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Interaction among bio-oil model components during oxidative degradation

Wei Lu, Qi Zhang^{*}, Chenguang Wang, Tiejun Wang, Jinxing Long, Ying Xu, Longlong Ma

Key Laboratory of Renewable Energy, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou, Guangdong 510640, China

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ABSTRACT

The oxidative degradation behavior and interactions of three model components (eugenol, vanillic aldehyde and levoglucosan) which are model of three classes of components, namely phenols, aromatic aldehydes and carbohydrate) in bio-oil were investigated by TG-FTIR and TG-MS analysis. TG-DTG profiles showed that the phenols had the greatest tendency to oxidative degradation, followed by aromatic aldehyde and carbohydrate. Volatilization and thermal oxidation are the main steps during eugenol and vanillin degradation. The TG-FTIR-MS results reveal that the interactions among three model components lead to mixture degrade at a higher temperature but completely oxidize at a lower temperature. The interactions may well be the reactions among aromatic substances, anhydrosugar and its disintegrating products to form nonvolatile component, polymers and char. The model compound oxidative degradation kinetic analysis data shows that the value of activation energy corresponds to the sequence of model compound oxidative degradation. Which also indicate the interactions among disintegrating products have effect on the mixture oxidative degradation and give rise to generation char.

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1. Introduction

Bio-oil obtained by biomass pyrolysis has the potential to be used as liquid transport fuel substitute [1,2]. As a primary liquid fuel, however, the unsatisfied properties of bio-oil, such as high oxygen and moisture content, low heating value, large surface tension, corrosiveness and instability [3,4], cause many problems when used in thermal and power equipment: low efficiency, poor flexibility, damaging combustion system (blocking injectors or cylinder pressure transducer and corrosion turbine blades etc.) [5–8]. In order to improve bio-oil for direct utilization, researchers make a

great effort by far: most of the light fractions are upgraded by hydro-deoxygenation, catalytic cracking, catalytic steam reforming and emulsification to generate a power fuel for direct utilization [9–12]. However, some relative complicated fractions are hard to decompose or convert during improving quality, owing to the deposition of carbon on the catalysts and the extremely instability of the oxygenated complex compositions [13,14]. Those unstable oxygenated fractions mainly include the degradation products of lignin (phenolic derivatives) and the saccharides, largely of the heavy fractions with high heating value. Their activity and effect depend on their exact form and the local chemical

^{*} Corresponding author. Tel.: +86 20 87057751; fax: +86 20 87057737.

E-mail address: Zhangqi@ms.giec.ac.cn (Q. Zhang).

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environment [1,15,16]. For instance, they are easy to form large molecules and polymers when subject to a relative high temperature. They do not act independently during combustion and have mutual effects lead to polymerization and coking [17–19]. The research results concerning the phenolic derivatives and saccharides complete oxidation process and their interactions are limited by far. Therefore, oxidative degradation characteristics and interactions of those model fractions during combustion are worth to be intensively studied.

The main interests in this work focus on the interactions among three model components and oxidative degradation behaviors during complete oxidation. The rapid thermal oxidation reactions provide insufficient the products' information during the bio-oil combustion in combustor or furnace. It is difficult to analyze the deep cause of carbon deposition and coking. In this work, we mainly studied the interaction among model components, which related to the carbon deposition and coking. A slow heating rate employed for investigating complete oxidation behavior would help to obtain more information about the degradation products and process reactions. The products' characteristics and interactions were used to identify the components and reactions leading to carbon deposition and coking. Thus, the technology of TG-FTIR and TG-MS analysis are adopted to record the data and predict the product-evolution patterns.

2. Experimental section

2.1. Materials

The model compounds used in the experiments are eugenol, vanillic aldehyde and levoglucosan, and their physical properties are shown in Table 1. The mixture contains eugenol, vanillic aldehyde and levoglucosan with the mass ratio of 2:3:5 in this work, referring to the mass ratio of phenols, aromatic aldehydes and saccharides in research reported [14]. All chemical reagents are analytically pure. Eugenol and vanillin were purchased from Guangzhou Chemical Co.,Ltd., Guangdong Province, China. Levoglucosan was purchased from Aladdin Industrial Inc.

2.2. Thermal analysis and gaseous products FTIR-MS analysis on sample combustion

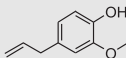
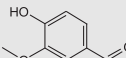
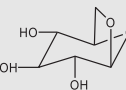
Combustion behavior of the model samples and their mixture were carried out using a Netzsch STA 449C Jupiter simultaneous thermogravimetric analyzer. Experiments were performed from 30 to 930 °C with a linear heating rate of 10, 20, 30, and 40 K min⁻¹. About 10 mg of sample and 20 cm³ min⁻¹ of a dry air flow rate were adopted. The gaseous products were detected by deuterated triglycine sulfate pyroelectric detector. The spectrum scope was 400–4000 cm⁻¹ and the resolution factor was 1 cm⁻¹. The gaseous products were led from TG to FTIR and MS through a pipe, heated to 200 °C. The heated pipe was approximately 1 m in length and the gas time delay between TG and FTIR was 20 s. The gas time delay between the TG and the MS was 40 s. Before starting an experiment, the furnace, the heated pipe and the gas cell were purged by N₂ for 30 min at least (20 cm³ min⁻¹). The TG and FTIR experiments were then begun simultaneously.

The mass spectrometer was operated at 70 eV and *m/z* was carried out from 1 to 250 amu to determine which *m/z* has to be followed during the TG experiments. The ion curves close to the noise level were omitted. Finally, only the intensities of 40 selected ions (*m/z* = 16, 17, 18, 28, 29, 30, 32, 40, 42, 44, 45, 46, 58, 60, 72, 74, 78, 80, 84, 88, 90, 92, 93, 94, 100, 102, 105, 106, 107, 108, 121, 122, 123, 124, 126, 131, 134, 137, 144 and 146) were monitored with the TG parameters. However, some MS fragments at *m/z* with very weak signal strength (*m/z* = 40, 45, 72, 84, 88, 105, 107, 121, 123, 131, 137, 144, 146 etc.) were not showed in the figures for analyzing model components thermo-oxide degradation, due to they are not the main fragments and reaction pathways.

3. Kinetic modeling

The extent of conversion or the fraction of combusted material, α , is defined by the expression $\alpha = (w_0 - w)/(w_0 - w_\infty)$ where *w* is the mass of the sample at a given time *t*; *w*₀ and *w*_∞ refer to values at the beginning and the end of the mass event of interest.

Table 1 – Physical property of model component of bio-oil.

Model component	Molecular formula	Molecular weight	Density (g cm ⁻³)	Boiling point (°C)	Melting point (°C)
Eugenol		164.2	1.06	254	-9.2 – -9.1
Vanillic aldehyde		152.14	1.06	255	80–81
Levoglucosan		162.14	1.60	383	182–184

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