Journal of Industrial and [Engineering](http://dx.doi.org/10.1016/j.jiec.2017.06.026) Chemistry xxx (2017) xxx–xxx

Journal of Industrial and Engineering Chemistry

journal homepage: where j

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

² � Hoda Shafaghat^{a,1}, Pouya Sirous Rezaei^{a,1}, Donghoon Ro^{a,1}, Jungho Jae^{b,c,1}, ³ Beom-Sik Kim^a, Sang-Chul Jung^d, Bong Hyun Sung^e, Young-Kwon Park^{a,*}

4 a School of Environmental Engineering, University of Seoul, Seoul 02504, Republic of Korea
5 b Clean Energy Perserch Center Korea Institute of Science and Technology Seoul 02702, Re

5 b Clean Energy Research Center, Korea Institute of Science and Technology, Seoul 02792, Republic of Korea
6 **b** Characteristic of Clean Energy and Characteristic Maria Wave University of Grimman A Technology Devi

6 c Department of Clean Energy and Chemical Engineering, Korea University of Science and Technology, Daejeon 34113, Republic of Korea

20 department of Environmental Engineering, Sunchon National University, Suncheon 57922, Republic of Korea
28

^e Bioenergy & Biochemical Research Center, Korea Research Institute of Bioscience & Biotechnology, Daejeon 34141, Republic of Korea

A R T I C L E I N F O

Article history: Received 6 March 2017 Received in revised form 3 June 2017 Accepted 17 June 2017 Available online xxx

Keywords: In-situ catalytic pyrolysis Lignin Bio-oil Aromatic hydrocarbons Phenolics

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 \degree 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.

© 2017 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.

> pyrolysis and catalytic upgrading. Thus far, ZSM-5 zeolite has been $\frac{45}{100}$
used in in situ and av situ catalytic pyrolygis [25, 29]. Vildiz et al. used in *in-situ* and *ex-situ* catalytic pyrolysis [35–[38\].](#page--1-0) Yildiz et al. 46
[38] who examined the non-catalytic and in citylex city establise 47 [\[38\]](#page--1-0), who examined the non-catalytic and in-situ/ex-situ catalytic 47
fact, purplyist of biomass, using $75M_5$, reported, ophanced 48 fast pyrolysis of biomass using ZSM-5, reported enhanced ⁴⁸
deovymention of pyrolygic vapors and reduced eil viold using a 49 deoxygenation of pyrolysis vapors and reduced oil yield using a 49
catalyst lisa et al. [36] reported that faster catalyst deactivation 50 catalyst. Iisa et al. [\[36\]](#page--1-0) reported that faster catalyst deactivation 50
occurred in the *in-situ* pyrolysis of pine biomass over 51 occurred in the *in-situ* pyrolysis of pine biomass over 51
HZSM-5 compared to ex-situ pyrolysis Enhanced production of 52 HZSM-5 compared to *ex-situ* pyrolysis. Enhanced production of 52
valuable aromatics and olefins was reported in both the *in-situ* and 53 valuable aromatics and olefins was reported in both the *in-situ* and $\frac{53}{2}$ ex-situ pyrolysis of hybrid poplar biomass using the

⁹ Introduction

10 Lignocellulosic biomass, consisting of cellulose, hemicellulose
11 and lignin is considered a major sustainable aperay researce that ¹¹ and lignin, is considered a major sustainable energy resource that $\frac{12}{12}$ m this regard 12 might be a substitute for depleting fossil fuels $[1-3]$ $[1-3]$. In this regard,
13 the thermochamical conversion of lignocally logic highest to 13 the thermochemical conversion of lignocellulosic biomass to 14 biofuels or biobased epomicals materials has attracted consider 14 biofuels or biobased chemicals/materials has attracted consider-
 15 belo interest [4, 16]. Among the various thermoshemical converable interest $[4-16]$ $[4-16]$. Among the various thermochemical conver- 16 sion processes, the fast pyrolysis of biomass can convert solid
 17 biomass directly to a liquid fuel called pyrolygic oil or bio oil [2,17] ¹⁷ biomass directly to a liquid fuel, called pyrolysis oil or bio-oil [\[2,17\].](#page--1-0)
¹⁸ Lignin constitutes 15, 20% of the biomass weight and 40% of the ¹⁸ Lignin constitutes 15–30% of the biomass weight and 40% of the biomass approximates in the biomass weight and 19 19 biomass energy $[18-20]$ $[18-20]$, and is an asymmetric macromolecule
 20 bights assembly approximately recordinated and highly happened ²⁰ with a complex, amorphous cross-linked and highly branched
²¹ etrusture Lignin is composed mainly of the huilding blocks of 21 structure. Lignin is composed mainly of the building blocks of 22 securing conjecture and signal dependent of 22 securing 21 . The complex 22 p-coumaryl, coniferyl, and sinapyl alcohols $[19-21]$. The complex
 23 three dimensional structure of limin includes polymerized phopul 23 three dimensional structure of lignin includes polymerized phenyl
24 propaga units linked through C_1 , $O(\text{other})$ or C_2 , C_3 bonds [22, 25] 24 propane units linked through C- \sim O (ether) or C- \sim C bonds [22–[25\].](#page--1-0)

