



# Co-pyrolysis of waste newspaper with high-density polyethylene: Synergistic effect and oil characterization



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## ABSTRACT

Biomass from waste newspaper (WP) was first co-pyrolyzed with high-density polyethylene (HDPE) in order to enhance the oil yield and its fuel properties. The synergistic effects during co-pyrolysis were investigated in terms of entire pyrolysis process, products yield and properties of liquid products (aqueous phase and oil phase) using thermogravimetric analysis coupled with infrared spectroscopy (TG-FTIR), physical properties analysis, elemental analysis, Fourier transform infrared spectroscopy (FT-IR), and gas chromatography/mass spectrometry (GC/MS). The results showed that synergistic effect occurred at 400–500 °C resulting in an obviously increase in oil phase by 31.59% as compared to theoretical data. Positive synergistic effects on fuel properties of co-pyrolysis oil were observed, especially demonstrating dramatically decrease in viscosity and total acid number by 75.96% and 216.04% in comparison to theoretical data. WP pyrolyzed alone gives mainly oxygenated compounds in its derived oil, while HDPE give hydrocarbons. No cross reaction products appeared in co-pyrolysis oil, implying that the synergistic effects were determined by altering its compounds content rather than generating cross reaction products. Unfortunately, aqueous phase and oil phase exhibit similar composition.

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## 1. Introduction

Massive consumption of fossil fuel resources has caused serious environmental issues and prompted great interest in renewable resources which can be converted into clean energy and high-valued feedstock. The huge annual worldwide production of municipal solid waste (MSW) such as waste daily newspaper and plastic reached almost two hundred million tons in China. Thermal conversion of MSW for fuels attracted considerable attention nowadays as traditional recycling processes (e.g. compost and incineration) cannot fundamentally solve the environmental and clean energy recycling issues. This thermal conversion process applied for MSW recycling not only can reduce its volumes, but also can recover chemicals and convert them into clean fuels in place of fossil fuels [1–6].

In recent years, co-processing has been focused in its clean products such as bio-gas [7], bio-oil [8,9], and bio-char [10] which have potential for replacing fossil fuels. However, the derived bio-fuels have many unstable properties as compared to conventional fossil fuels due to their high oxygen, acid, and water contents. These shortcomings greatly limit the application of bio-fuels in

energy field. High-density polyethylene could offer hydrogen in co-pyrolysis to organic natural materials with less hydrogen content such as waste newspaper and balance the carbon, oxygen, and hydrogen in the feedstock. This synergistic effect would lead to strong improvement on the properties of their derived products [11]. Moreover, co-pyrolysis process can solve the problem that different components of MSW are not easily separated from the post-consumer stream.

Previous studies have demonstrated that biomass pyrolyzed alone produces highly oxygenated derived oil due to low carbon content of 45–50 wt.% and high oxygen content of 35–45 wt.% in the feedstock [12,13], while synthetic polymers such as high-density polyethylene have high carbon content of 84 wt.% and contain nearly no oxygen generating mainly hydrocarbons in its derived oil [14]. Co-pyrolysis of biomass with synthetic polymer could adjust the content of C, H, and O in the derived products leading to positive synergistic effects on derived bio-oil properties [14–30]. Biomass from lignocellulosic biomass [14–22], cellulose [23–26], model compound of hemicellulose [27], and lignin [28–30] were co-pyrolyzed with synthetic polymers, which were considered as an effective way to enhance the yields and fuel properties of liquid product. However, since lignin mainly generates solid product during thermal degradation [28,29], pyrolysis of cellulose gives higher liquid yield than lignocellulosic biomass and

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lignin. Especially, Solak et al. [25,26] reported that co-pyrolysis of cellulose with polyethylene at 500 °C gives the highest bio-oil yield of 79.5 wt.%, while Brebu et al. [22,28] reported that the liquid yield obtained from co-pyrolysis of lignin with synthetic polymers (polyethylene, polypropylene, polystyrene, and polycarbonate) only reached 53.2–62.7 wt.% and also reported that co-pyrolysis of pine cone with synthetic polymers gives the liquid yield of 63.9–69.7 wt.%. Therefore, waste newspaper which mainly consists of cellulose was selected as biomass in this study aiming at enhancing the yield and fuel properties of liquid product during co-pyrolysis with high-density polyethylene.

In this study, co-pyrolysis of waste newspaper with high-density polyethylene was performed to investigate the synergistic effect in terms of its entire pyrolysis process, products yield, and oil properties. Such understanding is essential for development of co-pyrolysis products applications in energy source and technology for the production of industrial wastes with improved value.

## 2. Experiment

### 2.1. Materials

The feedstock used in this study included waste newspaper (WP) and high-density polyethylene (HDPE). WP was obtained from local newsstand, milled, and sieved to a particle size of less than 1 mm using mesh screen [31], and dried for 24 h at 80 °C. HDPE was obtained from Yangzi (Nanjing) Chemical Plastic CO., LTD and first ground by a grinder. Then the crushed HDPE was sieved at a powder size of less than 500 µm using mesh screen which and dried for 8 h at 60 °C. The mass ratios of the WP/HDPE blend were 1:0, 2:1, 1:1, 1:2, and 0:1, respectively, and it was homogenized by mixing and subsequent rolling for 12 h. Some typical properties of WP and HDPE are presented in Table 1.

