Fuel 162 (2015) 47–54

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Reforming of lignin-derived tars over char-based catalyst using Py-GC/MS

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HIGHLIGHTS

- Catalytic reforming of lignin tar was performed in a Py-GC/MS.
- Gasification-derived char was used as precursor of reforming catalyst.
- Effects of temperature, pressure and atmosphere on reforming of tar were assessed.
- Char-based catalyst effectively decreased the lignin tar.

ARTICLE INFO

Article history:
Received 11 June 2015
Received in revised form 17 August 2015
Accepted 21 August 2015
Available online 2 September 2015

Keywords:
Lignin
Char
Activated carbon
Catalyst
Tar removal
Py-GC/MS

ABSTRACT

Tar removal is one of the major challenges in implementation of biomass gasification technology. Syngas tars causes formation of aerosols and soots, which plug filters, reactors and fuel lines. In this study, a char-derived catalyst was tested in removal of tar produced from pyrolysis of kraft lignin in a pyroprobe reactor. The effects of reaction temperature (700, 800 and 900 °C), water amount (5–10 μl), pressure (0.1–2.2 MPa) and atmosphere (inert and hydrogen) on catalytic conditioning of tar components were assessed. The tar components were analyzed by GC/MS. Catechols were the most abundant tar components followed with phenols and guaiacols during non-catalytic kraft lignin pyrolysis. Results indicated that the char-based catalyst effectively decreased the contents of lignin tar. Reaction temperature, water loading and reaction pressure significantly affected the tar removal. An increase in reaction temperature led to an increase in removal efficiency of most tar components except naphthalene. Excessive water loading (10 μl) decreased the tar removal efficiency of char-based catalyst. High pressure promoted the catalytic conversion of lignin tar. Tar contents decreased significantly when hydrogen was used as a reaction medium and thus promoted the conversion of lignin into non-condensable gas.

1. Introduction

Increase in global greenhouse gas emissions and concerns about global fossil fuels reserves have promoted the research in renewable energy. Biomass gasification is one type of efficient renewable energy technology converting lignocellulosic solid feedstocks into combustible gas. However, during gasification many contaminants are generated, such as NOx, SOx and tar. Particularly, the presence of considerable amount of tar in syngas leads to formation of aerosols and soots due to repolymerization and plugs filters and fuel lines due to tar condensation [1]. Therefore, tar removal is one of the major challenges in implementation of biomass gasification technology at commercial scales for fuels, chemicals and power production.

Biomass is mainly composed of cellulose, hemicellulose and lignin. Many studies have shown that cellulose, hemicellulose and lignin produce different tar compounds [1,2]. Primary tars produced from cellulose are furans and small molecule aldehydes [3]. Primary tars produced from hemicellulose are acetic acid [2] and those produced from lignin are furfurals and phenolics [4]. Approximately 20–40 wt.% of biomass, such as switchgrass, wheat straw and eastern red is composed of lignin [5]. Lignin is a complex polymer of p-hydroxyphenyl, guaiacyl and syringyl alcohols. Three species of hydroxycinnamyl alcohols (p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol) are considered as monoligol monomers incorporated in lignin polymer structure in the form of p-hydroxyphenyl, guaiacyl, and syringyl phenylpropanoid [1,6]. Since only the lignin fraction of the biomass is aromatic in nature, lignin represents a potential precursor for formation of

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http://dx.doi.org/10.1016/j.fuel.2015.08.064

polyaromatic hydrocarbon (PAH) in tar. The study of catalytic lignin-derived tar reforming is critical for understanding strategies to reduce syngas tar.

The tar formation is affected by reaction conditions such as pressure. The pressure will affect composition of syngas as well tar. Knight [7] studied the effect of pressure on the biomass gasification products and found that increasing pressure (from 0.8 to 2.2 MPa) decreased oxygenated species. Specifically, particularly phenols were almost completely eliminated; but the PAH fractions increased. Research was also conducted on pressurized gasification of coal [8]. Pressurized operation not only reduced the volatile evolution during coal pyrolysis and increased char gasification rate by influencing the physical structure of pyrolysis char, but also lowered the energy cost for compressing syngas prior to using in a gas turbine [8].

The tar formation is also affected by reaction atmosphere such as hydrogen. Many studies have found that hydrogen atmosphere promotes hydrocracking and deoxygenation reactions of biomass pyrolysis, thus decreasing the oxygen content of bio-oil while increasing the gas yield [9,10]. Thangalazhy-Gopakuma et al. [9] studied the hydrogen effect on formation of oxygenated compounds during pine wood pyrolysis. They found that the presence of hydrogen significantly enhanced hydrodeoxygenation, which rejected the bio-oil oxygen in the form of water [9]. As a result, yield of higher molecular weight oxygenated compounds under H_2 atmosphere was much lower than that under helium atmosphere [9]. Takarada et al. [11] studied coal pyrolysis in hydrogen and helium in a fluidized bed. The yields of permanent gases in hydrogen were about five times than those in helium. The yields of aromatic hydrocarbon (benzene, toluene and naphthalene, etc.) also enhanced.