25 Lignin is considered a high potential feedstock for the production

26 cf aromatic chemicals due the polyaromatic structure [19.22.26]. ²⁶ of aromatic chemicals due the polyaromatic structure $[19,22,26-27]$ $[19,22,26-27]$ and Monomeric phenols, such as guidagely syringels, allyeinha- $\frac{27}{28}$ [34\]](#page--1-0). Monomeric phenols, such as guaiacols, syringols, alkylphe-
 $\frac{28}{28}$ and sates help are the main products of the fast pyrolysis of nols, and catechols, are the main products of the fast pyrolysis of

E-mail address: [catalica@uos.ac.kr](undefined) (Y.-K. Park).

<http://dx.doi.org/10.1016/j.jiec.2017.06.026>

1226-086X/© 2017 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.

Please cite this article in press as: H. Shafaghat, et al., In-situ catalytic pyrolysis of lignin in a bench-scale fixed bed pyrolyzer, J. Ind. Eng. Chem. (2017), <http://dx.doi.org/10.1016/j.jiec.2017.06.026>

Corresponding author.

Co-first authors.

2 H. Shafaghat et al. / Journal of Industrial and Engineering Chemistry xxx (2017) xxx–xxx

 55 HZSM-5 catalyst [\[35\]](#page--1-0). An investigation of the effects of pyrolysis 56 and extending bod temperatures on the product distribution of 56 and catalytic bed temperatures on the product distribution of 57 57 HZSM-5 in the ex-situ catalytic pyrolysis of hybrid poplar biomass
 58 is distant that the appropriate temperature had as similar that of set 58 indicated that the pyrolysis temperature had no significant effect
 59 en the product selectivity, whereas high temperatures in the 59 on the product selectivity, whereas high temperatures in the 60 catalyst had shifted the product selectivity favorably from 60 catalyst bed shifted the product selectivity favorably from
 61 aromatics to olefins [35] 61 aromatics to olefins [\[35\]](#page--1-0).
 62 In this study the pote

 $\frac{62}{100}$ In this study, the potential of different types of lignin (kraft $\frac{63}{100}$ lignin deally line lignin organosoly lignin and klason lignin) for ⁶³ lignin, dealkaline lignin, organosolv lignin and klason lignin) for 64 bio-oil production was assessed using a bench-scale pyrolyzer. The 64 bio-oil production was assessed using a bench-scale pyrolyzer. The 65 effects of the pyrolysis temperature and pitrogen carrier gas flow. ⁶⁵ effects of the pyrolysis temperature and nitrogen carrier gas flow
 $\frac{66}{100}$ ante an the vial d and composition of his ail were also investigated ⁶⁶ rate on the yield and composition of bio-oil were also investigated $\frac{67}{2}$ rates with a feature and proposition 67 using kraft lignin as feedstock. A range of zeolite and non-zeolite 68 type catalytic weak for the in city catalytic pyrolysic of kraft ⁶⁸ type catalysts were tested for the *in-situ* catalytic pyrolysis of kraft
 $\frac{69}{100}$ lignin. The efficiency of the catalytic was evaluated in terms of the ⁶⁹ lignin. The efficiency of the catalysts was evaluated in terms of the $\frac{70}{10}$ product vields and selectivity product yields and selectivity.

⁷¹ Experimental

⁷² Materials

 73 The powder form of kraft lignin, dealkaline lignin, organosolv
 74 Units and klasse limin was used to kissues and also proposed 74 lignin, and klason lignin were used as biomass model components 75 in the fast pyrolysis experiments. The first two lignins were ⁷⁶ purchased from Sigma–Aldrich and Tokyo Chemical (Japan),
⁷⁷ secondatively and the last two liming were obtained from Sugaren 77 respectively, and the last two lignins were obtained from Sugaren
78 $\frac{1}{2}$ Co. (Korea), Table 1, summarizes the results of provimate and 78 Co. (Korea). Table 1 summarizes the results of proximate and 79 ultimate analysis of the liquing. The liquing samples were dried ⁷⁹ ultimate analysis of the lignins. The lignin samples were dried
⁸⁰ overnight at 110 °C before the experiments ⁸⁰ overnight at 110 \degree C before the experiments.
⁸¹ The catalytic materials used for the in

