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# Kinetics and reaction chemistry of pyrolysis and combustion of tobacco waste

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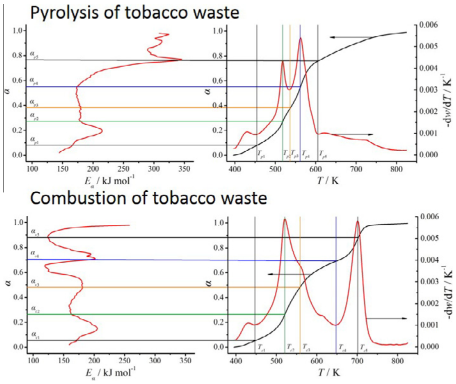
## GRAPHICAL ABSTRACT



Pyrolysis of tobacco waste

Combustion of tobacco waste

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## ABSTRACT

In this work, the kinetics and reaction chemistry of the pyrolysis and combustion of tobacco waste were investigated. The physicochemical analysis and thermogravimetric analysis under $N_2$ and air atmospheres of the tobacco waste sample mainly consisting of tobacco leaves were performed. The physicochemical analysis results showed that the tobacco waste sample contains more ash and N than other types of lignocellulosic biomass. The DTG curves obtained from the numerical differentiation of the experimental TGA curves have many fluctuations and need to be smoothed for subsequent kinetic analysis. The Savitzky–Golay smoothing algorithm was found to be effective for the smoothing the DTG curves of the pyrolysis and combustion of tobacco waste. The pyrolysis process of tobacco waste can be divided into four stages: (a) the water evaporation generated by the cleavage of aliphatic hydroxyl groups and strongly bonded hydrated compounds, and the degradation of simpler saccharides and other low temperature decomposing components of tobacco waste in the first stage; (b) the decomposition of hemicellulose and pectin, and the formation of nicotine in the second stage; (c) the decomposition of cellulose in the third stage; and (d) the decomposition of lignin and char formation in the final stage. The combustion process of tobacco waste can be divided into three stages: (a) the same as the first stage of the pyrolysis process; (b) the oxidative pyrolysis of tobacco waste components; (c) the combustion of the oxidative pyrolysis char. The Friedman differential and iterative linear integral isoconversional methods were used for the estimation of the effective activation energies of the pyrolysis and combustion of tobacco waste. The results showed that the effective activation energies of the pyrolysis and combustion of tobacco waste varied strongly with the extent of conversion. The obtained effective activation energies are in the ranges of 144–338 kJ mol$^{-1}$ and 118–257 kJ mol$^{-1}$ for the pyrolysis and combustion

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of tobacco waste, respectively. The relationship among the effective activation energies, temperature range, degree of conversion, reactions of tobacco waste components was also obtained.

## 1. Introduction

Over the past decades, global tobacco production has increased dramatically, particularly in developing countries [1]. According to the statistic from the website: http://www.statista.com, the global tobacco industry produced approximately 7.49 million tons in 2012. China was the leading producer with an amount of 3.2 million tons of tobacco produced in the same year. The production of tobacco generates about 25% of tobacco waste [2]. Thus, an estimate of about 0.8 million tons of tobacco waste was generated in China in 2012 [3]. This waste poses an environmental problem as it contains some harmful and toxic components (e.g., nicotine) [4]. It can be used as an organic fertilizer to improve soil fertility because of its relative high contents of C, N, exchangeable K, Ca and Mg, and available P [5,6], the source of plant pesticide [1], some chemicals [7] and pulp [8,9].

Like other types of lignocellulosic biomass, tobacco waste mainly contains cellulose, hemicellulose, and lignin. Therefore, high value-added biofuel or heat can be generated from the pyrolysis and combustion of tobacco waste [10]. Pyrolysis is a thermally assisted decomposition process in the absence of oxygen, during which lignocellulosic biomass can be converted into syngas, bio-oil and biochar [11–13]. Syngas and bio-oil have high heating values and can be used for energy recovery. Bio-oil can also be further upgraded into renewable transportation fuels to replace gasoline, diesel, and chemicals currently derived from nonrenewable sources [14–18]. Biochar can be used as a fuel [19], activated carbon [20], or as a fertilizer replacement offering an advanced option for biological sequestration of carbon [21–23]. Combustion of tobacco waste can be used for electrical and heat energy [24].

