phenols, such as guaiacols, syringols, alkylphenols, and catechols, are the main products of the fast pyrolysis of

lignin [15,20]. Catalytic pyrolysis, which is pyrolysis in the presence of catalyst, is an efficient technique for enhancing the production of monomeric phenols from lignin and further deoxygenating phenolic compounds to aromatic hydrocarbons. During catalytic pyrolysis, the catalysts can eliminate the oxygen content of pyrolysis vapors through reactions, such as decarboxylation, decarbonylation and dehydration.

Catalytic pyrolysis can be classified into in-situ and ex-situ configurations. In in-situ pyrolysis, catalyst is mixed with feedstock, while in ex-situ pyrolysis, the catalyst bed is separated from the pyrolyzer and thus pyrolysis vapors are passed through a catalyst bed after pyrolysis [35]. Compared to ex-situ pyrolysis, the lower capital and operating costs are expected for in-situ pyrolysis because of its one reactor configuration [36,37]. On the other hand, separate zones of pyrolysis and catalytic reactions in the ex-situ configuration allows optimization of the reaction conditions for pyrolysis and catalytic upgrading. Thus far, ZSM-5 zeolite has been used in in-situ and ex-situ catalytic pyrolysis [35–38]. Yildiz et al. [38], who examined the non-catalytic and in-situ/ex-situ catalytic fast pyrolysis of biomass using ZSM-5, reported enhanced deoxygenation of pyrolysis vapors and reduced oil yield using a catalyst. Iisa et al. [36] reported that faster catalyst deactivation occurred in the in-situ pyrolysis of pine biomass over HZSM-5 compared to ex-situ pyrolysis. Enhanced production of valuable aromatics and olefins was reported in both the in-situ and ex-situ pyrolysis of hybrid poplar biomass using the

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HZSM-5 catalyst [35]. An investigation of the effects of pyrolysis and catalytic bed temperatures on the product distribution of HZSM-5 in the *ex-situ* catalytic pyrolysis of hybrid poplar biomass indicated that the pyrolysis temperature had no significant effect on the product selectivity, whereas high temperatures in the catalyst bed shifted the product selectivity favorably from aromatics to olefins [35].

In this study, the potential of different types of lignin (kraft lignin, dealkaline lignin, organosolv lignin and klason lignin) for bio-oil production was assessed using a bench-scale pyrolyzer. The effects of the pyrolysis temperature and nitrogen carrier gas flow rate on the yield and composition of bio-oil were also investigated using kraft lignin as feedstock. A range of zeolite and non-zeolite type catalysts were tested for the *in-situ* catalytic pyrolysis of kraft lignin. The efficiency of the catalysts was evaluated in terms of the product yields and selectivity.

Experimental

Materials

The powder form of kraft lignin, dealkaline lignin, organosolv lignin, and klason lignin were used as biomass model components in the fast pyrolysis experiments. The first two lignins were purchased from Sigma–Aldrich and Tokyo Chemical (Japan), respectively, and the last two lignins were obtained from Sugaren Co. (Korea). Table 1 summarizes the results of proximate and ultimate analysis of the lignins. The lignin samples were dried overnight at 110 °C before the experiments.

The catalytic materials used for the *in-situ* lignin pyrolysis experiments were commercial alumina, spent FCC (from a local company in Korea), HZSM-5 (SiO_2/Al_2O_3 of 30, Zeolyst International), HBeta (SiO_2/Al_2O_3 of 25, Zeolyst International), HY (SiO_2/Al_2O_3 of 30, Zeolyst International), and MgO (Samchun Chemical). With the exception of MgO, all the catalysts were calcined at 550 °C for 3 h. MgO was not calcined to prevent the possibility of carburization of MgO to $MgCO_3$. Silica sand and lignin char were also used in the *in-situ* pyrolysis of lignin.

Thermogravimetric analysis (TGA) of lignin

TGA (PerkinElmer, US/Pyris Series) was conducted to study the pyrolysis behavior of kraft lignin, dealkaline lignin, organosolv lignin, and klason lignin. A 5 mg sample of lignin was heated from ambient temperature to 700 °C at a rate of 30 °C/min under a nitrogen carrier gas at a flow rate of 20 ml/min.

