



## Full Length Article

# Pyrolysis oil polymerization of water-soluble fraction during accelerated aging



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## ABSTRACT

Pyrolysis oil is a promising material for renewable energy through a hydrogenation process. However, the polymerization, initiated especially by pyrolysis oil water-soluble fraction (PS), is a big hurdle to hydrogenation. The types and structures of the polymerization chemicals, their polymerization mechanisms are very important for upgrading pyrolysis oil. This study firstly compared the polymerization rates of water-soluble fraction (PS) and water-insoluble fraction (PL) by accelerating aging fresh PS and PL at different temperatures (80 °C, 90 °C, 100 °C and 110 °C) for 24 h and at 110 °C for different durations (12 h, 24 h, 36 h, 48 h and 60 h), respectively. The thermogravimetric and differential thermogravimetry analysis results showed that PS polymerized much more rapidly than PL. Then, PS polymerization was further investigated by evaluating the changes in its physical properties (water content, viscosity and element content) and chemical compositions (gas chromatography and liquid chromatogram) before and after aging. The results showed that hydroxy aldehydes and ketones (especially glycoaldehyde, hydroxyacetone and levoglucosan), dicarbonyl compounds (especially succindialdehyde) and  $\alpha$ ,  $\beta$ -unsaturated carbonyl compounds (especially 3-methyl-2-cyclopenten-1-one and dehydrate resultants of some aldol condensation products) were mainly responsible for PS polymerization.

## 1. Introduction

Pyrolysis oil, a liquid product, is obtained from biomass materials under conditions of rapid heating, moderate temperatures (around 500 °C) and absence of oxygen [1]. It has characteristics of low nitrogen and sulfur and is easy to transport and store. It has the potential to replace traditional fossil fuels [2]. However, pyrolysis oil contains > 300 substances and various polymerization reactions could happen, even under ambient conditions [3]. The polymerization, initiated especially by the cellulose-derived fraction, was regarded as a great challenge to hydroprocessing of pyrolysis oil [4]. Mercader et al. [5] found that the hydrodeoxygenation process was a combination of polymerization and hydrogenation, and the polymerization was even faster than the hydrogenation. Moreover, the polymerization can result in production of char, plugging of reactor, deactivation of catalyst and minimal yield of hydrocarbon fuels, etc [6].

Pyrolysis oil can be fractionated into water-soluble (PS) and water-insoluble fractions (PL) through water extraction. PS is the most abundant products derived from holocellulose pyrolysis. Therefore, studying the polymerization reactions in PS is very important to providing the guidance for hydroprocessing of pyrolysis oil. Currently, reactivities of PS or some substances within it have been reported in

some literatures. For example, Hu et al. [7] performed a polymerization study based on bio-oil model compounds and found that some substances (such as sugars and sugar derivatives) within PS were highly reactive and tended to polymerize. But given that the reaction environment of model compounds was simple compared to that of real pyrolysis oil water-soluble fraction, the work was deemed significant but incomplete. Based on this, Meng et al. [8]. conducted an accelerated aging test on pyrolysis oil water-soluble fraction (WS) and observed evident aging behavior (such as increased molecular weight and solid formation) with increasing aging temperature. And it was concluded that acid-catalyzed sugar decomposition played an important role in polymerization. But the WS was obtained through a separation method described in literature [9] and its water content was higher than 96 wt%. Such high water content made stratification easy to occur during accelerated aging, and then resulted in a two-phase environment. But notably, in order to investigate compounds within pyrolysis oil in a more consistent matrix, it was emphasized in some studies [10,11] that the sample should remain a single phase before and after aging. Therefore, in this paper, the PS, with low water content (15 wt%) and no phase splitting before and after aging, was used to explore the polymerization by an accelerated aging experiment.

In this work, two key points were discussed. Firstly, the accelerated

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aging experiments of fresh PS and PL were conducted at different aging temperatures for 24 h and at 110 °C for different durations, respectively. The polymerization rates of PS and PL were compared. And thermogravimetry (TG) and differential thermogravimetry (DTG) was used to characterize the pre-aging and post-aging samples of both fractions. Then PS polymerization was further explored by employing other analysis techniques, such as water content and viscosity measurement, elemental analysis, gas chromatography (GC) and liquid chromatogram (HPLC). Finally, the main chemicals contributing to polymerization and their polymerization mechanisms were proposed based on the analysis results.

## 2. Experimental

### 2.1. Experimental material

The pyrolysis oil used in this work was supplied by the Shanxi Yingjiliang Bio-Energy Co., Ltd. It was produced from rice straw in a fluidized bed reactor operating at 500 °C, 1.5–2.2 kPa with 500 °C/s heating rate. The water-soluble fraction (PS) and water-insoluble fraction (PL) were prepared by mixing pyrolysis oil with water (V:V = 1:1). The PS was further concentrated through rotating evaporation (70 mbar, 39 °C) until its water content reached approximately 15 wt%. The PL was used without further processing. Levoglucosan (> 99%) was purchased from TCI (Shanghai) Development Co., Ltd. And glycolaldehyde dimer (97%) was purchased from Energy Chemical Industrial Co., Ltd. Dibutyl phthalate (> 99.5%) was purchased from Shanghai Aladdin Industrial Co., Ltd.

