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Synergistic effects on char and oil produced by the co-pyrolysis of pine wood, polyethylene and polyvinyl chloride

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ABSTRACT

The synergistic effects of the woody biomass (pine wood (PW)) and plastics (polyethylene (PE) and polyvinyl chloride (PVC)) during co-pyrolysis on the properties of char and oil were examined by thermogravimetric analysis (TGA) and fixed bed reactor. The results showed that PW-PE interaction increased the maximum weight loss rate of PW by 8.0–23.7%. Co-pyrolysis of PW-PE blends produced lower quantity of char (13.8–22.4%) and higher quantity of oil (3.7–4.4%) as compared to the theoretical results. PW-PVC interaction decreased the temperature corresponding to the maximum weight loss rate of PW by 47–51 °C. Co-pyrolysis of PW-PVC blends yielded more char (15.5–27.9%) and less oil (7.2–14.4%) than expected values. Also, the interaction of biomass and plastic materials decreased the H/C atomic ratio of char, which resulted in a higher chemical stability of char. The fuel quality of oil produced from mixtures was improved due to a lower O/C atomic ratio of oil as compared to the theoretical results.

1. Introduction

Renewable hydrocarbons (e.g. biomass) and fossil fuel hydrocarbons (e.g. plastics) are the major combustible fractions in municipal solid waste (MSW) [1]. The safe utilization of these materials is considered a significant challenge for the sustainability of the planet. Biomass as widely distributed huge reserves of emerging green energy is expected to play an important role in the development of renewable energy systems around the world [2]. It is mainly composed of cellulose (40–60%), hemicelluloses (15–30%), lignin (10–25%) and a small fraction of extractives and inorganics [3]. Plastic materials contain different types of polymers, such as polyvinyl chloride (PVC), polyethylene (PE), polypropylene (PP), polystyrene (PS) and polyethylene terephthalate (PET), which are extensively used in various forms daily [4]. However, the environmental pollution and the great loss of resources from the disposal of biomass and plastic wastes have become common challenges around the world. Also, the recent ban of plastic waste imports in China will accelerate the need and development of units to beneficially use plastic materials. Pyrolysis is one of the most promising methods for the treatment of biomass and plastic wastes. This is associated with the high efficiency, remarkable volume and mass reduction, energy recovery and variety of sellable products (syngas, char and oil) that thermal treatment processes indicate.

The pyrolysis of biomass and plastics has been extensively studied

[5–13]. The three major components of biomass are hemicellulose that decomposes between 200 and 350 °C, cellulose that decomposes between 300 and 375 °C and lignin that reacts in a wide temperature range of 160–500 °C [5]. The main product of lignin is char since it is not readily cleaved to lower molecular weight fragments [6]. The pyrolysis mechanisms of plastics are different due to the complexity of polymer structures. PE and PVC are two of the most commonly used polymers [4]. The thermal decomposition of PE occurs at temperatures between 350 and 500 °C. The polymer chain breakdowns and primary products (C₁–C₅ and C₁₀–C₂₄ aliphatic compounds) are formed, which are then cracked to mainly C₃–C₅ olefins. The reactions are accelerated by the free radicals formed [7]. The Diels-Alder type reactions are observed as the pyrolysis temperature is increased, and the C₃–C₅ olefins are transformed to aromatics [8,9]. Wax is the main product in the oil produced from the pyrolysis of PE, which can be used as a substitution of fossil fuels or petrochemicals [14]. One of the first to break during thermal decomposition of the PVC materials is the C-Cl bond. This is followed by the intermolecular chain transfer, that results via dehydrochlorination (DHC) in the evolution of HCl at 200–300 °C [10]. The residual polyene undergoes further thermal degradation at a higher temperature range of 400–550 °C [11–13]. The disposal of PVC wastes by thermal methods is hampered by the release of Cl, which leads to serious issues, such as the corrosion, the formation of chlorinated compounds and dioxins, and the poisoning of catalysts [15].

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The pyrolysis/gasification of plastics in fluidized bed often faces the agglomeration of bed particles with plastic particles and the subsequent defluidisation [16]. Biomass oil has high contents of oxygen, acid compounds and water, which lower the bio-oil quality and restrict its use. These facts have led to extensive investigations of co-treatment of different materials, such as plastics, biomass, coal, MSW and sewage sludge to make degradation easier while maintaining productivity and profitability [2,6,15–20]. Particularly, the co-pyrolysis of plastics and biomass materials is potential for the production of various chemicals and fuels [15,17,21–26]. The synergistic effect of these two materials is also unavoidable during the thermal conversion of some mixed wastes, such as MSW and refuse derived fuels (RDF) [17]. Co-pyrolysis is an important and efficient strategy to counter the lack of off-seasonal biomass supply, to provide efficient conversion of low-grade feedstock [27], and to modify the quantity or quality of oil produced [17,21–23].