Char is a byproduct of gasification and pyrolysis. Char's variable and tailorable surface properties (surface functional groups, porosity and surface area) offer great potential value for its applications in renewable energy, agriculture and environmental remediation, etc. [12,13]. As for syngas cleaning, char and char derived catalysts were proved to be effective alternatives to traditional catalysts for tar removal [14,15]. However, limited studies have investigated the reaction conditions, such as pressure and atmosphere on the formation of lignin tar and the performance of char based catalyst in catalytic tar removal.

The objective of this study was to study the effects of reaction conditions, such as pressure and atmosphere on non-catalytic and catalytic reforming of lignin tar. The catalytic and non-catalytic pyrolysis of kraft lignin was conducted at 700–900 °C and 0–300 psig in a pyroprobe reactor in presence of 5 or 10 μl water. Char-based catalyst was used for catalytic pyrolysis. Since hydrogen is the primary component of syngas and is found to have significant effect on tar formation, the effect of hydrogen on tar cracking was also investigated.

2. Material and methods

2.1. Catalyst preparation

Catalysts were prepared by loading nickel on char-derived activated carbon. The char was produced by downdraft gasification of red cedar [16]. The red cedar char was then mixed with KOH (Fisher Scientific, Pittsburgh, PA, USA) and activated at 800 °C for 1.5 h under nitrogen flow of 200 ml/min in a fixed-bed tubular reactor. Activated carbon obtained was then impregnated with nickel nitrate solution (Sigma Aldrich, St. Louis, MO, USA) and then dried at 105 °C for 3 h. The dried catalyst was reduced in 100 ml/min hydrogen flow at 350 °C for 3 h. Reduced catalyst was then kept in vacuum desiccator for further test.

2.2. Pyrolysis of kraft lignin using Py-GC/MS

Catalytic reforming was performed using a commercial micro-pyrolyzer (Pyroprobe model 5200/high pressure, CDS Analytical Inc., Oxford, PA). The pyrolyzer was connected with a gas chromatograph/mass spectrometer (GC/MS, Agilent 7893, Agilent, Santa Clara, CA, USA). The probe of Pyroprobe consisted of a platinum heating coil, which can be heated up to 1400 °C. The lignin, named as Indian AT, (Mead Westvaco, Richmond, VA, USA). Indian AT is a purified form of kraft pine lignin. It is derived by hydrolysis of kraft lignin, removing the sodium the hemicellulose [17]. About 0.5 mg of the lignin powder and 5 mg of catalyst were packed in a quartz tube (approximately 25 mm long and 1.9 mm inner diameter), which was then held in the platinum heating coil. To make sure all tar volatiles passed through the catalyst layer, one layer of catalyst was kept on each side of the lignin powder. The catalyst layer and lignin layer were separated by quartz wool. In order to simulate steam gasification, 5 μl water was injected into lignin powder during non-catalytic pyrolysis. The sample was pyrolyzed at a heating rate of 1500 °C/s in presence of different gases (He, 100% and H_2 100%). To make sure the sample was completely pyrolyzed, the sample was held at pyrolysis temperature for 20 s. To use helium as reactant gas, 40 ml/min helium was purged for about 1 min to remove air. To use H_2 as reactant gas, 40 ml/min helium was also purged for about 2 min to remove air and residual hydrogen before switching to reactant gas (H_2) with flow rate of 40 ml/min. The actual temperature of biomass inside the quartz tube was, typically, about 50–100 °C lower than that of the filament temperature [18,19].

2.3. Tar composition analysis

The reactant gas carried the pyrolysis vapors (tars) from the probe to a trap (adsorbent). The trap adsorbed the condensed vapors. Non-condensable gases escaped from the trap and were not analyzed in this study. The adsorbed tar was desorbed by heating the trap to 300 °C and purging with helium. The gaseous tar was then carried by helium gas and injected into the GC/MS through a transfer line for compositional analysis. The transfer line was heated at 300 °C to prevent tar condensation. A capillary column (HP-5, 0.03 mm OD, 3 m length) was installed in the GC for separating the tar components. The injector of the GC was held at 250 °C. The column temperature was maintained at 40 °C for 2 min and then increased to 280 °C with a heating rate of 5 °C /min. Helium of ultra-high purity (99.999%) was used as a carrier gas at a flowrate of 1.25 mL/min.

The mass spectrometer was configured for electron impact ionization at 70 eV, with an interface temperature of 250 °C. Tar compounds were identified by comparing the mass spectra with the NIST (National Institute of Standards and Technology) mass spectral library and the retention time of the standard compounds. The concentration of tar components were determined using an external standard method. 26 tar components were quantified using 24 external standards including 10 aromatic hydrocarbons, 8 phenols, 6 phenol-guaiacols, 1 furan and benzoic acid. 2-methyl-phenol and 4-ethylcatechol were quantified using corresponding standard from similar structure compounds [20] (P-cresol for 2-methyl-phenol and methylcatechol 4-ethylcatechol).

2.4. Experimental design and data analysis

For non-catalytic pyrolysis of lignin, a full factorial design was performed at five pressures of 0, 0.5, 0.8, 1.1 and 2.2 MPa (0, 50, 100, 150 and 300 psig) and three temperatures of 700, 800 and 900 °C. For catalytic pyrolysis of lignin, a full factorial design was performed at three pressures of 0.1, 0.5 and 1.1 MPa (0, 50 and