Contents lists available at ScienceDirect

Fuel

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Full Length Article

Tar formation and evolution during biomass gasification: An experimental and theoretical study



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ARTICLE INFO

Keywords: Tar formation Biomass Gasification DFT

ABSTRACT

The present research employed experimental and numerical methods to develop a tar formation model for the gasification of *Camellia sinensis* branches. Gasification experiments using lignin and cellulose extracted from *Camellia sinensis* branches were conducted to provide insights on the reaction mechanisms of *Camellia sinensis* branches because of the its complex components and structure. The extracted biomass was characterized by Fourier transform infrared spectroscopy and nuclear magnetic resonance spectroscopy, while the gasification products were analyzed by gas chromatography and mass spectrometry to figure out the tar compounds relationship between *Camellia sinensis* branches, the reaction energetics, structure of precursors, intermediates, transition of *Camellia sinensis* branches, the reaction energetics, structure of precursors, intermediates, transition states, products were examined by density functional theory. Theoretical results were in good agreement with experimental observations and showed that the tar compounds concentration increased with temperature, while the tar composition partially shifted from single ring hydrocarbons to polyaromatic compounds. The major compounds in tar were lignin-derived phenolics, while ketones, aldehydes and alcohols mainly originated from the decomposition of cellulose. The presence of phenol and cresol was attributed to both lignin and cellulose, but had different formation pathways.

1. Introduction

The use of biomass and agricultural waste in thermochemical conversion processes has spurred tremendous interests in renewable energy generation [1–3]. In particular, biomass gasification has the potential to become a viable alternative to limit the dependence on fossil fuels and reduce greenhouse gas emissions. Gasification is a well-established technology, which consists of the partial oxidation of solids (i.e. coal or biomass) in the presence of an oxidizing agent (i.e. steam, air or oxygen) into combustible gaseous products with small quantities of char, ash, and condensable compounds [4,5]. The latter comprises a mixture of single-ring to five-ring aromatic compounds plus other oxygen-containing hydrocarbons and complex polyaromatic hydrocarbons (PAH) known as tar. The formation of tar is one of the main challenge in the implementation of gasification processes and can cause serious operational issues, such as plugging of filters due to coking and attrition of the reactor and transfer lines due to condensation in the cold spots of the system. These deposits can evolve in other more complex molecular arrangements due to polymerization reactions, further increasing the difficulty for tar treatment. Besides hampering gasification

efficiency and increasing maintenance costs, tar also poses a possible threat on human health due to its carcinogenic nature. This is especially relevant when biomass is utilized as feedstock, because the lower fixed carbon, and higher moisture and volatile matter contents of biomass promotes tar formation. Typical biomass gasification systems, including fluidized bed reactors, downdraft and updraft gasifiers yield approximately 1–150 g/Nm³ of tar [6–8]. However, the minimum tar tolerances for applications in fuel cells and gas turbines are less than 1.00 g/Nm³ and 0.05 g/Nm³, respectively.

As previous literatures reported, biomass starts decomposing into primary tar around 500 °C, forming a mixture of oxygenates and condensable organic compounds, which in turn generate non-condensable light gaseous products (CO₂, CO, CH₄, H₂, and C_xH_x), and secondary tar comprising heavier molecules, such as benzene, toluene, and indene, at higher temperatures. When primary tar is fully decomposed, tertiary tar (PAHs) is produced[9–12]. Despite extensive research, the mechanism of tar formation during biomass gasification remains unclear. This is likely attributed to the complex nature of biomass with large variations in chemical composition, including different polymeric units and crosslinkages in lignin, cellulose, and hemicellulose, generating various

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https://doi.org/10.1016/j.fuel.2018.07.105

Received 10 May 2018; Received in revised form 4 July 2018; Accepted 24 July 2018 0016-2361/ © 2018 Elsevier Ltd. All rights reserved.





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 Table 1

 Ultimate, proximate analysis and LHV of Camellia sinensis branches, lignin, and cellulose.

| | Ultimate analysis (%, ad) | | | | | Proximate analysis (wt%, ad) | | | | LHV (MJ/kg) | Composition (wt%) |
|-----------|---------------------------|------|-------|------|------|------------------------------|--------------|----------|------|-------------|-------------------|
| | С | Н | 0 | Ν | S | Volatiles | Fixed carbon | Moisture | Ash | | |
| CSB | 44.74 | 3.49 | 48.93 | 1.01 | 0.12 | 79.00 | 11.92 | 7.24 | 1.84 | 13.83 | - |
| Lignin | 58.90 | 2.92 | 27.40 | 1.14 | 0.23 | 65.31 | 25.28 | 6.10 | 3.31 | 20.28 | 27.80 |
| Cellulose | 41.46 | 1.83 | 48.51 | 0.03 | 0.02 | 83.97 | 7.88 | 7.98 | 0.17 | 11.56 | 35.31 |

types of tar [13]. Because of its aromatic nature, lignin is considered as the main tar precursor [14,15] and primary byproducts of lignin pyrolysis, such as vanillin, guaiacol, catechol and anisole are often used to examine tar formation pathways [12,16,17]. A free radical mechanism has been suggested as a major route in the early lignin decomposition, followed by free radical, homolytic and concerted reactions with the lowest dissociation energy of different bonds and transferring of atoms (hydrogen, oxygen, and carbon) to form new bonds [18-22]. In addition, byproducts of cellulose decomposition, such as furans and aldehydes, can also be found in relatively large quantities in tar [23]. However, the formation of tar from cellulose derivatives has been mostly studied within the scope of fast pyrolysis in inert gas where an active cellulose generated in the first step and depolymerized into volatiles with levoglucosan which could be fragmentated or dehydrated to form aldehydes, ketones, and furans [24-26]. And limited works have been reported on gasification processes of cellulose. Therefore, considered the biomass complex components and structure, identifying the contributions of the different precursors, intermediates, transition states, and products on tar during the gasification of raw biomass and its lignin and cellulose are critical to unravel the formation mechanism of tar and its properties in the gasification of raw biomass.