⁸¹ The catalytic materials used for the *in-situ* lignin pyrolysis
⁸² experiments were commercial alumina spent ECC (from a local ⁸² experiments were commercial alumina, spent FCC (from a local
⁸³ company in Korea), HZSM-5 (SiO_s/Al-O_p of 30, Zeolyst Interna-⁸³ company in Korea), HZSM-5 (SiO₂/Al₂O₃ of 30, Zeolyst Interna-
⁸⁴ tional), UPsta (SiO₂/Al₂O₂ of 25, Zealyst International), UV (SiO₄) ⁸⁴ tional), HBeta (SiO₂/Al₂O₃ of 25, Zeolyst International), HY (SiO₂/
⁸⁵ Al Q of 20 Zeolyst International), and MgQ (Samshun Chamical) 85 A_2O_3 of 30, Zeolyst International), and MgO (Samchun Chemical).
86 With the exception of MgO all the extal veta vera salcined at 550 °C. ⁸⁶ With the exception of MgO, all the catalysts were calcined at 550 °C
⁸⁷ for 3b, MgO, was not calcined to prevent the possibility of 87 for 3 h. MgO was not calcined to prevent the possibility of 88 carburization of MgO to MgCO. Silica sand and limin characters ⁸⁸ carburization of MgO to MgCO₃. Silica sand and lignin char were $\frac{89}{1}$ also used in the *in-situ* pyrolysis of lignin.

⁹⁰ Thermogravimetric analysis (TGA) of lignin

⁹¹ TGA (PerkinElmer, US/Pyris Series) was conducted to study the ⁹² pyrolysis behavior of kraft lignin, dealkaline lignin, organosolv
⁹³ lignin and klason lignin, A.5 mg sample of lignin was beated from ⁹³ lignin, and klason lignin. A 5 mg sample of lignin was heated from $\frac{94}{28}$ exists the ligning of $\frac{1}{28}$ 94 ambient temperature to 700 °C at a rate of 30 °C/min under a
95 antrogen carrier gas at a flow rate of 20 ml/min nitrogen carrier gas at a flow rate of 20 ml/min.

⁹⁶ Fast pyrolysis experiments

97 The fast pyrolysis experiments were carried out in a bench-
98 scale pyrolyzer (ID 50 mm height 400 mm) (Fig. S1). The ⁹⁸ scale pyrolyzer (ID 50 mm, height 400 mm) (Fig. S1). The pyrolyzer was beated by a slidable furnage controlled by a PID ⁹⁹ pyrolyzer was heated by a slidable furnace controlled by a PID
¹⁰⁰ controller. A down flow of purified pitrogen (99.9%) was used to ¹⁰⁰ controller. A down flow of purified nitrogen (99.9%) was used to $\frac{101}{2}$ provide an oxygen-free atmosphere for pyrolysis. The characteristic 101 provide an oxygen-free atmosphere for pyrolysis. The char, which 102 is the solid residue of pyrolysis remaining inside the reactor was is the solid residue of pyrolysis, remaining inside the reactor was