Most of the previous studies on the pyrolysis and combustion of tobacco or its waste focused on the determination of the chemical components of tobacco smoke [25–28]. Limited information is available in the literature concerning the production of fuel or heat from the pyrolysis and combustion of tobacco or its waste. Liu et al. [24] found that furfural and phenol were the major products in the low temperature pyrolysis of tobacco stem, while in the high temperature pyrolysis indene and naphthalene were the major products. Encinar et al. [29] compared the pyrolysis behavior of tobacco waste with that of maize, sunflower, and grape residues, and found that the pyrolysis of tobacco waste led to biochar with the lowest carbon content. Akalin and Karagöz [30] reported that the pyrolysis products mainly contained N-containing compounds, phenols, alkanes, alkenes, steroids, acids and esters during the pyrolysis of tobacco waste. Pütün et al. [31] compared the slow and fast pyrolysis of tobacco waste, and found that the liquid bio-oil from fast pyrolysis has lower C content and higher H/C ratio than that from slow pyrolysis.

The pyrolysis and combustion kinetics of tobacco waste can help to produce sub-models that can be coupled with transport phenomena to describe practical conversion processes and design more efficient reactors [32]. Some papers focused on the kinetic description of the thermochemical conversion of tobacco waste. Valverde et al. [33] studied the pyrolysis of tobacco dust by using thermogravimetric analysis (TGA) and used a four-parallel-first-order-reaction model to describe its pyrolysis kinetic behavior. Cardoso et al. [34] used an multiple *n*th-order reactions model to describe the pyrolysis kinetics of tobacco waste. Várhegyi et al. [35,36] developed the model consisting of multiple distributed activation energy model (DAEM) reactions to describe the pyrolysis and combustion of tobacco waste. Strezov et al. [37] divided the pyrolysis process of tobacco waste into the following four stages: dehydration, torrefaction, charring, and carbonization according to the derivative thermogravimetric curve peaks of tobacco waste pyrolysis.

It is expected that the reactions involved in the pyrolysis and combustion of tobacco waste are very complex and the corresponding activation energies may vary with the degree of conversion. This variation of the activation energies can be obtained by means of isoconversional kinetic methods. These methods yield the effective activation energies as a function of the degree of conversion and permit us to draw reliable mechanistic conclusions [38]. The isoconversional kinetic analysis of the pyrolysis and combustion of tobacco waste and their corresponding reaction chemistry are still missing in the literature. This is the scope of the present work. Because the reactions studied in this work also occur in the pyrolysis and combustion of other lignocellulosic materials, the considerations, data processing algorithms, kinetic methods and results of this work are also expected to be applicable to the research on the thermochemical conversion of other types of lignocellulosic biomass.

## 2. Materials and methods

### 2.1. Materials

The tobacco waste samples mainly consisting of tobacco leaves were collected from a local cigarette factory in Huanggang City, Hubei Province, China in October, 2013. The samples for experimental analysis were prepared in accordance with ASTM standard E1757-01.

### 2.2. Physicochemical analysis

Proximate analysis is used to estimate the relative amounts of moisture, ash, volatile matter, and fixed carbon in tobacco waste [39]. The determination of moisture, ash, volatile matter, and fixed carbon contents should follow the procedures outlined in the ASTM standards E1756-08, E1755-01, E872-82, and E870-82, respectively. Moisture content is determined by drying at 378 ± 3 K (105 ± 3 °C) in a drying oven for at least 3 h but not longer than 72 h. Ash content is determined after dry oxidation at 848 ± 25 K (575 ± 25 °C) in a muffle furnace for a minimum of 3 h. Volatile matter content is determined by a muffle furnace in which the sample is maintained at a temperature of 1223 ± 20 K (950 ± 20 °C) for 7 min. And fixed carbon content is calculated by difference. The higher and lower heating values are measured by using an oxygen bomb calorimeter (XRY-1A+, Shanghai Changji Geological Instrument Co., Ltd, China) in accordance with the ASTM standard D2015-00.

Elemental analysis is a process where the sample is analyzed for its elemental composition. In this work, the contents of C, H, N and S in tobacco waste were measured by means of an elemental analyzer (Model vario EL cube, Elementar Company, Germany) and the content of O was determined by difference.

The contents of the metallic and non-metallic (excluding C, H, O, N, and S) elements in tobacco waste were measured by an