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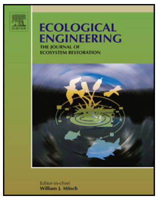

Optimisation of corn straw biochar treatment with catalytic pyrolysis in intensive agricultural area

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ABSTRACT

The crop biomass treatment is the challenging issue in the intensive agricultural area and the catalyst has the potential to solve this problem. This preliminary study examined the response of the corn straw biochar treatment to the catalytic pyrolysis and applications of catalyst to the sustainable agricultural with cost savings. The surface morphology of corn straw after pyrolysis was compared with the electron microscope scanned images. The pyrolytic characteristics and kinetics of corn straw were studied using a thermogravimetric analyser from ambient temperature to 900 °C under a nitrogen atmosphere at heating rates of 10, 20, 30 and 40 °C min^{-1}. The mass loss and the rate of mass loss curves derived from the pyrolysis of corn straw biochar and the biochar with the addition of 5% (wt.%) ammonium dihydrogen phosphate (ADP) catalyst. The pyrolysis process was consisted of three distinct stages, and impact of catalyst on the temperature distribution was distinguished. The catalytic pyrolysis process was mainly categorised by removal of water including free water and combined water, decomposition of hemicellulose, cellulose and lignin; and carbonisation. With the increase of pyrolysis rate, the maximum weight loss temperature shifted to lower temperatures. The kinetic process characteristics of corn straw biochar at three levels of ADP addition and four kinds of temperature were calculated. The activation energies and pre-exponential factors of the pyrolysis process were calculated by the Flynn–Wall–Ozawa method, modified Coats–Redfern model-free method and Kissinger method. The detailed information of kinetic parameters also helped to improve the biomass pyrolysis process. The analysis demonstrated that the ADP had a catalytic effect on the pyrolysis behaviour of biomass and was able to reduce the activation energy of biomass pyrolysis. Therefore, the catalyst can improve the pyrolysis process and have great potential to increase crop residue treatment efficiency, especially in the intensive agricultural area.

1. Introduction

The intensive agricultural management introduced by food safety have to meet the need about the sustainable development with the considerations of soil conservation, diffuse pollution, climate change and residue management (Singh et al., 2015). In the agriculture area, the biomass waste is also a renewable and abundant organic resource. Approximately 0.8 billion tonnes of various crop residues are generated annually in China, of which corn and wheat straw make up 216 and 135 million metric tonnes, respectively (National Bureau of Statistics of China, 2010). In many areas of the country, crop straws are burned in the open, which result in increased greenhouse gas emissions into the atmosphere. Therefore, the proper and efficient treatment of crop straw has important significance to maintain the environmental quality and the sustainable development (Malińska et al., 2014). The regular crop residue reuse is difficult in the freeze-thawing intensive agricultural area, but the biochar treatment with the assistance of the catalyst is an effective method and needs the mechanism study.

Crop residues biochar treatment has been studied worldwide for the soil amendment and agricultural waste management, which also provides the biofuel with the economic advantage (Masto et al., 2013). The crop residue is the main issue during the tillage practice, which is more serious in the freeze-thawing agricultural area due to the slow decomposition rate. However, the crop residue cycle is also the best solution to maintain soil organic matter stocks, which is important for soil fertility and properties (Neill, 2011). With the assistance of the pyrolysis process and the addition of the catalyst, the biomass treatment can be completed in shorter time

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and with higher carbon content (Zabeti et al., 2012). This advance leads to less economic cost and advocates the application during the sustainable tillage. The corn is the dormant crop in this freeze-thawing intensive agricultural area and catalytic pyrolysis stages have special patterns, which also helps to optimise the biomass treatment.

The thermal pyrolysis is the conversion measurement for biomass into biochar, bio-oil and biogas (Jain et al., 2014). Pyrolysis behaviour is influenced by many factors, which include the biomass species, temperature range, heating rate, pyrolysis atmosphere and certain treatment methods (Kloss et al., 2012; Garcia-Maraver et al., 2013). Hence, the content and composition of main products must be determined under a range of pyrolysis conditions, which is influenced by catalyst treatment. The presence of CaO for certain pyrolysis phases has been shown to increase the conversion of the resource and capture the CO_2 produced (Zhang et al., 2014). The biochar with more content of carbon suits for the soil fertility conservation and numerous porous structures are helpful for the diffuse pollution control (Houben et al., 2013; Bayabil et al., 2015). The catalyst can be used to control the reaction process and products of biomass pyrolysis, which has been extensively studies in the past few decades.

The kinetic pattern is the direct factor for biochar treatment and also the effective chain to adjust the pyrolysis process. The thermogravimetric analysis (TGA) is the common technique to evaluate kinetic parameters about pyrolysis process description (Teh et al., 2014). There are mainly two types of methods to calculate kinetic parameters through non-isothermal TGA data, which are model-fitting and iso-conversional method. The model-fitting method estimate kinetic parameters based on prior assumptions of the reaction mechanism model. For iso-conversional method, the activation energy is calculated from data of the same conversion in a series of TGA curves, which are obtained at different heating rate without using a reaction function. Therefore, they are also termed as model-free methods (Ceylan and Topcu, 2014; Slopiecka et al., 2012). Both methods are usually used to verify each other's parameters and support the treatment optimisation.

