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Characteristics of tar formation during cellulose, hemicellulose and lignin gasification

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HIGHLIGHTS

- The tar yield decreased with increasing temperature and excess air ratio.
- Gasification tar derived from lignin was more stable and harmful.
- PAHs were primary component of gasification tar at relatively higher temperature.
- Gasification tar of biomass components had different composition.
- Tar formation mechanisms for biomass components were different.

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ABSTRACT

This study compares the major biomass components (i.e., cellulose, hemicellulose and lignin) with respect to their differing tar formation characteristics during the gasification process. To better understand the tar formation mechanism, the tar content and composition were analysed via gas chromatography coupled with mass spectrometry (GC–MS). The tar yields of the three components all decreased with increasing temperature or excess air ratio (ER). However, lignin has a higher tar yield and produces more stable components in tar due to its molecular structure. At higher temperatures, the tar composition shifts toward higher-molecular-weight substances, such as polycyclic aromatic hydrocarbons (PAHs). For lignin, PAHs are derived primarily from phenols and its derivatives. For cellulose and hemicellulose, PAHs are derived primarily from benzene, toluene, ethylbenzene and xylene isomers (BTEX) and miscellaneous hydrocarbons. During the gasification process of real biomass materials, it is crucial to remove the tar compounds derived from lignin for tar control.

1. Introduction

The depletion of fossil fuel sources and concerns over environmental pollution have motivated the exploration of renewable and clean energy [1]. Because of its large reserves and environmentally friendly nature, biomass is considered a potential source of sustainable energy [2]. Various technologies have been developed to convert biomass into other more valuable forms of energy. Gasification is one of the most interesting alternatives because of its flexibility in accepting different types of materials and its ability to produce a wide range of products with high efficiency [3]. However, the commercialization of biomass gasification continues to present challenges due to technical problems related to tar and other issues. The gas generated during the gasification process typically contains an unacceptable level of tar, which can cause operational problems by blocking gas coolers, filter elements and engine suction channels [4,5]. Although many efforts have been made to remove gasification tar through physical and chemical methods, such as filtration and catalytic cracking, tar removal continues to be a major research objective in the field of biomass gasification. Such research would be aided by an increased understanding of the tar formation mechanism.

Tar formation is the result of a series of complex thermochemical reactions, such as chemolysis, depolymerisation, oxidation, polymerisation and cycloaddition, that depend on many factors, including feedstock properties, reactor configurations and reaction conditions. Extensive studies have been conducted to investigate the effects of reaction conditions such as temperature, pressure, heating rate and excess air ratio (ER) on the concentration and composition of gasification tar in flue gas [6,7]. Feedstock properties also have notable effects on tar formation. Researchers have studied the effect of physical properties, such as particle size and shape, on tar formation [8,9]. However effects of chemical properties such as biomass composition on tar formation are limited in literature.

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Cellulose, hemicellulose and lignin are major components of general biomass materials. The amounts of cellulose, hemicellulose and lignin vary substantially with the type of biomass materials. For example, woody materials contain more lignin but less cellulose and hemicellulose as compared to agricultural residues or herbaceous crops [10]. Besides, the polymer structure and length, and the cross-linkages of cellulose, hemicellulose and lignin are very different. The difference of chemical composition and nature of the biomass polymers result in different tar formation characteristics for different types of biomass during gasification. Researchers have used typical biomass materials which have obviously different composition, such as wood and straw, to study effects of biomass composition on tar formation [8,11]. But these studies have not distinguished among the major components of biomass and examined their individual characteristics with regard to tar formation. To get better understanding of the effects of biomass composition on tar formation in gasification process, it is necessary to examine the individual tar formation characteristics of biomass major components. However, there is no such literature according to the author's best knowledge.

In this work, gasification experiments involving the three major biomass components were conducted in a lab-scale entrained-flow reactor to investigate the effects of process parameters, especially temperature and ER on tar generation. To better understand the characteristics of tar formation, gas chromatography coupled with mass spectrometry (GC–MS) was used to analyse the tar composition. By comparing tar amounts and compositions among cellulose, hemicellulose and lignin, insight into tar formation during the gasification process can be gained.

