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Thermal behavior and kinetic study for co-pyrolysis of lignocellulosic biomass with polyethylene over Cobalt modified ZSM-5 catalyst by thermogravimetric analysis

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ABSTRACT

The thermal behavior and kinetic study of lignocellulosic biomass (rice straw (RS)) and linear low-density polyethylene (LLDPE) pyrolysis over modified ZSM-5 catalyst were investigated using thermo-gravimetric analysis (TGA). Cellulose and lignin were used as model compounds of biomass in order to investigate the reaction mechanism of lignocellulosic biomass and polyethylene co-pyrolysis. Results showed that RS & LLDPE co-pyrolysis was more complicated than that of the individual components. The activation energy (E) of RS, and RS & LLDPE pyrolysis were 79.61 kJ/mol and 59.70 kJ/mol respectively, suggesting that there was a positive synergistic interaction between RS and LLDPE. The addition of LLDPE with lignin co-pyrolysis obtained a lower apparent activation energy (33.39 kJ/mol) compared to raw lignin pyrolysis (53.10 kJ/mol). Results indicated that the Cobalt modified ZSM-5 catalyst was able to improve the reaction rate of RS and LLDPE co-pyrolysis; also the addition of Co/ZSM-5 catalyst resulted in a lower apparent activation energy during cellulose and LLDPE co-pyrolysis.

1. Introduction

With the continuous development of society, human dependence on energy is always increasing. Petroleum fuel is one of the most widely used sources of energy and is considered as a non-renewable source of energy because its consumption is higher than regeneration (Abnisa and Wan Daud, 2014). The continuous use of large quantities of fossil fuel has contributed to the release of vast amounts of contaminants, such as sulfur dioxide, nitrogen oxides and carbon dioxide into the atmosphere and has caused serious environmental problems (Kalogirou, 2004). Apart from the use of petroleum as a fuel source, its derived products such as plastics have been significant contributors to environmental degradation. Most of the plastic that is used in everyday society is derived from petroleum based chemicals; the versatility of the material has caused its use to be in almost every part of our daily lives. Singh and Sharma (2016) reported that annually about 300 million tons of new plastic material is produced which adds to the already existing plastic; the secondary use of this material has been the subject of recent investigations (Singh and Sharma, 2016).

In order to produce an environmentally friendly source of fuel, biomass has been considered as a potential source of energy material that can replace fossil fuels in the future due to its abundance and carbon neutral processing (Fazlollahi and Maréchal, 2013). Biomass has been known to have several benefits: it is clean (less greenhouse gas emissions), it can be obtained at low costs (agriculture, forestry waste, etc.), it has great compound diversity and it is very easy to grow (González et al., 2009). Biomass is primarily composed of a complex biopolymer consisting mainly of cellulose, hemicellulose and lignin (Bajpai, 2016; Huber et al., 2006; Morgan et al., 2017). In China, agricultural residues is one of the most abundant sources of biomass, according to statistics, China's crop residues have been almost 750 million tons per year since 2010 (Qiu et al., 2014). These sources of materials are normally burned in fields which contribute to environmental pollution but in recent years there have been investigations that are focused towards the use of these materials for the production of energy compounds.

In general, there are two main pathways that are typically used for biomass conversion to fuels and chemicals: biochemical conversion

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(enzymatic hydrolysis by mild conditions) and thermochemical conversion (under high temperature and high pressure conditions) (Bridgwater and Peacocke, 2000). The thermochemical method typically consists of three main pathways: gasification, pyrolysis and liquefaction, and hydrolysis (Bu et al., 2015; Huber et al., 2006). Biomass pyrolysis is normally described as a thermal decomposition process that occurs in the absence of oxygen where bio-oil, syn-gas and bio-char are produced (Bu et al., 2012; Mohan et al., 2006). Out of the three products that are obtained from biomass pyrolysis, bio-oil is the one that has been investigated thoroughly because it is the most valuable; however it is a well known fact that the bio-oil obtained via pyrolysis cannot be utilized directly for substitutes of fossil fuels due to its low quality (such as high oxygen content, high viscosity, high water content and low heating value) (Duan and Savage, 2011; Gunawan et al., 2013). Therefore, in order to improve the quality of bio-oil derived from biomass pyrolysis, plastics have been investigated for their potential use as feedstock addition (Han et al., 2014; Paradela et al., 2009). Plastics are rich with hydrogen compounds which make them highly suitable for co-pyrolysis with biomass in order to improve compound diversity and bio-oil quality (Zhang et al., 2016b). Catalysts have also been reported to be used in biomass co-pyrolysis investigations for the purpose of improving the reaction efficiency and bio-oil quality; it was also reported that the use of catalyst does not interfere with the decomposition mechanism (Bhattacharya et al., 2009b; Xue et al., 2016). Catalytic co-pyrolysis of biomass and plastics includes two types of interaction: the interaction between biomass and plastics during thermal decomposition by pyrolysis and the interaction between the decomposing products at the catalyst site (Bhattacharya et al., 2009b; Li et al., 2014). Biomass catalytic co-pyrolysis using plastics as feedstock addition have been suggested to have a more complex reaction pathway than pyrolysis conducted without the presence of plastics (Dorado et al., 2013; Dorado et al., 2015; White et al., 2011). Zeolite catalysts have traditionally been used in the petroleum industry when processing desired fuels and chemicals; for this reason these same zeolite catalysts have been investigated in the production of bio-based compounds through biomass co-pyrolysis with plastics (Li et al., 2014; Xue et al., 2016; Zhang et al., 2015b). Literature reports have suggested that the modification of zeolite (ZSM-5) catalysts was able to change their crystalline and physical structure while improving their chemical behavior and functionality (Zhang et al., 2015a; Zhang et al., 2015c). Results indicated that metal oxides and transition metals were frequently used to modify the structure of zeolite catalyst so as to improve compound selectivity during chemical reactions (Bu et al., 2014; Wang et al., 2012; Zhang et al., 2015a). Even though previous investigations have been conducted, there are seldom investigations that have focused on studying the effects transition metal modified ZSM-5 catalyst have on the internal thermal degradation of lignocellulosic biomass and plastics during co-pyrolysis reaction process along with the reaction mechanism and reaction kinetics of the entire process.