The crop residue is the main concern for the sustainable development in intensive agricultural area, which also has direct connections with soil carbon cycle and greenhouse gas emission (Kumar et al., 2013; Suthar, 2008). The biochar is also the effective materiel for the agricultural diffuse pollution control (Lucchini et al., 2014). In order to achieve the best treatment performance, the ammonium dihydrogen phosphate (ADP) was chosen as the catalyst for the pre-treatment of corn straw. The main objectives of this study are to (1) investigate the impact of the catalyst on the pyrolytic characteristics and pyrolysis kinetics of corn straw; (2) identify the kinetic parameter values of pyrolysis with the model-fitting and free-model methods after the TGA of the corn straw with different additions of catalyst; and (3) optimise the biomass utilisation and agricultural waste management with the theoretical basis at four heating rates.

2. Materials and methods

2.1. Sample preparation

The catalyst used in this study was ADP (analytical grade) purchased from Xilong Chemical Co., Ltd. (Beijing, China). Deionised water (18 MΩ) used in this study was produced using a Millipore Simplicity 185 (Merck Millipore, US). The corn straw biomass was obtained from the Sanjiang Plain in Northeast China, which is the typical intensive agricultural area in China (Ouyang et al., 2014). As the freeze-thawing condition, the crops grow from May to October and the massive crop residue is the challenge for the tillage in the next year. The natural decomposition is slow due to the cold condition, therefore the biochar treatment is the potential method and can provide effective material for diffuse pollution control (Angst et al., 2014).

The corn straw was washed in deionised water and dried in the oven at 105 °C, which was then smashed in a crushing machine and passed through a 100 mesh (0.154 mm) screen. The corn straw biochar sample with no catalyst (0%) was labelled as CS. In order to study the impact of different ADP loads on pyrolysis process, the corn straw was treated by dipping it in 1%, 5% or 10% (wt.%) ADP solutions for 24 h. After being sufficiently impregnated, the corn straw was dried in an oven at 80 °C for 2 days. The CSA1, CSA5 and CSA10 were the labels for straws with three levels of ADP concentrations, which were characterised by TGA. The corn straw has three components (hemicellulose, cellulose and lignin), which has special pattern in pyrolysis stages and was compared by two types of materials. The CS and CSA5 were pyrolysed in ceramic pots with lids under a nitrogen atmosphere at different target temperatures (350 °C, 450 °C, 550 °C and 650 °C) for 4 h. The comparison presented the structure change in different pyrolysis stages. The treated biochar was named as CS-350, CS-450, CS-550, CS-650, CSA5-350, CSA5-450, CSA5-550 and CSA5-650.

2.2. Material analysis

To observe the surface morphology pattern of corn straw after pyrolysis, the CS, CS-450 and CSA5-450 samples were imaged using scanning electron microscopy (SEM) (Hitachi S-4800, Japan). The functional groups of the corn straw (CS and CSA5) and biochars from corn straw after pyrolysis at different temperatures were detected with a Nexus 670 FTIR spectrophotometer (Thermo Nicolet Corporation, US). This process can determine how the functional groups of corn straw changed during the pyrolysis process. The spectra were recorded from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}. The samples were prepared with a tableting method after being mixed with KBr in an agate mortar. The pyrolysis of four corn straw samples (CS, CSA1, CSA5 and CSA10) was conducted with TGA by TA Q50 analyser (TA Instruments, US) in a nitrogen flow of 60 ml min^{-1} (Zhao et al., 2013). The pyrolysis experiments were performed at heating rates of 10 °C, 20 °C, 30 °C and 40 °C min^{-1} from ambient temperature to 900 °C. Approximately 4 mg of biomass sample was used in each experiment.

2.3. Kinetic methods

The biomass pyrolysis process is mainly about the biomass converted into char and some part of volatiles gas (White et al., 2011). The conversion rate (α) of pyrolysed biomass is defined as:

$$\alpha = (m_0 - m_t)/(m_0 - m_\infty) \quad (1)$$

where m_0 is the initial mass, m_t is the mass at each time instant t at a temperature T and m_∞ is the final mass.

The conversion rate of a solid state kinetic reaction over time, $d\alpha/dt$ can be described as a function of $k(T)$ and $f(\alpha)$ as

$$d\alpha/dt = k(T)f(\alpha) \quad (2)$$

where k is the rate constant and T is a function of temperature. The $f(\alpha)$ is a function of the reaction mechanism.

The rate constant k is described by the Arrhenius equation:

$$k = A \exp(-E_\alpha/RT) \quad (3)$$

where A is the pre-exponential or frequency factor (min^{-1}), E_α is the apparent activation energy (kJ mol^{-1}), R is the gas constant (8.314 JK^{-1} mol^{-1}), and T is the absolute temperature (K).

$$d\alpha/dt = Af(\alpha)e^{(-E_\alpha/RT)} \quad (4)$$