Catalytic fast pyrolysis of cellulose for increasing contents of furans and aromatics in biofuel production

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ABSTRACT

The catalytic fast pyrolysis of cellulose, cellobiose and glucose with the zeolite catalyst of NaY was carried out using thermogravimetric analyzer (TG) and pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). Results from TG showed that all samples presented significant mass loss at low temperature and exhibited high residual chars with NaY. The activation energies of cellulose, cellobiose and glucose were significantly decreased with NaY. PY-GC/MS showed that saccharides were significantly decreased or even completely eliminated and converted into furans, aromatics, phenols and light oxygenates with NaY. The contents of furans of cellulose, cellobiose and glucose with NaY were increased from 17.48%, 18.79% and 28.77% to 46.71%, 52.11% and 67.81%, respectively. Pyrolysis of cellulose and cellobiose presented high selectivity of BTX (Benzene, Toluene, and Xylene). The furans are mainly formed on the surface of NaY by dehydration, fragmentation/retro-aldol condensation, decarbonylation, or decarboxylation. The pyrolysis intermediates of anhydro-oligosaccharides dominated the formation of aromatics and phenols during the catalytic fast pyrolysis of cellulose in the zeolite catalyst pores at the active sites.

1. Introduction

Lignocellulosic biomass is a promising feedstock for the production of renewable liquid fuels and valuable chemicals due to its abundance and special chemical composition [1]. Pyrolysis is an attractive way for converting the abundant biomass resource into valuable liquids. Cellulose is the major component of lignocellulosic biomass and accounting for nearly 50% of biomass. Its pyrolysis behavior significantly influenced the thermochemical conversion of the whole biomass. Therefore, it is of critical importance to understand the cellulose pyrolysis in order to clarify the biomass pyrolysis. Cellulose is composed of *d*-glucose units linked by β-1,4-glycosidic bonds to form a linear homopolysaccharide. The pyrolysis of cellulose is complicated and involves multiphase reactions, complex chemical pathways, highly unstable intermediates, and heat and mass transfer effects [2]. Cellulose pyrolysis can generate hundreds of volatile species such as levoglucosan (LGA), furans and light oxygenates (such as glycolaldehyde and formic acid). [3–5]. However, the uncontrollability and complexity of pyrolysis products from cellulose limited the development of cellulose conversion. Many studies have been carried out and found that catalytic fast pyrolysis (CFP) is a promising way to produce the target products and has gained extensive attention in recent years.

CFP allows the direct conversion of solid materials into high value-added liquid products. Results have been reported previously on the effect of product distribution of CFP of carbohydrates with zeolites catalysts. It was reported that CFP of glucose with HZSM-5 can produce aromatics by two steps [6]. Karanjkar et al. [7] also used ZSM-5 as the pyrolysis catalyst and achieved 39.5% carbon aromatic yields for the CFP of cellulose. Wei et al. [8] found that CFP of cellulose with the solid acid catalyst can produce levoglucosenone (LGO) with a 7.25% yield. Yang et al. [9] obtained 22.0% selectivity of 5-Hydroxymethylfurfural (HMF) from the depolymerization of cotton cellulose using SO_4^{2-}/M_xO_y solid superacid catalyst. Some Researchers [10] found the acid-catalysed cellulose pyrolysis was dominantly contributed by dehydration reactions at low temperatures. CFP of cellulose using MCM-41 type catalysts can promote dehydration reactions and decrease the production of LGA [11].

In conclusion, furans and aromatics, which have a relatively high energy density and are cleaner to replace petroleum fuels or as fuel additives, were generated during the CFP of cellulose using the zeolites catalysts. However, the yields were generally low and the mechanism for the conversion was not fully understood because of the

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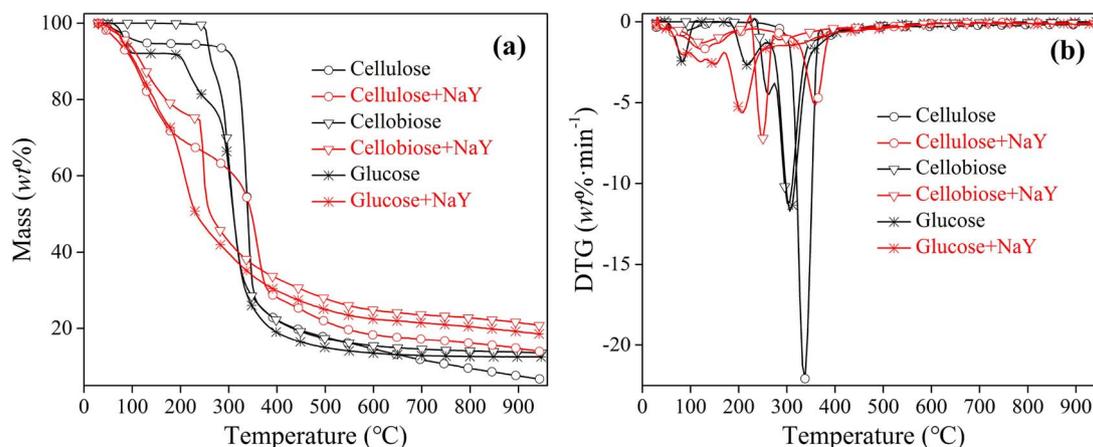
Fig. 1. TG (a) and DTG (b) curves of catalytic pyrolysis of cellulose, cellobiose and glucose.

