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Evaluating the bioenergy potential of Chinese Liquor-industry waste through pyrolysis, thermogravimetric, kinetics and evolved gas analyses

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ABSTRACT

Baijiu (Chinese liquor) industry is the world-renowned industry to produce high-quality liquor using mixed biomass feedstocks including sorghum, wheat, and rice bran. A huge amount of *Baijiu Diuzao* (residual solid waste) is produced every 1–3 months after the fermentation. The present study was focused on evaluating the bioenergy potential of the Chinese liquor industry waste for the very first time. The collected sample was subjected to thermal degradation in an inert environment at three heating rates including 10, 30 and 50 $Kmin^{-1}$. It was shown that pyrolysis of this waste followed a three-stage degradation pattern, with a loss of 7.49% of the mass during the first stage at T ≤ 130 °C. While the second stage showed two zones ranging from 130 to 373 °C with an overall 51.12% of the mass loss. The third stage occurred above 373 °C and showed 16.08% loss in the mass. The released gases were subjected to TG-FTIR-MS analyses to monitor the composition and abundance of the gases where C═O groups (aldehydes, ketonic and carboxylic) and hydrocarbons were shown to be the dominating functional groups. Moreover, the data were subjected to kinetics, thermodynamics and reaction mechanism analyses using KSA (Kissinger-Akahira-Sunose), FWO (Flynn-Wall-Ozawa), Vyazovkin and CR (Coats-Redfern) methods. Where, the activation energies (70–195 kJ mol^{-1}), Gibbs free energy (177–185 kJ mol^{-1}) and lower difference of enthalpy ($\Delta H = \sim 5$ kJ mol^{-1}) indicated remarkable bioenergy potential of this waste either through pyrolysis or co-pyrolysis. The artificial neural network ($R^2 = 0.99$) and reaction mechanism analyses indicated that the best thermal degradation chemistry was performed and described. This study will lead to establishing a thermal transformation strategy of this abundant and low-cost biological resource into energy and valuable chemicals in the cleanest manner.

1. Introduction

In view of recent issues related to food security, environment, and depletion of fossil fuels, a renewed interest bioenergy from waste-biomass sources has become an emerging trend across the globe. China, being a heavily industrialized country, is one of the most energy demanding countries in the world, while energy production and industrial activity is always associated with waste production. Recent massive economic growth in China has raised serious environmental concerns. Hence, the focus is to minimize the industrial waste, developing waste-recycling technologies and to develop cleaner energy technologies. Among various industrial wastes, the residual solid biomass of Chinese Liquor-industry which is locally called "*Baijiu Diuzao*" is produced from *Baijiu* Industry and is one of the major waste biomasses particularly in Sichuan province. In traditional *Baijiu* solid fermentation process sorghum is the main fermentation resource, rice bran is used to adjust the fraction void, and fermented wheat which is called "*Daqu*" [1], is used as the raw fermentation starter. In some *Baijiu* industries, five grains including sorghum, rice, glutinous rice, corn, and wheat are used as main fermentation feedstocks. *Baijiu Diuzao* contains residual biomass of sorghum, wheat, and rice bran. Annual production of *Baijiu* is estimated to be more than five million metric tons [2], which reflects the huge amount of associated solid waste. This waste is abundant and low-cost, hence may be used to produce bioenergy and high-value industrial chemicals through thermal conversion.

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Several processes are available for the cleaner transformation of biomass to bioenergy ranging from thermochemical to biological transformation. Although, the biological methods are the cleanest methods to produce fuel alcohols, yet these methods are not suitable for the liquor industry waste because the residual waste is produced after fermentation and does not contain enough fermentable sugars. Moreover, thermal conversion is dominant over biological methods in terms of speed and efficiency [3]. Hence, pyrolysis (thermal degradation in an invert environment) offers another cleanest way to retrieve the energy stored in the liquor industry waste and to produce chemicals of industrial value. Pyrolysis can transform the subjected biomass into various products including bio-oil, syngas, and biochar leaving almost no waste. While the process is highly influenced by the nature of biomass along with temperature parameters. For this reason, establishing an efficient thermal conversion requires a clear understanding of pyrolysis conditions and behavior of the biomass. Previously, several waste-biomasses including Corn cobs, Sorghum weeds [4], manure [5] and tobacco stem [6] have been studied for their bioenergy potential using thermogravimetric analyses. Other than these biomass sources, Sawdust biomass waste was subjected to pyrolysis at five heating rates ranging from 5 to 25 °C min^{-1} followed by estimation of kinetic parameters using various models [7] namely Kissinger-Akahira-Sunose (KAS), Ozawa-Flynn-Wall (OFW), Friedman, Coats-Redfern, and Distributed Activation Energy Model (DAEM). The activation energy was found to be ranging from 148 to 206 kJ mol^{-1}. Similarly, different residual waste biomasses were collected from agricultural practices and forests and were studied to evaluate their bioenergy potential using proximate analyses. Different waste biomasses namely forest leaves, wheat straw, cotton waste and soybean waste using charcoal as a reference showed high heating values of 20.9 MJ kg^{-1}, 17.62 MJ kg^{-1}, 16.65 MJ kg^{-1}, 18.77 MJ kg^{-1}, and 26.07 MJ kg^{-1}, respectively [8], which indicated the remarkable bioenergy potential of these biomasses. However, pyrolytic products of the most biomass sources have not been studied.

