



Full Length Article

Conversion of bio-derived phenolic compounds into aromatic hydrocarbons by co-feeding methanol over γ -Al₂O₃



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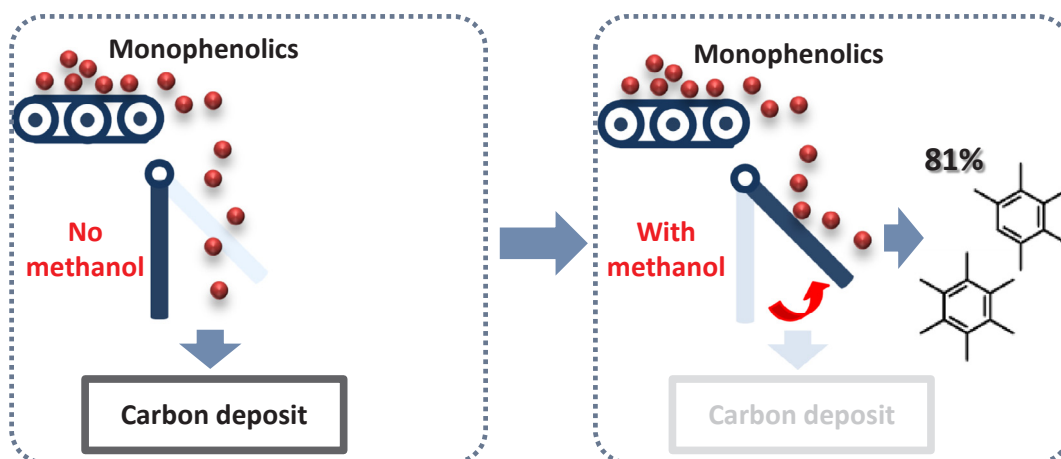
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GRAPHICAL ABSTRACT



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ABSTRACT

In the present study, a novel route of upgrading lignin pyrolysis vapor to aromatic hydrocarbons was investigated. Guaiacol was used as model compound to investigate the coupling conversion of pyrolysis vapor and methanol. Co-feeding methanol obviously facilitated the conversion of guaiacol to aromatic hydrocarbons and inhibited coke formation. HZSM-5, Al-MCM-41 and γ -Al₂O₃ catalysts were screened, and γ -Al₂O₃ showed the best catalytic activity for the catalytic co-cracking reaction due to the appropriate acid property. The effects of methanol to guaiacol molar ratio, reaction temperature and W/F_{guaiacol} on product distribution over γ -Al₂O₃ were studied in a fixed bed reactor to reveal the reaction mechanism. As hydrogen donor, the co-fed methanol promoted the deoxygenation of guaiacol. The water formed through methanol dehydration was an efficient agent for attenuating coke deposition. The highest yield of aromatic hydrocarbons was 81.2% when the methanol to guaiacol molar ratio was 25 at 400 °C. The investigation of W/F_{guaiacol} indicated that the synergistic

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effect of co-feeding was sensitive at lower W/F_{guaiacol} . Co-feeding methanol with phenol, anisole and the phenolic mixture were also investigated, and high yields of aromatic hydrocarbons were obtained, which demonstrated that co-feeding methanol was a promising process for upgrading complicated pyrolysis products.

1. Introduction

Lignocellulosic biomass, as a renewable, abundant and CO_2 -neutral energy source, has been studied as an attractive alternative energy to produce fuels and chemicals. Fast pyrolysis is one of the most promising routes to convert biomass into liquid products (i.e. pyrolysis oil) [1,2]. Due to the high oxygen content, raw pyrolysis oil has some drawbacks like corrosiveness and instability. Therefore, catalytic upgrading of raw pyrolysis oil is essential [3]. Numerous studies focused on the transformation of cellulose and hemicellulose [4,5]. Unlike the sugar based components, lignin is an amorphous biopolymer formed from three aromatic alcohols: p-coumaryl, coniferyl, and sinapyl alcohol [6]. The products of lignin pyrolysis are mainly aromatic oxygenates instead of relatively small oxygenates [7]. The lignin derived phenolics, especially oligomers with high molecular weight, are difficult to be catalytically converted. These oligomers are non-volatile and prone to generating coke through condensation reactions [8]. Patwardhan and co-workers proposed that lignin pyrolysis primarily produced volatile phenolic monomers, which could be immediately converted to oligomers through secondary reactions [9]. Bai et al. also demonstrated that phenolic oligomers were formed from reoligomerization of primary products [10]. Hence, catalytic upgrading of phenolic monomers to aromatic hydrocarbons to inhibit coke formation and improve the quality of bio-oil is highly desirable.

Catalytic cracking and hydrotreating have been intensively studied and taken as two main methods for upgrading the pyrolysis oil. Catalytic cracking could be operated at atmospheric pressure without external source (e.g. H_2). However, severe coke formation is a major defect of zeolite cracking, which significantly reduces the efficiency of carbon utilization. Chen et al. introduced the hydrogen to carbon effective ($\text{H}/\text{C}_{\text{eff}}$) ratio and suggested that severe coke formation occurred when the feedstock $\text{H}/\text{C}_{\text{eff}}$ ratio was less than 1 [11]. This suggests that co-feeding with a high $\text{H}/\text{C}_{\text{eff}}$ ratio feedstock is an efficient way to suppress the coke formation and increase the yield of hydrocarbons. Hydrotreating is a suitable approach to convert biomass-derived phenolic compounds to aromatic hydrocarbons [12]. However, conventional hydrotreating is conducted at high pressure over transition metal sulfide catalysts, which are prone to leaching sulfur, leading to a reduction of product yield and catalyst deactivation. In addition, the aromatic rings may be hydrogenated to form aliphatic hydrocarbons, which reduce the hydrogen efficiency [13].