Table 1
Kinetic parameters of catalytic pyrolysis of cellulose, cellobiose and glucose.

Sample	T_s (°C)	T_{max} (°C)	w (%)	E (kJ mol^{-1})	A (min^{-1})	R^2
Cellulose	306–354	337	6.66	182.34	1.40×10^{12}	0.97
Cellulose + NaY	326–381	362	13.81	48.82	1.83×10^3	0.96
Cellobiose	274–327	304	13.54	106.72	1.09×10^6	0.99
Cellobiose + NaY	240–260	250	20.74	67.70	1.63×10^3	0.95
Glucose	275–337	306	12.48	74.57	1.04×10^6	0.98
Glucose + NaY	178–235	207	18.55	23.33	2.73×10^3	0.99

T_s: Temperature section; T_{max}: Temperature of the maximum rate of weight loss; w: The final Residual mass fraction; E: Activation energy; A: Pre-exponential factor; R^2: correlation coefficient.
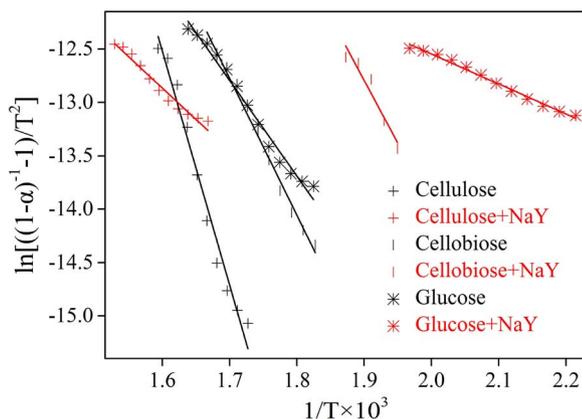
Fig. 2. Fitting curves for the kinetics of catalytic pyrolysis of cellulose, cellobiose and glucose.

heterogeneous structure of the materials and the occurrence of large number of reactions [12]. Consequently, the objective of this study was to investigate the product distribution of CFP of cellulose and elucidate the converted pathways for producing biofuels production of furans and aromatics from CFP of cellulose.

2. Material and methods

2.1. Material preparation

The microcrystalline cellulose (CAS: 9004-34-6) was used as the cellulose sample, which was purchased from Alfa Aesar. The d-(+)-cellobiose (CAS: 528-50-7) was used as the cellobiose sample, which was purchased from Sinopharm chemical reagent Co., Ltd. The d-(+)-glucose (CAS: 50-99-7) was used as the glucose sample, which was purchased from Sigma.

The zeolite catalyst of NaY was purchased from liaoning haitai sci-tech development Co., Ltd., Liaoning province, China. The NaY catalyst had the cage structure of faujasite and its BET surface area was 715 m^2/g. The molar ratio of Si/Al was 5.2 and the lattice parameter of NaY was 24.65×10^{-10} m. Prior to use, the NaY was calcined at 1000 °C for 2 h under N_2 atmosphere in muffle furnace.

2.2. Experimental methods

Catalytic pyrolysis of cellulose, cellobiose and glucose in the presence of NaY catalyst were conducted using TG (The NETZSCH STA449F3 thermo-gravimetric analyzer) and Py-GC/MS analyzer (The CDS 5150 pyrolyzer coupled with Shimadzu GCMS-QP2010Plus gas chromatography/mass spectrometry). The cellulose, cellobiose and glucose were mixed with NaY catalyst with the mass ratio of 1:5, respectively. The mass loss and mass loss rate of the samples with NaY were calculated after removing the weight of NaY.

The TG experiment was carried out with a flow rate of 50 mL/min and a heating rate of 10 °C/min under the nitrogen atmosphere. The pyrolysis temperature ranged from 30 to 950 °C. The Coats-Redfern method [13] was used to analyze the pyrolysis kinetic characteristics. The Coats-Redfern formula used to calculate the kinetic parameters of the first order reaction is as follows:

$$\ln[\frac{-\ln(1 - \alpha)}{T^2}] = \ln[\frac{AR}{\beta E}(1 - \frac{2RT}{E})] - \frac{E}{RT} \tag{1}$$

where α is the mass loss fraction, E is the activation energy (kJ mol^{-1}), A is the pre-exponential factor (min^{-1}), β is the heating rate (°C min^{-1}), R is the universal gas constant (8.314 J K^{-1} mol^{-1}) and T is the temperature (K).

The PY-GC/MS was used to observe the characteristics of the pyrolysis vapor. GC/MS had EI source, DM-5 (60 m × 0.25 mm × 0.25 μm) and NIST08 MS data base. A heating rate of 20 °C/ms, a holding temperature of 600 °C and a time-duration of 10 s were used for the