Fast pyrolysis experiments

The fast pyrolysis experiments were carried out in a bench-scale pyrolyzer (ID 50 mm, height 400 mm) (Fig. S1). The pyrolyzer was heated by a slidable furnace controlled by a PID controller. A down flow of purified nitrogen (99.9%) was used to provide an oxygen-free atmosphere for pyrolysis. The char, which is the solid residue of pyrolysis, remaining inside the reactor was weighed after the experiment. The pyrolysis-derived vapors were passed through four condensers. The first condenser was cooled by the surrounding air and the other condensers were cooled using an anti-freezing liquid at −30 °C. The condensable products were collected in the oil samplers connected to the condensers. The mass of pyrolysis oil including the aqueous and organic phases was obtained by weighing the condensers and oil samplers after the reaction. The organic phase was separated and analyzed by gas chromatography/mass spectrometry (GC/MS 7890A Agilent Technologies) using acetone as the solvent. An Ultra alloy-5 column (30 m × 250 μm × 0.25 μm) was employed and the GC was equipped with a split injector at 300 °C with a split ratio of 10:1. Pure helium was used as the carrier gas with a flow rate of 1 ml/min. The GC oven temperature program was as follows: 40 °C for 4 min, 40–200 °C at 5 °C/min, 200–300 °C at 20 °C/min, an 300 °C for 10 min. Compound identification was carried out using the NIST (National Institute of Standards and Technology) library. Non-condensable gases were collected in a 20 l gas bag to be analyzed by gas chromatography/thermal conductivity detector/flame ionization detector (GC/TCD/FID). The GC/TCD was equipped with a Carboxen 1000 (15 ft × 1/8 in.) column and the carrier gas was helium (20 ml/min) with injector and detector temperatures of 150 °C. The GC/TCD oven temperature program was as follows: 35 °C for 5 min, 35–225 °C at 15 °C/min, and 225 °C for 10 min. The GC/FID was equipped with a HP-plot Al_2O_3/KCl (50 m × 0.322 m × 8 μm) column with a split ratio of 10:1 and injector and detector temperatures of 200 and 250 °C, respectively. The GC/FID oven temperature program was as follows: 40 °C for 5 min, 40–160 °C at 4 °C/min, 160–200 °C at 2 °C/min, and 200 °C for 40 min.

In the non-catalytic fast pyrolysis experiments, lignin (100 g) was loaded inside the reactor. The pyrolysis temperature and nitrogen carrier gas flow rate were optimized in the ranges of 400–700 °C and 400–700 ml/min, respectively.

In-situ catalytic fast pyrolysis was carried out by loading the kraft lignin (50 or 100 g) with silica sand (100 g), lignin char (100 g), alumina (100 g), spent FCC (100 g), HZSM-5 (50 g), HBeta (50 g), HY (50 g), and MgO (50 g) inside the feedstock zone of the reactor. All catalytic pyrolysis experiments were carried out at a pyrolysis temperature of 500 °C and a nitrogen flow rate of 600 ml/min.

The yields of char (solid residue), oil, and gas produced from the fast pyrolysis of lignin were calculated using the following equations:

Char yield (wt.%) = (weight of reactor loaded with lignin-weight of reactor after experiment)/initial weight of lignin

Oil yield (wt.%) = (weight of the collected condensable products)/initial weight of lignin

Gas yield (wt.%) = (initial weight of lignin-weight of char-weight of oil)/initial weight of lignin

Table 1
Physical properties of kraft lignin, dealkaline lignin, organosolv lignin, and klason lignin.

	Ultimate analysis (wt.%)					Proximate analysis (wt.%)			
	C	H	O[a]	N	S	Moisture	Volatiles	Fixed carbon	Ash
Kraft lignin	62.45	5.68	30.61	0.56	0.7	1.8	62.9	32.6	2.7
Dealkaline lignin	47.99	4.33	44.45	0.14	3.09	1.7	57.3	34.7	6.3
Organosolv lignin	58.04	4.82	37.14	0	0	2.3	60.4	36.5	0.8
Klason lignin	65.45	5.71	26.99	0.37	1.48	1.4	53.5	37.6	7.5

a By difference.