### 2.2. Accelerated aging experiment

During accelerated aging of both fractions for pyrolysis oil, approximately 2 g of PS (the water content was 15 wt%) or PL was added into a 10 mL sealed glass bottle and heated in an oven. Both fractions were aged at different temperatures (80 °C, 90 °C, 100 °C and 110 °C) for 24 h to investigate the effects of temperature. And they were aged at 110 °C for different durations (12 h, 24 h, 36 h, 48 h and 60 h) to examine the effects of time. In this paper, the fresh water-soluble sample was denoted as PS. The aged water-soluble samples at 80 °C, 90 °C, 100 °C and 110 °C for 24 h were denoted as PS-80 °C, PS-90 °C, PS-100 °C and PS-110 °C, respectively. And the aged water-soluble samples at 110 °C for 12 h, 24 h, 36 h, 48 h and 60 h were denoted as PS-12 h, PS-24 h, PS-36 h, PS-48 h and PS-60 h, respectively. The fresh water-insoluble sample was denoted as PL and the aged water-insoluble samples were denoted by reference to the rule above. The masses of the bottles were weighed before and after PS aging and the results showed that the mass loss was within 0.5 wt%.

### 2.3. Sample analysis

Firstly, the pre-aging and post-aging samples of both fractions were characterized by using TG. Secondly, the properties of the pre-aging and post-aging samples of PS, such as water content, viscosity and element content, were measured. And their chemical compositions were detected by using the GC and HPLC.

Thermal stabilities of both fractions were analyzed by using TG (Netzsch, 209-F3, Germany). Approximately 10 mg of sample was heated from 40 °C to 900 °C at a heating rate of 10 °C/min under nitrogen atmosphere. The flow rate of nitrogen was 80 mL/min.

Water contents in the pre-aging and post-aging PS samples were measured by using the method of Karl-Fischer Coulometric titration with a METTLER TOLEDO C20s titrator. The titrant was applicable for the samples containing aldehydes and ketones.

Viscosities of the pre-aging and post-aging PS samples were measured by using a RheoSense  $\mu$ VISCTM viscometer. According to Oasmaa et al. [9], the measurement was carried out at 40 °C.

Contents of elements (C, H, N and S) in the pre-aging and post-aging PS samples were determined by using an Elementar Vario Micro cube. The oxygen content was obtained according to the calculation formula as follows:

$$O(\%) = 1 - C(\%) - H(\%) - N(\%) - S(\%).$$

Chemical compositions of the pre-aging and post-aging PS samples were identified and quantified by using GC-MS and GC-FID, respectively. GC-MS is Thermo ISQ (America), with capillary column DB-1 (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu$ m), injector temperature of 300 °C, detector temperature of 300 °C, and oven temperature initially of 55 °C (held for 5 min), then raised to 230 °C (at 10 °C/min, kept for 5 min). Nitrogen was used as the carrier gas with a flow rate of 20 mL/min. GC-FID is Beijing Beifen SP-3420A (China), with capillary column DB-1 (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu$ m), and its temperature program was consistent with GC-MS. Dibutyl phthalate was chosen as the internal standard, and compounds in samples were roughly quantified by comparing the peak areas of them and internal standard under the assumption that the response factor for all substances was 1. Specifically, 1 g sample was diluted with 2 g methanol, and then 0.003 g dibutyl phthalate was added into the mixture.

In addition, levoglucosan and glycolaldehyde in the pre-aging and post-aging PS samples were accurately quantified with HPLC. Specifically, 0.5 g sample was fully dissolved into 10 g deionized water under ultrasonication, and then the suspension was filtered with a Büchner funnel. After filtering, the filtrate was collected for HPLC analysis and its volume was measured. HPLC is Waters 2695 equipped with an Aminex HPX-87H column and a differential detector. The mobile phase was aqueous solution of H<sub>2</sub>SO<sub>4</sub> (5 mmol/L) with a flow rate of 0.6 mL/min and the column temperature was 70 °C. Levoglucosan and glycolaldehyde were quantified by plotting a 7-point standard curve.

## 3. Results and discussion

### 3.1. Comparison the polymerization rates between water-soluble fraction (PS) and water-insoluble fraction (PL)

TG and DTG techniques were used to compare the thermal stabilities of PS and PL. Figs. 1 and 2 presented the TG curves of the pre-aging and post-aging samples of both fractions, respectively. And Table 1 summarized the detailed information obtained from the TG curves. The effects of aging temperature on PS and PL were shown in Fig. 1(a) and 2(a), respectively. Fig. 1(a) showed that compared to that of fresh PS, TG curves of aged PS samples tended to stabilize at higher level and the phenomenon was more obvious for the samples aged at higher temperatures. However, the TG curves of the pre-aging and post-aging PL samples in Fig. 2(a) were almost overlapping and exhibited little difference. The effects of aging duration on PS and PL were shown in Figs. 1(b) and 2(b), respectively. The PL TG curves were more overlapped than the PS TG curves. Therefore, qualitative results showed that either aging temperature or aging duration, had greater influence on PS than PL. Moreover, quantitative comparison of the polymerizations between PS and PL was also made by estimating the final residue. Generally, if the yield of final residue was higher, more polymers were formed during aging and the sample was more stable. And the residue aging indexes [8] of various samples were calculated with Eq. (1) and the results were also summarized in Table 1. It could be found that whether with increasing aging temperature or prolonging aging duration, the residue aging indexes of PS samples were far greater than those of PL samples. Consistent with qualitative results, this further indicated that more pronounced polymerization took place in PS rather than PL, and polymerization degrees of PS were far greater than those of PL under the same condition.

The findings above were also confirmed by the DTG curves. Fig. 3(a) and (b) presented the DTG curves of four representative PS samples (PS,

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