Therefore, in this study, transition metal (Cobalt) modified ZSM-5 catalyst was prepared to investigate its influence on co-pyrolysis of lignocellulosic biomass with plastic. The thermal decomposition behaviors of rice straw (RS), linear low-density polyethylene (LLDPE) and RS & LLDPE blends during pyrolysis were investigated using thermogravimetric analysis (TGA). In order to identify a possible reaction pathway which will shed light on a possible reaction mechanism of lignocellulosic biomass and plastics co-pyrolysis with the influence of the modified ZSM-5 catalyst; cellulose and lignin were used as model compounds during co-pyrolysis of biomass with polyethylene. A kinetic study of non-catalytic and catalytic lignocellulosic biomass and polyethylene co-pyrolysis over Co/ZSM-5 was also conducted.

2. Materials and methods

2.1. Materials

Rice straws (RS) (4 mm in diameter and 8 mm in length) biomass feedstock was collected from the countryside of Zhenjiang City, Jiangsu Province, China. Linear low-density polyethylene (LLDPE) powder were purchased from Dongguan Haosheng Plastic Co., Ltd., Guangdong Province, China. Parent ZSM-5 (SiO_2/Al_2O_3 Mole Ratio: 46) was purchased from Nankai University Catalyst Co., Ltd. The $Co(NO_3)_2{\cdot}6H_2O$ was purchased from Sinopharm Chemical Reagent Co., Ltd. which was used for the catalyst modification. The cellulose was purchased from Alfa Aesar (China) Chemicals Co. Ltd., and lignin was purchased from Tokyo chemical industry Co. Ltd.

2.2. Catalyst preparation

In this experiment, catalyst preparation was done using the excessive wetness method. This modification technique has been used by other investigations conducted by (Lee et al., 1997). Forty (40) grams of the ZSM-5 catalyst was weighed and poured into a 250 ml beaker. Five percent (5% wt) of the 40 g of ZSM-5 was used to determine the quantity of the metal salt needed for modification and mixed with the ZSM-5 catalyst. An excess amount of de-ionized water was added to the beaker to dissolve the mixture. The mixture was then placed in a magnetic stirrer with a water bath that was maintained at a temperature of 60 °C for six (6) hours. After thorough mixing, the catalyst was separated from the excess water and molded into the desired form. The modified ZSM catalyst was subsequently dried in an oven at a constant temperature of 105 °C for twelve (12) hours at vacuum. After drying, the catalyst was crystallized in a tube furnace for four (4) hours at 550 °C in 99.96% nitrogen atmosphere that was maintained at a constant flow rate of 50 mL/min. The transition metal modified ZSM-5 catalyst was prepared and stored for biomass pyrolysis analysis. The prepared catalyst was characterized by XRD and NH_3-TPD analysis as shown in the supplementary material.

2.3. Thermogravimetric analysis

The thermal degradation behavior of lignocellulosic biomass (RS, cellulose and lignin) with polyethylene (LLDPE) was evaluated by a thermogravimetric analyzer (PerkinElmer TGA 4000, America). In preparation for the experiment the rice straw was ground to powder and then sieved to particle sizes of about 0.3 mm. In each experiment, approximately 5 mg of the sample was placed in a crucible and heated from 25 °C to 600 °C at a temperature ramp rate of 30 °C/min, a nitrogen flow rate of 20 ml/min. The thermal decomposition of RS and LLDPE were carried out separately. The mixture of RS and LLDPE were thermally decomposed at a mixing ratio of 4:1. Catalytic decomposition of the feedstock was carried out with modified and unmodified catalyst respectively. Co-pyrolysis experiments were conducted also using a 4:1 biomass/LLDPE ratio and 25% catalyst was used for catalytic experimental runs. The methodology used for the analysis of cellulose or lignin co-pyrolysis was the same as that described previously, the catalyst ratio was the same as well.

2.4. Biomass pyrolysis kinetic method

Biomass decomposition kinetics is normally calculated using iso-conversional methods. One of the main principles of iso-conversional methods is that the heating rate and temperature changes does not affect the reaction mechanism (Sun et al., 2012). In general, the rate of non-isothermal solid decomposition can be expressed as:

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{1}$$