Isoconversional mathematical models play a backbone role to calculate the energy values like activation energy, enthalpy, and Gibbs free energy. Lower activation energy reflects weak bonding between the molecules, and internal structure is easy to break with the subsequent release of pyrolytic products. Whereas, enthalpy indicates the internal energy of the sample under study. Moreover, the Artificial Neural Networks (ANN) were used to compare the thermogravimetric experimental data with the predicted results of mass loss using input parameters of temperature and heating rates. This comparison is a validation of the empirical and predicted data. Artificial Neural Networks (ANN) models are built on the principle of the human brain functioning. In the human brain, data is transferred among neurons through synapses with the help of chemicals which are called neurotransmitters. Based on the same principle, the ANNs contain multiple neuron layers including input, hidden, and output layers to learn their inter-relationship to further validate the experimental and predicted data [9], Previously, the ANNs have been employed to predict the reaction chemistry [10] and to validate the thermal data [11].

The present study was focused to elucidate the pyrolytic behavior and bioenergy potential of the Chinese Liquor Industry Waste for the very first time. The pyrolytic products were monitored through TG-FTIR-MS and the experimental data was validated through ANN analysis. Our data demonstrated the considerable potential of this biological resource to produce energy and chemicals through pyrolysis.

2. Materials and methods

2.1. Elemental composition and proximate analyses

The *Baijiu Diuzao* (BD) was collected from the fermentation facility at Sichuan Province, China. The BD sample was heated at 80 °C for 48 h in the oven and passed through a sieve to get particles of size ranging from 200 to 250 μm. Later, it was subjected to proximate analyses to determine volatile matter (VM%), ash (%) moisture content (%) using the standard methods as described in ASTM (E872-&82 2006, E871-82 2006, E1755-01 2007). To determine the VM and moisture content, known mass was put in oven-dried at 380 K in triplicate for 24–48 h to get a constant mass. The loss in mass reflected the moisture content. Similarly, known mass from the oven dried sample was put into pre-weighed ceramic crucibles in triplicate and left at 775 K in a Muffle furnace for 3–4 h to get a constant mass. Where, loss in mass reflected the volatile matter (VM) and residual mass reflected the ash content. The composition of organic elements including Carbon (C), Hydrogen (H), Sulphur (S), Nitrogen (N) and Oxygen (O) in the sample was estimated using Vario EL Cube elemental analyzer (Germany). Where, Argon was used as the carrier gas.

The High calorific value (also referred as High Heating Value) is a measure of the amount of energy which would evolve from any biomass in response to thermal degradation. It was measured using an Oxygen Bomb calorimeter available at Foshan Ceramics Research Institute Testing Co., Ltd. China, following the GBT 213-2008 test standards.

2.2. Coupled TGA-DSC experiment

A coupled TG-DSC experiment was carried out in thermogravimetric STA-409, NETZSCH-Gerätebau GmbH, Germany. The milled and weighed (with an approximation of 10 mg) BD sample was put into aluminum crucibles with continuous heating from room temperature to 1273 K at three different heating rates 10, 30 and 50 K min^{-1} under nitrogen environment in a reaction chamber.

2.3. Coupled TG-FTIR-MS experiment

To investigate the evolved gasses and the functional groups of their released major compounds advance coupled TG-FTIR-MS experiment was performed using TG-FTIR-GCMS (PerkinElmer, Model: TGIRGCMS*/TGA8000*). A 10 mg sample was loaded into the equipment and initial temperature of 105 °C was maintained for 15 min to ensure the loss of retained moisture. Later, the sample was degraded at increasing temperature with the heating rate of 40 °C min^{-1} and the gases evolved were analyzed using the same equipment. The GC–MS analyses were conducted in positive electron impaction (EI) ionization mode at 70 eV. The oven was set at an initial temperature of 50 °C for 3 min then ramped the temperature @ 10 °C min^{-1} up to 280 °C and kept for 5 min. The injector was kept at 150 °C. Both the transfer line and ion source temperatures were at 50 °C each. For the separation of sample components, 30 m × 250 μm TR-5MS column was used. The Helium (He) gas was used as the carrier.

2.4. ANN model development

An Artificial Neural Network (ANN) model was established to monitor the pyrolysis experiment. Data was evaluated by selecting the feed-forward Levenberg Marquardt back-propagation algorithm in MATLAB® R2014b. The model consisted of the input, hidden and output layers of the multi-layer network topology. Temperature and heating rate were selected as two inputs whereas, mass loss was selected as the output layer. 1073 data points were used that were divided into training (70%), validation (15%) and testing (15%) phases. The Mean Square Error (MSE) function was used (Eq. (1)) to optimize the network model based on output values (o) and the target (t) shown in Eq. (2).

$$MSE = \frac{1}{n[\sum_{i=1}^{n}(\lambda_i - \beta_i)^2]} \quad (1)$$

where λ_i: experimental values; β_i: predicted values; n: number of data points