### 2.2. Pyrolysis process and products

The pyrolysis experiments were established as seen in Fig. 1 under 20 mL/min N<sub>2</sub> flow. Approximately 6 g of feedstock material was used for each experiment and heated up to final decomposition temperature of 500 °C with the heating rate of 10 °C/min. The condensable pyrolysis products were collected from U-tube and naturally separated into aqueous phase and oils phase. Water content higher than 30 wt.% leads to phase separation according to Chiaramonti's study [32]. Diethyl ether was used to extract most part of organic compounds from the aqueous phase. Then, the extracted aqueous phase was separated by density from the ether

one and it was washed several times with diethyl ether for advanced extraction of organic compounds. The diethyl ether fraction was further analyzed by FT-IR and GC/MS. Condensed liquid products including water were weighed and recovered in dichloromethane. Solid yield was determined by the overall weight losses of the quartz tube. Non-condensable gas yield was determined by overall material balance.

### 2.3. Synergistic effect

The synergistic effect can be observed by comparing the co-pyrolysis product yields with theoretical value calculated by the additivity rule from the yields corresponding to the individual components as seen in Eq. (1) [33].

$$y = (x_1 \cdot w_1 + x_2 \cdot w_2) \quad (1)$$

where  $y$  represents the theoretical value;  $x_1$  and  $x_2$  represent the experimental products yield, physical properties value, and elements content of oils obtained from individual WP and HDPE pyrolysis, respectively;  $w_1$  and  $w_2$  are the mass proportion of WP/HDPE blend. Thus, a synergistic effect occurs during co-pyrolysis if the experimental value is higher than the theoretical value.

### 2.4. Characterization methods

Thermogravimetric analysis coupled with infrared spectroscopy (TG-FTIR) was conducted on a NETZSCH STA449C and Bruker FT-IR Tensor 27 spectrometer in high purity N<sub>2</sub>. A total of 5–10 mg of sample was heated up to 600 °C under 20 mL/min N<sub>2</sub> flow with the heating rate of 10 °C/min. The FT-IR instrument was connected to the thermogravimetric analyzer by a pipe and a flow cell, which were preheated to 180 °C to prevent condensation of the evolved gases. The volatiles released during pyrolysis can be recorded by means of the FT-IR real-time tracking mode with the scanning range from 4000 to 400 cm<sup>-1</sup>.

The physical properties and element components of obtained oils were characterized using the items of ultimate composition (Carlo Erba EA1108), calorific value (IKA C-2000), water content (Crison Titromatic by Karl-Fischer titration), total acid number and pH (Mettler Toledo T50), density (Anton-Paar DMA35N), and viscosity (Brookfield LVDV-E) according to ASTM E203-96. Only averaged values over four repeated analysis were considered to compensate for an eventual heterogeneity of the sample.

Fourier transform infrared spectroscopy (FT-IR) was used for chemical structure analysis in NEXUS870, using a KBr disc containing 1% samples. Sixteen scans were conducted for each sample in the range from 4000 to 400 cm<sup>-1</sup>, with a resolution of 4 cm<sup>-1</sup>. The precision was no more than 0.01 cm<sup>-1</sup>.

Oil phase and diethyl ether fraction of aqueous phase were characterized using gas chromatography/mass spectrometry (GC/MS) for qualitative analysis, which was carried out on an Agilent 6890N gas chromatograph (GC) coupled with 5975 inert XL mass selective detector (MSD) instrument working at an ionizing voltage of 70 eV. A HP5-MS column was used (30 m × 0.25 mm × 0.25 µm, 5% – phenyl–95% – methyl polysiloxane). The column program is: injector temperature, 240 °C; split ratio, 50:1; volume of injected sample, 0.2 µm; initial column temperature, 40 °C, hold for 2 min; heating rate, 12 °C/min; final temperature, 260 °C, hold for 10 min; carrier gas, Helium with purity of 99.999%, 1 mL/min. Qualitative identification for compounds was performed based on library data from MS spectra.

**Table 1**  
Ultimate and proximate analyses for WP and HDPE.

	WP	HDPE
<i>Elemental analysis<sup>a</sup>, wt.%</i>		
C	39.78	85.43
H	5.50	14.21
O <sup>c</sup>	54.62	0.15
N	0.10	0.08
H/C molar ratio	1.66	1.99
O/C molar ratio	1.03	0.001
Calorific value <sup>b</sup> , kJ/g	14.57	38.66
<i>Proximate analysis, wt.%</i>		
Volatile	72.8	100
Moisture	6.5	–
Ash	11.2	–
Fixed carbon <sup>c</sup>	9.5	–

<sup>a</sup> Dry basis and ash-free.

<sup>b</sup> Dry basis.

<sup>c</sup> Calculated by difference.

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