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Pyrolysis characteristics of bean dregs and in situ visualization of pyrolysis transformation

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ABSTRACT

Biomass is an important renewable and sustainable source of energy. Waste products from biomass are considered as attractive feedstocks for the production of fuel. This work deals with the pyrolysis of bean dregs, a biomass waste from soybean processing industry. A technique has been developed to study bean dregs pyrolysis by in situ visualization of bean dregs transformation in a quartz capillary under a microscope using a charge-coupled device (CCD) camera monitoring system. The technique enables us to observe directly the processes and temperatures of bean dregs transformation during pyrolysis. In situ visualization of reaction revealed that how oily liquids are generated and expulsed concurrently from bean dregs during pyrolysis. Pyrolysis characteristics were investigated under a highly purified N_2 atmosphere using a thermogravimetric analyzer from room temperature to 800 °C at different heating rates of 10, 30 and 50 °C/min. The results showed that three stages appeared in this thermal degradation process. The initial decomposition temperature and the peak shifted towards higher temperature with an increase in heating rate. Kinetic parameters in terms of apparent activation energy and pre-exponential factor were determined.

1. Introduction

With the depletion of petroleum resource and fossil fuels, it is necessary and urgent that finding alternative and renewable fuels. Because of the global warming problem resulting from combustion of fossil fuels, a lot of efforts are pushing towards the replacement of fossil fuels with alternative energy sources. Due to inexhaustible and potential energetic application of biomaterials, the exploration to effectively utilize this sort of resource is very attractive. Biomass is an important renewable and sustainable source of energy. Since living biomass fixes carbon dioxide from atmosphere during photosynthesis to synthesize hydrocarbon in its structure, combustion of almost all of the fresh or waste biomass species does not cause to any significant contribution to the net carbon dioxide deposition in atmosphere (Haykiri-Acma and Yaman, 2008).

Pyrolysis has been widely used for utilizing biomass materials (Jeguirim and Trouve, 2009; Park et al., 2009a,b; Kumar et al., 2008). Among the various biomass materials, bean dregs are a potential source of energy and value-added products. Bean dregs come from soybean processing industry. Soybean is the main oil-bearing crop and an important food resource. Because soybean has comprehensive and rich nutrients, the soybean processing industries are in the ascendant. More than 80,000 tons wastes of bean dregs, the main by-product of soybean processing industry, are produced annually in recent years in China. However, only a small fraction of bean dregs were used for poultry and livestock feed. Most of them were arbitrarily dumped into fields. Bean dregs consist of cellulose, protein, fat and minor amount of other organics (Jiang and Hu, 2008; Zhu and Zheng, 2004). It is recommended to utilize bean dregs as a source of renewable energy and value-added products, based on both benefits of energy or value-added product recovery and environmental protection.

For the proper design and operation of the pyrolysis conversion systems, a thorough knowledge of the thermal behavior and pyrolysis kinetics of bean dregs are required. Up to now, bean dregs pyrolysis has not been visually investigated. In this paper, we present the visual characteristics of bean dregs during pyrolysis in a quartz capillary. The visual capability of the capillary technique provides direct observations showing how oil is generated and expulsed concurrently from bean dregs during pyrolysis. Thermogravimetric analysis (TGA) was also selected for the thermal decomposition process. The characteristics of the thermal degradation of bean dregs at different heating rates were studied. The kinetic parameters were obtained by Coats–Redfern method (Coats and Redfern, 1964), Kissinger–Akahira–Sunose (KAS) method (Kissinger, 1957) and Flynn–Wall–Ozawa (FWO) method

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Corresponding authors. Tel./fax: +86 21 66137727 (X. Zhu), +86 21 60873507 (Z. Xiao).(Flynn and Wall, 1966; Ozawa, 1965). The results of this study are very useful in helping us understand the thermal degradation processes and mechanisms, and provide information for designing a pyrolytic processing system using bean dregs as feedstock.

2. Methods

2.1. Material

Bean dregs wastes came from Shanghai University Canteen. Before the experiments, the dried bean dregs were milled for 10 min using a mixer (HR170, Philips Corp.) at the maximum speed setting, and then were further grinded with a high-speed rotary grinder (Pulverisette, Fritsch Corp.) to make even smaller particles. The small particles of bean dregs were sieved. The portion under 140 meshes was collected for tests. The particle size is in the range of 0.090 mm and 0.106 mm. The proximate analysis of bean dregs was carried out according to ASTM standard. In this work, we calculated HHV for bean dregs including C, H, O and N based on Francis and Lloyd method (Cordero et al., 2001). The ultimate sample analysis was carried out using a VARIO EL111 elemental analyzer. The analysis results are presented in Table 1.

The contents of crude protein, crude fat, and crude cellulose were determined by the Kjeldehl method, the Soxhlet extract method, and the intermediate filtration method respectively. The analysis results are shown in Table 2.