weighed after the experiment. The pyrolysis-derived vapors were 103
access the pyrolysis-derived vapors were scaled passed through four condensers. The first condenser was cooled 104
his the concentration site and the other condensers was cooled by the surrounding air and the other condensers were cooled 105
using a particle simulation using an anti-freezing liquid at -30° C. The condensable products 10°
were collected in the eil camplers connected to the condensary 10° were collected in the oil samplers connected to the condensers. 107
The mass of purclusis oil including the aqueous and erganic The mass of pyrolysis oil including the aqueous and organic 108
phases was obtained by weighing the condensers and eil phases was obtained by weighing the condensers and oil 109
samplers after the reaction. The organic phase was separated samplers after the reaction. The organic phase was separated 110
and analyzed by me chromatography/mass spectrometry/CC/MS and analyzed by gas chromatography/mass spectrometry (GC/MS) and $T2800A$ Agilent Technologies) using acetone as the solvent. An 7890A Agilent Technologies) using acetone as the solvent. An 112
Ultra alloy-5 column (30 m × 250 um × 0.25 um) was employed 113 Ultra alloy-5 column $(30 \text{ m} \times 250 \text{ }\mu\text{m} \times 0.25 \text{ }\mu\text{m})$ was employed 113
and the CC was equipped with a split injector at $300\degree$ C with a and the GC was equipped with a split injector at 300° C with a 114
split ratio of 10:1 Pure belium was used as the carrier gas with a split ratio of 10:1. Pure helium was used as the carrier gas with a 115
flow rate of 1 ml/min. The CC even temperature pregram was as flow rate of 1 ml/min. The GC oven temperature program was as 116
follows: $40\degree$ C for 4 min. $40\degree$ 200 \degree C at $5\degree$ C/min. 200 \degree C at follows: 40° C for 4 min, $40-200^{\circ}$ C at 5° C/min, 200–300 °C at 117
20 °C/min, an 300 °C for 10 min. Compound identification was 20 °C/min, an 300 °C for 10 min. Compound identification was 118
carried out using the NIST (National Institute of Standards and carried out using the NIST (National Institute of Standards and 119
Technology) library Non-condancable gases were collected in a ¹²⁰ Technology) library. Non-condensable gases were collected in a 201 gas bag to be analyzed by gas chromatography/thermal 121
conductivity detector/flame ionization detector (CCTCD/EID) 122 conductivity detector/flame ionization detector (GC/TCD/FID). 122
The GC/TCD was equivased with a Garbonic 1999 (15 ft. 1/9 in). The GC/TCD was equipped with a Carboxen 1000 (15 ft \times 1/8 in.) 123 column and the carrier gas was helium (20 ml/min) with injector 124
and ditactor temperatures of 150% . The GG/TCD sum temperature and detector temperatures of 150 °C. The GC/TCD oven tempera-
ture approximation of the subset of the General property of the 126 ture program was as follows: 35° C for 5 min, $35-225^{\circ}$ C at 126
15.00 km and 325.00 for 10 min. The CO/FID was explied with a 15 °C/min, and 225 °C for 10 min. The GC/FID was equipped with a 127
HP plot ALO *IVCL* (50 m \times 0.222 m \times 8 um) column with a split HP-plot Al_2O_3/KCl (50 m \times 0.322 m \times 8 μ m) column with a split 128
ratio of 10:1 and injector and detector temperatures of 200 and 129 ratio of 10:1 and injector and detector temperatures of 200 and ¹²⁹
250.06, respectively. The CC/EID over temperature program was 250 °C, respectively. The GC/FID oven temperature program was 130
as follows: $40\degree$ G for 5 min 40, 160 °C at $4\degree$ G/min 160, 200 °C at as follows: 40° C for 5 min, $40-160^{\circ}$ C at 4° C/min, $160-200^{\circ}$ C at 2° C/min, and 200° C for 40 min 2° C/min, and 200 °C for 40 min. 132
In the non-catalytic fast pyrolygic experiments lignin (100 g)

In the non-catalytic fast pyrolysis experiments, lignin $(100 g)$ 133
s loaded inside the reactor. The pyrolysis temperature and was loaded inside the reactor. The pyrolysis temperature and 134
pitrogen carrier gas flow rate were optimized in the ranges of nitrogen carrier gas flow rate were optimized in the ranges of 135
400, 700 °C and 400, 700 ml/min, recnestively 136 400–700 °C and 400–700 ml/min, respectively. 136
In situ extalutio fact purolusis was carried out by loading the

In-situ catalytic fast pyrolysis was carried out by loading the 137
ft lignin (50 or 100 g) with silica sand (100 g) lignin char kraft lignin (50 or 100 g) with silica sand (100 g), lignin char 138
(100 g) alumina (100 g) spent ECC (100 g) HZSM 5 (50 g) HBeta (100 g), alumina (100 g), spent FCC (100 g), HZSM-5 (50 g), HBeta 139
(50 g), HV (50 g), and MgO (50 g) inside the feedstock zone of the $(50 g)$, HY ($50 g$), and MgO ($50 g$) inside the feedstock zone of the 140
reactor All catalytic pyrolygic experiments were carried out at a reactor. All catalytic pyrolysis experiments were carried out at a 141
pyrolysis temperature of 500% and a pitrogen flow rate of pyrolysis temperature of 500 °C and a nitrogen flow rate of 142
600 ml/min 143 143
The vielde of char (colid residue) eil, and gas produced from the

The yields of char (solid residue), oil, and gas produced from the 144
the purclusing of digning the selection of the following 145 ¹⁴⁵ fast pyrolysis of lignin were calculated using the following equations:

Char yield $(wt.\%) = (weight of reactor loaded with lignin-weight of 147$
reactor after experiment)/initial weight of lignin reactor after experiment)/initial weight of lignin

Oil yield (wt.%) = (weight of the collected condensable products)/ 149
initial woight of lignin initial weight of lignin

Gas yield (wt.%) = (initial weight of lignin-weight of char-weight of 151
oil)/initial weight of lignin oil)/initial weight of lignin

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

^a By difference.

Please cite this article in press as: H. Shafaghat, et al., In-situ catalytic pyrolysis of lignin in a bench-scale fixed bed pyrolyzer, J. Ind. Eng. Chem. (2017), <http://dx.doi.org/10.1016/j.jiec.2017.06.026>

Download English Version:

<https://daneshyari.com/en/article/6667874>

Download Persian Version:

<https://daneshyari.com/article/6667874>

[Daneshyari.com](https://daneshyari.com)