



Response surface method for optimization of phenolic compounds production by lignin pyrolysis



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ABSTRACT

Lignin pyrolysis has a significant opportunity of producing commodity phenolic chemicals from natural biomass resources or industrial byproducts. Bio-oil production of lignin pyrolysis in a fixed-bed system was systematically characterized by response surface methodology (RSM) to optimize operating variables such as temperature, heating rate, and loading mass. According to the mathematical model of RSM, the predicted maximum bio-oil yield of 30.1% and the actual bio-oil yield of 29.3% were obtained under the optimum condition: 669 °C temperature, 15 °C/min heating rate, and 6.97 g loading mass. Temperature significantly influenced both the yield and the chemical composition of lignin bio-oils because pyrolytic decomposition of lignin consisted of temperature-dependent stepwise reactions. The bio-oil under the optimum condition produced not only the higher yield but also the higher content (43.2%) of the primary product (i.e., 2-methoxyphenol).

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1. Introduction

Pyrolysis can be used with many biomass feedstocks and is compatible as a subunit of other biorefinery methods (e.g., biological conversion) because it can directly convert organic substrates to lower molecular weight compounds, regardless of compositional characteristics of the substrate [1]. Wide range of biomass feedstock can be thermally degraded into the form of bio-oil, biochar, and gas. Particularly, various lower molecular weight compounds present in the bio-oil phase can be utilized as renewable fuels or as a source of commodity chemicals. The chemical composition and properties of bio-oils depend on the type of feedstock and the conversion technology [2]. Many studies of biomass pyrolysis have focused on utilizing total lignocellulosic biomass for bio-oil production [3,4]. However, lignocellulosic biomass is composed of three components (cellulose, hemicellulose, and lignin), which have inherently different chemical structures, so the pyrolysis products contain a variety of chemical compounds such as alcohols, aldehydes, organic acids, and phenols [5].

Compared to cellulose and hemicellulose, lignin is an attractive single feedstock as a natural resource of aromatic compounds

because it is composed of hydroxyphenyl (H), guaiacyl (G), and syringyl (S) building units [6]. The biological lignocellulosic bio-fuel production industry has used 200–300 million tons per year of lignocellulosic biomass. However, lignin has been left by 15% of the biomass as a byproduct because lignin is hardly degraded by microorganisms due to its chemical structural rigidity [7,8]. Thus pyrolysis of this lignin can be a promising approach to renewable production of various aromatic compounds such as guaiacols, syringols, catechols, pyrogallons, cresols, xylenols, phenols, and benzofuran [6].

Yields and quality of lignin pyrolysis products are influenced by various operational parameters such as reaction temperature, heating rate, substrate loading, particle size, residence time, catalyst, and reactor types. In accordance with operating conditions such as heating rate and residence time, thermal degradation of lignin is categorized to slow, intermediate, and fast pyrolysis. Fluidized-bed system under the fast pyrolysis conditions (heating rate higher than 1000 °C/min and residence time lower than 2 s) is usually appropriate for lignocellulosic biomass to obtain higher bio-oil yields (up to 75%) [9]. However, the fluidized-bed system of lignin might not be effective to produce higher yield of bio-oil because further decomposition and repolymerization reactions of lignin would lead to formation of adhered clumps of bed material and lignin coke causing performance degradation [10].

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This study used response surface methodology (RSM) to quantify how oil production of lignin pyrolysis in a fixed-bed system is affected by operating temperature, heating rate, and loading mass. The optimum conditions of the lignin pyrolysis for the highest bio-oil yield were determined using a response mathematical model obtained by RSM. To understand the stepwise conversion process of lignin into monomeric phenolic compounds, and to ascertain the effectiveness of recovering value-added aromatic commodity chemicals from the lignin pyrolysis, the influence of the most effective variable on yield and on each chemical component of the bio-oil was also analyzed.

2. Materials and methods

2.1. Materials and pyrolysis

Lignin (catalog number: 370959, Sigma-Aldrich Co., USA) was applied to a substrate of a pyrolysis system. The lignin was oven-dried and cooled down to remove moisture included in original lignin chemicals before the pyrolysis reaction. The lignin samples were pyrolyzed from room temperature to final temperatures at certain heating rates in a fixed bed pyrolysis system. The reactor was made of quartz with the dimension of 240 mm in height and 25 mm i.d. and was externally heated by an electric furnace controlled by thermocouples inside. N₂ gas was flowed at 100 ml/min to maintain an oxygen depleted atmosphere in the reactor. After each reaction, the pyrolysis products existed in three phases: biochar, bio-oil, and non-condensable gas. The vapor product that were produced during the pyrolysis reaction passed a connecting condenser between the reaction zone and a post-condensing column at -4 °C along with the carrier gas (N₂), and then it was divided into condensable liquid (i.e., bio-oil), and non-condensable gas. The bio-oil was collected in the downside of the condensing column at -4 °C and the non-condensable gas that left the column was accumulated in Tedlar® gas sampling bags. Yields of bio-oil, and biochar were calculated gravimetrically; the gas yield was estimated from the difference of the total amount of bio-oil, and biochar.