Co-pyrolysis of plastics and biomass materials usually results in a higher yield of oil with acceptable quality. Some co-pyrolysis examples are newspaper-high density polyethylene (HDPE) [17], plywood-PP [21], pine cone-PE/PP/PS [22] and cotton stalk/hazelnut shells/sunflower residues/ard land plant-PVC/PET [23]. The improved quality of co-pyrolysis oil is resulted from the increase of aliphatic compounds and the decrease of oxygen, water and acid contents [17,28]. The synergistic effect of different plastics with biomass materials varies. About 25% deviation between the experimental and theoretical thermogravimetric analysis (TGA) results was observed during the co-pyrolysis of high density polyethylene (HDPE) and biomass (bamboo, empty fruit bunch and sawdust), and up to 40% deviation was reached for that of PS and biomass [24]. Whereas, no significant synergistic effect in the derivative thermogravimetric analysis (DTG) curves was found for the co-pyrolysis of low density polyethylene (LDPE) and cellulose [25]. During the co-pyrolysis, polymers may act as H-donors and lead hydrogen transferring from polymer chains to biomass derived radicals [23]. This effect may stabilize the primary products from cellulose thermal degradation resulting in a higher yield of liquid and a lower yield of char [29,30]. Furthermore, the radicals derived from biomass with relatively lower stability may promote the polymer degradation [31]. The overlap of temperature regimes of plastic and biomass pyrolysis is necessary for the occurrence of interaction [27]. However, the specific co-pyrolysis mechanisms of plastic-biomass mixtures are still unclear and vary with different feedstock. Some contradictions concerning this topic exist. For example, Tang et al. [15] observed a lower oil yield from the co-pyrolysis of food waste and PVC, which was contradictory to others' findings [17,21–23]. Also, there are no many studies discussing the synergistic effects on the quality of co-pyrolysis products, especially char and oil. This research was designed to fill in these gaps.

In this paper, one of the most widely used plastics (PE) and a troublesome plastic (PVC) were co-pyrolyzed with woody biomass material (pine wood) to study the synergistic effects on char and oil. The kinetic parameters of the co-pyrolysis of the materials were determined by thermogravimetric analysis (TGA). This was helpful for the understanding of the synergistic effects on the products quality. Fixed bed reactor was used to determine the yields of products (char and oil). The H/C atomic ratio, the carbon structure and the textural property of the char produced were characterized. The elemental composition and the component classification of oil were analyzed. The experimental results were compared with the theoretical calculation results to identify the synergistic effects.

2. Materials and methods

2.1. Materials

PE and PVC were obtained from Sigma-Aldrich. Pine wood (PW) was provided by Zhejiang Zhongyuan Electric Co., Ltd., China. The particle size of materials was less than 500 μm . The batches of PW-PE

Table 1
Proximate and Ultimate analyses of materials (dry basis, wt%).

Analyses	PW	PE	PVC
<i>Proximate analysis</i>			
Volatile matters	77.0	100.0	94.9
Ash	5.0	0	0
Fixed carbon	18.0	0	5.1
<i>Ultimate analysis</i>			
C	47.9	85.7	39.6
H	5.5	14.3	4.9
O ^a	40.9	0	0
N	0.6	0	0.5
S	0.1	0	1.8
Cl	0	0	53.2

^a By difference.

and PW-PVC were prepared with mass ratios of 3:1, 1:1 and 1:3. The materials were kept at dry atmosphere and well mixed before each test. The ultimate and proximate analyses of materials were measured by Carbon-Hydrogen-Nitrogen analysis (5E Series-CHN2000 Ultimate Analyzer) and thermogravimetric analysis (5E Series-MAG6700 Proximate Analyzer), respectively. The analyses results are presented in Table 1.

2.2. Thermogravimetric experiments and kinetic analysis

Thermogravimetric analysis (TGA) was carried out using a thermal analyzer (TA-Q500). TGA experiments were conducted on 8 mg samples (individual feedstock and blends) in inert atmosphere (N_2), using a ramp rate of 10 $^\circ\text{C}/\text{min}$, to the final temperature of 600 $^\circ\text{C}$. The flow rate of N_2 was 60 ml/min. All experiments were conducted at least three times. The expression of the kinetics of heterogeneous reactions combined with the Arrhenius equation can be described as follow:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (1)$$

where t is time (min), A is pre-exponential factor (min^{-1}), E is activation energy (kJ/mol), R is gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), T is temperature (K) and α is conversion ratio which is given as follow:

$$\text{Conversion } (\alpha) = \frac{m - m_0}{m_f - m_0} \quad (2)$$

where m_0 and m_f are the weights of sample at initial and final state, m is the weight at a given time t (min). Considering the heating rate $\beta = dT/dt$, Eq. (1) can be transformed to Eq. (3).

$$\frac{d\alpha}{dT} = \left(\frac{A}{\beta}\right) \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (3)$$

The pyrolysis adopts independent first-order reaction model expressed by Eq. (4).

$$f(\alpha) = 1 - \alpha \quad (4)$$

Eq. (3) is then integrated using the integral method based on Coats and Redfern equation [18,24] and the result is given as Eq. (5).

$$\ln \left[\frac{-\ln(1-\alpha)}{T^2} \right] = -\frac{E}{R} \left(\frac{1}{T} \right) + \ln \frac{AR}{E\beta} \quad (5)$$

Thus, the activation energy and pre-exponential factor can be obtained from the slope and intercept of line determined by plotting $\ln[-\ln(1-\alpha)/T^2]$ vs. $1/T$.

The calculated derivative thermogravimetric analysis (DTG) was defined as Eq. (6) according to the mass ratio of blends.

$$\frac{d\alpha}{dT} = m_b \frac{d\alpha_{\text{biomass}}}{dT} + (1 - m_b) \frac{d\alpha_{\text{plastic}}}{dT} \quad (6)$$

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