2.2. In situ observational technique

In this study, bean dregs pyrolysis has been visualized directly using a capillary technique. A quartz capillary approximately 1.5 cm in length was flame sealed at one end using an oxyhydrogen flame machine. The inner and outer diameters of the capillary are 300 and 665 μm respectively. Approximately 0.1 mg of bean dregs was filled into the capillary, and then the other end of capillary was flame sealed. The capillary was inserted in a sample holder equipped in the hot and cold plate (HCP) which was connected to a temperature controller (INSTEC). The sample holder has a sample slot (1 mm wide, 2.5 mm deep, and 40 mm long) located at the middle part of the HCP. The schematic diagram of the in situ observation system and the pictures of the instrument are shown in Fig. 1. Image of sample was observed by a microscope and transferred to a computer through a CCD camera. Temperature was displayed and controlled by an intelligent digital control instrument. The heating rate adopted in the test for the in situ visualization was 30 °C/min.

2.3. Thermogravimetric analysis

The experiments were carried out in a STA 409 PC thermogravimetric analyzer (manufactured by Netzsch in Germany). In each experiment, approximately 7.3 mg of bean dregs were spread uniformly on the bottom of the ceramic crucible of the thermal analyzer. The pyrolysis experiments were performed at heating rates of 10, 30, and 50 °C/min in a dynamic high purity nitrogen flow of 20 ml/min. The temperature of the furnace was programmed to rise from room temperature to 800 °C.

Table 2
The chemical content analysis results of bean dregs (on dry basis).

Crude cellulose (%)	Crude protein (%)	Crude fat (%)
52.6	20.5	12.5

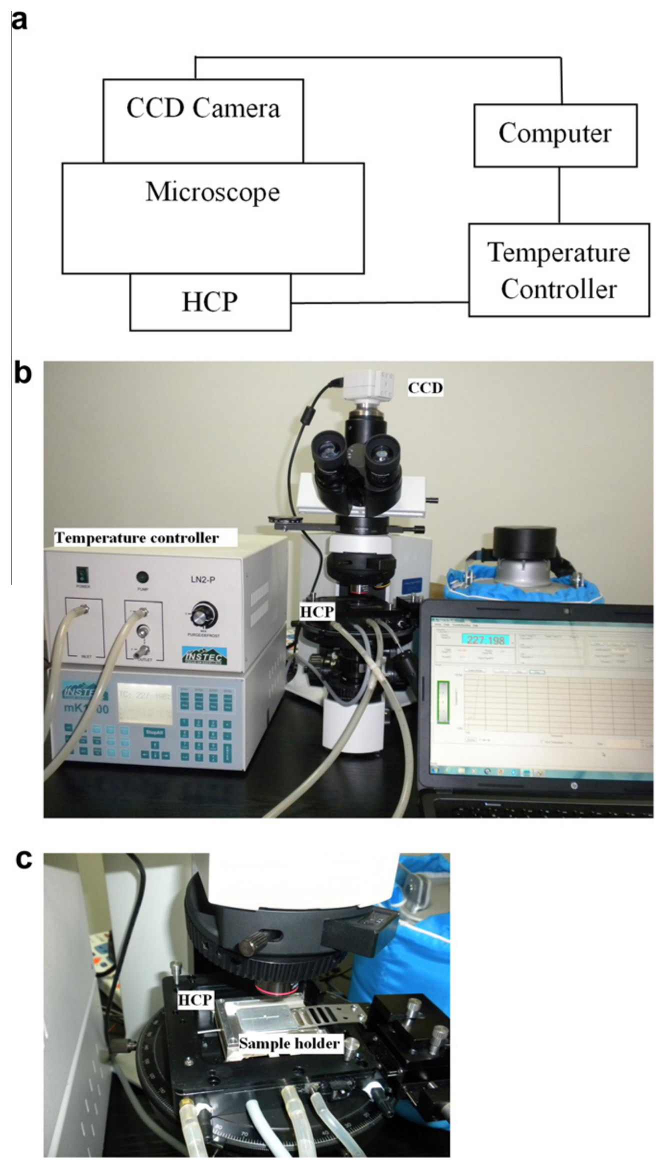

Fig. 1. Schematic diagram and pictures of the visualization system (a) Schematic diagram, (b) pictures of the instruments, (c) sample holder.

3. Results and discussion

3.1. In situ visualization of bean dregs pyrolysis transformation

Some micro-photographs showing transformations of bean dregs at different temperatures are given in Fig. 2.

Table 1
Sample characteristics of bean dregs.

Sample	Moisture (%)	Ash (%)	C (%)	H (%)	N (%)	O (%)	HHV (MJ kg^{-1})
Bean dregs	5.93	3.70	46.00	6.667	3.634	43.699	15.92