2.2. Experimental design using response surface methodology

To identify and optimize the effects of reaction conditions on lignin pyrolysis, a 3^k factorial Box-Behnken design (BBD) was applied. The BBD is efficient to estimate quadratic polynomials and to combine values for optimization of the response within a three-dimensional observation space [11]. To develop the regression equation, the relation between the coded- and actual values is expressed as follows:

$$x_i = \frac{(X_i - X_i^*)}{\Delta X_i} \quad (1)$$

where x_i is the coded value of the i th independent variable, X_i is the uncoded value of the i th independent variable, X_i^* is the uncoded value of the i th independent variable at the center point and ΔX_i is the step change value [12].

To analyze effects of different reaction conditions on lignin pyrolysis, the final temperature, heating rate, and loading mass were chosen as the independent variables of the BBD (Table 1). The relationship between response Y and input variables X_i is described as follows:

$$Y = \alpha_0 + \sum_{i=1}^3 \alpha_i X_i + \sum_{i=1}^3 \alpha_{ii} X_i^2 + \sum_{i=1}^3 \sum_{j=2}^3 \alpha_{ij} X_i X_j \quad (2)$$

where α_0 is the offset term, α_i is the i th linear coefficient, α_{ii} is the quadratic coefficient and α_{ij} is the j th interaction coefficient. The values of X_1 , X_2 , and X_3 that correspond to the maximum value of

Table 1
Experimental design and levels of the independent variables.

Variable	Code	Range and levels		
		-1	0	+1
Temperature (°C)	A	400	600	800
Heating rate (°C/min)	B	5	10	15
Loading mass (g)	C	3	5	7

Y were solved by setting the partial derivatives of the functions to zero and solving [12].

The number of experiments (N) for the analysis is defined as follows:

$$N = 2k(k - 1) + C_0 \quad (3)$$

where k is the number of factors and C_0 is the number of central points. It is recommended that the center point is run three times to allow for a more uniform estimation of the prediction variance over the entire design block [13]. Therefore, totally 15 runs were performed in this study with coded factor levels of a three-variable (Table 2).

2.3. Analytical methods

The methanol-soluble fraction of crude bio-oils obtained by lignin pyrolysis was analyzed using a Gas Chromatogram (GC)-Mass Spectrometer (MS) (Varian CP-3800 GC and Varian 320 MS models, Varian Inc., USA). The methanol-soluble fraction samples were filtered using 0.2 μm pore sized PTFE syringe filters before the analysis. The GC was equipped with a fused silica capillary column coated with (5% phenyl)-methylpolysiloxane (DB-5 ms, 60 m × 0.25 mm × 0.25 μm, Agilent J&W, USA). The GC oven temperatures were programmed as follow: from 100 °C (hold for 3.5 min) to 160 °C at 15 °C/min (hold for 20 min); from 160 °C to 200 °C at 15 °C/min (hold for 15 min); from 200 °C to 280 °C at 5 °C/min (hold for 5 min). The carrier gas was He (99.999%), flowing at 0.8 ml/min. The oven temperature program was modified to reduce a hindrance of minor peaks at the beginning of analysis and to improve peak separation over the end of analysis. The spectra of each of the lignin pyrolysis products were identified by retention time and NIST mass spectral libraries using AMDIS32 computer software. The relative content of the phenolic compounds was defined by measuring each peak area using the AMDIS32 software.

Gas composition (e.g., H₂, CH₄, CO, and CO₂) was analyzed using GC (model 6890N, Agilent Inc., US) equipped with a Supelco Carboxen-1010 PLOT capillary column (30 m × 0.32 mm, Sigma-Aldrich Inc., US) using a pulsed-discharged ionized detector and He as a carrier gas. The temperatures were 150 °C at the injector, 120 °C at the oven, and 240 °C at the detector.

3. Results and discussion

3.1. Statistical analysis model of lignin pyrolysis

The actual response values were clearly described using the experimental design matrix of lignin pyrolysis (Table 2). The actual values of the independent factors and the response were used to predict a model equation. Experimental results were fitted to a linear model and a second-order mathematical model for the bio-oil yield of lignin pyrolysis in terms of coded factors as follows:

$$\text{Bio-oilyield (\%)} = +23.33 + 4.83A + 1.10B + 4.60C - 3.40AB - 2.30AC + 2.55BC - 3.52A^2 - 0.22B^2 - 0.42C^2 \quad (4)$$

where A is pyrolysis temperature (°C), B is heating rate (°C/min), and C is loading mass (g). A , B , and C are linear terms of factors;

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