It is interesting to note that aliphatic alcohols are co-fed to improve the overall $\text{H}/\text{C}_{\text{eff}}$ ratio during the upgrading process. Valle et al. proved that co-feeding methanol in bio-oil upgrading process could significantly attenuate coke deposition on Ni/HZSM-5 [14]. Analogous results were obtained by Asadieraghi et al. in the in-situ catalytic upgrading of pyrolysis vapor with methanol. The yield of aromatic hydrocarbons increased from 1.03 wt% to 50.02 wt% and the yield of char decreased from 34.3 wt% to 9.6 wt% due to the addition of methanol [15]. To investigate the synergistic effect between methanol and bio-oil, Zheng and co-workers studied the coupling conversion of methanol and biomass derived furans over HZSM-5 catalyst [16]. They observed that methanol was converted to olefins, which would further react with furans through Diels-Alder reaction, resulting in the formation of aromatic hydrocarbons. Methanol could also cause alkylation reaction that converted benzene to polymethylbenzene.

Guaiacol is a typical model compound since it contains major functional groups of lignin-derived phenolic such as hydroxyl ($-\text{OH}$) and methoxy ($-\text{OCH}_3$). Tran et al. reported the vapor phase hydrogenation of guaiacol to aromatics over Al-MCM-41 supported Ni and Co

catalysts under atmospheric pressure. Total conversion of guaiacol was obtained over Co/Al-MCM-41, with the aromatic yield of about 35% [14]. In this work, we propose a co-cracking process which can effectively convert guaiacol to aromatic hydrocarbons in the presence of methanol over $\gamma\text{-Al}_2\text{O}_3$ catalyst. The conversions of phenol, anisole and phenolic mixture are also investigated. Both the phenolic reactants and methanol could be derived from inexpensive biomass. The aromatic products obtained by catalytic co-cracking could be blended with other fractions from petroleum to give high-octane gasoline. In addition, the aromatics could be utilized by the chemical industry for the production of chemicals. Thus, catalytic co-cracking of bio-derived phenolic compounds and methanol is economically beneficial for the production of aromatic hydrocarbons.

2. Materials and methods

2.1. Materials

Guaiacol (AR), anisole (AR), phenol (AR) and CH_3OD (AR) were obtained from Aladdin Reagent Co., Ltd (Shanghai, China). CH_3OH (AR) and acetone (AR) were purchased from Guangzhou chemical reagent factory. All chemicals were used as purchased without any pre-treatment. The catalysts used in this work including $\gamma\text{-Al}_2\text{O}_3$, HZSM-5 ($\text{Si}/\text{Al} = 25$), Al-MCM-41 (Al content: 25%) were purchased from the Catalyst Plant of Nankai University (Tianjin, China). Prior to reactions, all catalysts were calcined for 3 h at 550°C .

2.2. Catalyst characterization

The textural properties of catalysts were determined by N_2 adsorption/desorption analysis using a QUADRASORB SI analyzer. All samples were degassed at 200°C for 8 h before N_2 adsorption. The surface areas were analyzed by the Brunauer-Emmett-Teller (BET) method. The micropore size distribution was obtained from Density Functional Theory (DFT) method and the micropore volume (V_{micro}) was derived by the t-plot method using the adsorption data of $0.2 < p/p_0 < 0.6$. The mesopore size distribution and mesopore volume (V_{meso}) was evaluated by Barret-Joyner-Halenda (BJH) method applied to adsorption branch data. Finally, the total pore volume was determined at $p/p_0 = 0.99$ [17]. The acidity of catalyst was determined by ammonia temperature programmed desorption ($\text{NH}_3\text{-TPD}$) on a Chemisorption Analyzer (Quantachrome ChemStar TPx). A total of 100 mg of sample was first pre-treated at 400°C for 60 min in Helium ($60\text{ cm}^3/\text{min}$), then cooled to 100°C and exposed to a 10% NH_3/He stream for 60 min. Afterwards, the sample was flushed with Helium for 1 h at 100°C . Then, desorption was carried out by increasing the temperature from 100°C to 800°C at a ramp of $5^\circ\text{C}/\text{min}$, and the effluent NH_3 was measured by a mass spectrometer. The types of acid sites were measured using Fourier transform infrared (FT-IR) spectroscopy for pyridine-adsorbed samples. Prior to adsorption, the samples were pretreated at 500°C under vacuum for 2 h. A background spectrum was measured after cooling down to room temperature and then pyridine vapor was introduced to the catalyst for 0.5 h. The FT-IR spectra were measured at room temperature after evacuation at 200°C and 450°C , which represented the total and strong acid sites, respectively. The coke on the spent catalyst was characterized using a thermogravimetry analyzer (TA Instruments SDT 650). A sample of 10–20 mg was heated from 30°C to 800°C at a heating rate of $10^\circ\text{C}/\text{min}$ in air.

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