2. Materials and methods

2.1. Materials

In biomass, cellulose is the major structural polymer of a plant cell wall and typically exists as long thread-like fibres called microfibrils. Microfibrils are typically embedded in a matrix that contains hemicellulose and lignin. Hemicellulose is a branched polysaccharide comprised of different sugar monomers, such as glucose, xylose, mannose, galactose, arabinose and uronic acids. Lignin is the cementing material that provides elasticity and mechanical strength to the wood. It is a phenolic macromolecule with a high degree of cross linking between the phenylpropane units [12,13].

In this study, avicel Cellulose (PH 105, Mingtai Bio-tech, Taichung, Taiwan), beech wood xylan (Sigma Aldrich, St. Louis, MO, USA) and alkali lignin (Sigma Aldrich, St. Louis, MO, USA) were used as models of cellulose, hemicellulose and lignin, respectively. The results of the ultimate and proximate analyses for all model components are shown in Table 1.

2.2. Entrained-flow reactor gasification

The experiments were conducted on the gasification platform shown in Fig. 1. The system consists of a biomass feeding system, which enables the supply of a controlled biomass flow, an entrained-flow gasification reactor based on a Badzioch-type reactor [14,15], a gas supply system that supplies the gasifying agent to the reactor at a constant volumetric flow rate, a tar collecting system and other auxiliary facilities.

After the reactor tube reached the selected temperature, the gasifying agent was introduced into the reactor according to the selected flow. Biomass was then fed into the reactor at a constant volumetric flow rate. The gasification run started as soon as the biomass entered the reactor. Reaction products exited the reactor into a hopper and filter, where char and ash were collected. The tar collecting system collected the tar contained in the flue gas. Finally, a dry, clean producer gas sample was obtained. The products that were collected were properly sampled and stored for subsequent measurement and analysis.

The applied experimental conditions are listed in Table 2. In this study, four reaction temperatures were selected: 800 °C, 900 °C, 1000 °C and 1100 °C. The ER was varied between 0.2 and 0.35. In addition to the gasifying agent, a large amount of nitrogen was used as a balance gas to obtain a flat temperature profile and an isothermal condition in the reactor, leading to a low oxygen concentration in the combined reaction gas. The particle residence time in the reactor was approximately 1.5–2.2 s, which was determined by the mean gas residence time under the assumption that there was no relative velocity between the gas and solid phases [9,16]. The effects of reaction temperature and ER were investigated by maintaining a constant feeding rate and total input gas flow.

2.3. Tar analysis techniques

The tar collecting system was designed based on the protocol described in CEN/TS 15439 Biomass Gasification-Tar and Particles in Product Gases-Sampling and Analysis [16]. As shown in Fig. 1, the system consists of four parts: a particle filter that removes particles contained in the flue gas, tar collection impinger bottles that collect tar, a volume meter that measures the flow volume and a pump that adjusts and controls the flow. After the flue gas passes through the particle filter, the particle-free gas was led to the series of impinger bottles, which contained water or solvent to absorb the tar contained in the flue gas. The impinger bottles were placed in an external ice-water bath to remove heat released by gas cooling and condensation. After the completion of the experiment, the tar collected was extracted and separated for further measurement and analysis.

In this study, the tar amounts and compositions of cellulose, hemicellulose and lignin under various experimental conditions were measured. Tar amounts were evaluated using the index tar yield, which indicates the weight of tar generated from 1 g of feedstock [17]. This index was calculated according to Eq. (1).

$$\mathrm{Tar}_p = M_{tar}/(M_{daf} \cdot t) \quad (1)$$

where Tar_p is the tar yield from 1 g of material (mg/g), M_{tar} is the weight of tar collected (mg), $M_{d.a.f}$ is the material feeding rate on a dry-ash-free basis (g/min) and t is the reaction time (min).

Table 1
Ultimate and proximate analysis (wt.%) of the model components.

Components	Ultimate analysis					Proximate analysis				
	C_{ar}	H_{ar}	O_{ar}	N_{ar}	S_{ar}	M_{ar}	A_{ar}	V_{ar}	FC_{ar}	$Q_{net.ar}$ (kJ/kg)
Cellulose	41.85	6.35	45.75	1.06	0.004	4.94	0.04	90.37	4.65	16,531
Xylan	37.21	5.86	39.49	0.02	0.009	14.23	3.14	66.62	16.01	15,008
Lignin	41.44	4.90	31.44	0.16	4.25	6.05	11.76	64.56	17.63	17,522

ar = As received basis.