This study focuses on depleting tar formation by examining the influence of different parameters, such as temperature, pressure, and nature of feedstocks on the gasification process. The present work relies on both experimental and numerical methods to develop a tar formation model useful for the gasification of raw biomass in a fixed bed reactor. *Camellia sinensis* branches (CSB) were chosen as feedstock of interest because it is one of the most widely used economic crops in China for the production of tea, especially in the Jiangsu's province with more than 353.34 km² of tea land area [27]. *Camellia sinensis* branches are typically removed from tea trees to promote their growth, hence offering great opportunities for the gasification industry.

Gasification experiments of both *Camellia sinensis* branches and its extracted lignin and cellulose components (27.80% and 35.31% in the *Camellia sinensis* branches) [27] were conducted at various temperatures ranging from 500 to 900 °C and the different products were analyzed by gas chromatography/mass spectrometry (GC/MS) to figure out their tar compounds relationship. According to tar relationship and the extracted lignin and cellulose structures characterized by Fourier transform infrared spectroscopy (FTIR) and two-dimensional heteronuclear single quantum coherence NMR (2D HSQC NMR), *Camellia sinensis* branches replaced by structural models were simulated and calculated the pathways of main tar compounds generation. Then the experimental results were compared with Density Functional Theory (DFT) calculations to elucidate the mechanism for tar formation during biomass gasification.

2. Materials and methods

2.1. Biomass preparation and characterization

2.1.1. Preparation and isolation

Camellia sinensis branches, obtained from Jiangsu Tea Exposition Park (Jurong city), were smashed by a high speed pulverizer (RHP-100, Shenlian, China), prior to sieving using mesh sizes ranging between 0.075 and 0.150 mm. Cellulose was extracted from the *Camellia sinensis* branches as follows. First, *Camellia sinensis* branches were washed with acetone to remove undesirable compounds, such as extractives and inorganic impurities. The material (15 g) was then placed in an acetone bath for 6 h at 75 °C and air-dried before being added to 300 ml acidic solution (pH 4.5, adjusted with 10% acetic acid). The mixture was heated to 75 °C for 4 h and 3 g of sodium chlorite (AR: > 99.8%) was added every hour to remove the lignin. The resulting holocellulose was soaked in an alkaline solution (10% NaOH, 1:20 w/v) for 8 h at 25 °C. The mixture was filtered and rinsed with copious amount of deionized water until reaching neutral pH, and the extracted cellulose (4.29 g) was obtained by freezedrying in a lyophilizer (FreeZone[®] 4.5L, Labconco, USA).

The lignin extraction process was based on the well-established klason method [28]. First, 30 g of purified *Camellia sinensis* branches was placed in 200 ml H_2SO_4 solution (72%) and the mixture was stirred for 2 h at 50 °C. Deionized water was added until the H_2SO_4 concentration was below 10% and the mixture was refluxed under constant agitation for another 2 h at 100 °C. Finally, the extracted lignin (7.26 g) was recovered by filtration, washing and freeze-drying. Ultimate, proximate analysis and LHV of *camellia sinensis* branches, lignin, and cellulose were listed in Table 1.

2.1.2. Biomass characterization

The ultimate analysis was carried out in triplicates using a Vario EL-I elemental analyzer (Elementary, Germany) with 70, 50 and 50 mg of raw biomass, char and tar, respectively.

Fourier transform infrared (FTIR) spectroscopy was performed using a VERTEX 80 V FTIR spectrophotometer (Bruker, Germany) by pressing 1 mg of sample into a KBr-disc with an analyte: KBr mass ratio of 1:45. The spectra were collected in the [500–4000] cm⁻¹ range with a spectral resolution of 4 cm⁻¹.

The chemical structure of lignin was examined by 2D-HSQC NMR based on a previously established procedure [29]. Briefly, 1.8 g klason lignin was dispersed in 4 ml N-Methyl Pyrrolidone (NMP) by bath sonication for 3 h. The lignin dispersion (0.3 ml) was mixed with 0.3 ml DMSO- d_6 and the mixture was analyzed using a Bruker AVANCE 600 MHz (Bruker, Germany) spectrophotometer equipped with a 5 mm BBO probe using an inverse gated proton decoupling sequence. For data collection, 1024 points were acquired (160 blocks per scan) in the F2 (¹H) dimension with an acquisition time of 53 ms and 256 data points were recorded in the F1 (¹³C) dimension with an acquisition time of 5.14 ms.

Thermogravimetric analyses (TGA, PerkinElmer STA 8000, USA) coupled with a FTIR spectrometer (PerkinElmer Frontier, USA) were performed in pure nitrogen to characterize the mass loss and release of volatiles during the pyrolysis of Camellia sinensis branches, cellulose and lignin. Each sample weight was 14 mg and the nitrogen flow rate was 50 ml/min (purity: 99.999%). The sample was heated from 25 °C to 900 °C at a rate of 50 °C/min. The volatiles released during heating were quickly swept into the FTIR spectrometer by pure nitrogen carrier gas and the temperature of the transfer line between the TGA and FTIR was kept at 280 °C. The FTIR spectra were collected from 500 to 4000 cm⁻¹ with a spectral resolution of 4 cm⁻¹, corresponding to a scanned interval of 3 s.

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