Thermal Oxidative Decomposition of Soybean Straw: Thermo-Kinetic Analysis via Thermogravimetric Analysis and Artificial Neural Networks

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Abstract. Keeping in view the energy shortage problem, the bioenergy potential of soybean straw have been evaluated by thermos-kinetic study using thermogravimetric analysis and artificial neural networks. TG-DTG curves at 10, 20, and 30°C min⁻¹ revealed that the thermal oxidative decomposition of soybean straw could be divided into three stages and the second stage (180 to 380°C) would be the most suitable for thermal conversion of soybean straw into energy and chemicals. Kinetics analysis results showed that the activation energy values of models ranges were: KAS (87.57-819.24 KJ mol⁻¹), and OFW (92.01-790.85 KJ mol⁻¹), respectively. The variation of activation energy indicated the thermal decomposition process of soybean straw is complicated and may be consisting of several reactions. Furthermore, an ANN model was applied to predict the thermal decomposition of soybean straw. The good fitness between experimental and predict data (R² = 0.999) validated the accuracy of the model in predicting the mass loss of thermal oxidative decomposition process.

1. Introduction

Recent issues related to energy shortage and environmental deterioration have motivated a growing interest in the potential utilization of renewable energy sources. Among various renewables, biomass resources have attracted particular attention for their CO2 neutral property and abundant availability at cheaper prices [1, 2]. As a great agricultural country, China generates a large annual production of agricultural residues that can be used for energy production [3]. Soybean straw is one of the profusely available residues in China in terms of resource potential. Efficient exploitation of such agricultural residues will produce good benefits of society, environment, and economy.

Various thermochemical conversion (TCC) technologies have been developed to realize the resource utilization of the agricultural residues. Among them, combustion is one of the relatively common, efficient, and inexpensive TCC technologies, accounting for around 97% bioenergy production in the world [4]. The results of combustion (or called as thermal oxidative decomposition) and kinetic studies can provide certain technical guidance prior to the design, upgrading and operation of biomass combustor.

According to previous literature [4-6], the thermogravimetric analysis (TGA) is widely employed to evaluate the thermal decomposition behaviors of different solid materials. By using TGA, Chen et el. evaluated the kinetics and thermodynamics of rape straw, rapeseed meal, camellia seed shell, and camellia seed meal [4]. Islam et al. investigated the combustion characteristics of Karanj fruit hulls...
char [5]. Arenas et al. assessed the pyrolysis kinetics of five biomass wastes [6]. Hence, TGA can provide information on the continuous mass loss under non-isothermal conditions to analyze the thermal oxidative decomposition processes and kinetics of soybean straw. Moreover, many researchers are devoting to apply computational methods for the thermal data to reduce the number of the ordinary experiments [7, 8]. Among several computational methods, ANN is widely applied to predict the non-linear relationship between input and output data [9], which shows its potential in prediction of the non-linear relationship in thermal processes. Accordingly, once the ANN model is optimized successfully, it is possible to predict the thermal oxidative decomposition behaviors of soybean straw accurately.

Although previous studies have exhibited the thermochemical conversion process of various biomasses, these researches mainly focused on the pyrolysis behavior in an inert atmosphere. Since there are few researches on the application of ANN to predict the thermal oxidative decomposition of soybean straw, the present study attempts to (1) investigate the thermal behavior of soybean straw by thermogravimetric analysis, (2) estimate the kinetics of soybean straw at different heating rates according to the Kissinger Akahira-Sunose (KAS) and Ozawa-Flynn-Wall (OFW) methods, and (3) establish an ANN model to predict thermal decomposition of soybean straw. The present research could help to establish a thermal conversion strategy to convert soybean straw into energy or high-value chemicals in the cleanest manner.

2. Materials and methods

2.1. Raw materials and characterization

The soybean straw was obtained from a biomass production workshop in the town of YiChun City, JianXi Province, China. To characterize the basic properties of the sample, the proximate and ultimate analyses of samples are depicted in Table 1. The proximate results show that soybean straw has a low content of ash (3.72 %), which is lower than that of coal (34.28 %) [10]. Higher ash content can be a disadvantage to the combustion process considering the formation of aggregates and it may decrease the energy conversion efficiency [11]. For ultimate analysis, it can be observed that the contents of N (0.73 %) and S (0.33 %) are very low, which implies a less toxic substance emission and a good candidate for thermochemical conversion.

|                          | Proximate analysis | Ultimate analysis |
|--------------------------|-------------------|-------------------|
|                          | (wt,%, db)        | (wt%, daf)        |
| Moisture Content         | Volatile Matter   | Ash Dry Matter    | Fixed Carbon | Ash Dry Content | Carbon | Hydrogen | Oxygen | Nitrogen | Sulfur |
| 8.66                     | 54.35             | 32.27             | 3.72         | 42.75     | 6.15   | 44.83   | 0.73   | 0.33     |

a Calculated by difference

2.2. Thermogravimetric analysis

Thermal oxidative decomposition experiments of soybean straw were performed on a NETZSCH SAT 449 F3 Jupiter (NETZSCH, Germany) thermogravimetric analyzer. Specimens about 9±0.5 mg were heated from room temperature to 800 °C at the heating rates of 10, 20 and 30 °C min⁻¹. For oxidative atmosphere, dry air with a flow rate of 50 mL min⁻¹ was continuously passed into the furnace. The NETZSCH Proteus software was applied to record the thermogravimetric mass loss (TG) and differential thermogravimetric (DTG) profiles.

2.3. Kinetic analysis

The thermal oxidative decomposition kinetics analysis of soybean straw could be calculated by the
non-isothermal methods of KAS [12], and OFW [13], which were expressed respectively as follows:

\[
\ln \frac{\beta}{T^2} = \ln \frac{A_e R}{E_a g(\alpha)} - \frac{E_a}{RT}
\]

(1)

\[
\log \beta = \log \frac{A_e E_a}{Rg(\alpha)} - 2.135 - 0.4567 \frac{E_a}{RT}
\]

(2)

where, \(\alpha, \beta, A\) and \(E\) indicate the conversion rate, the heating rate, the pre-exponential factor (s\(^{-1}\)) and the activation energy (KJ mol\(^{-1}\)), respectively. \(g(\alpha)\) refers to the integral form of reaction model. By plotting \(\ln(\beta/T^2)\) and \(\log\beta\) against \(1/T\), the activation energy \(E_\alpha\) can be obtained by the slope \(-E_\alpha/R\) for KAS methods, and \(-0.4567 E_\alpha/R\) for OFW method, in which \(R\) is the gas constant (8.314 J mol\(^{-1}\)K\(^{-1}\)).

### 2.4. Artificial neural networks

In this study, MATLAB R2017b software has been applied to develop an ANN model to predict the mass loss of soybean straw. The main features of the ANN model are presented in Table 2. A learning algorithm called Levenberg-Marquardt (LM) was selected for data prediction[14]. Heating rate (°C min\(^{-1}\)) and temperature (°C) were selected as the input neurons in input layer, while mass loss (%) was selected as the output neuron in output layer. To improve the network efficiency, the data for input and output have been normalized. The data division was set to 70%, 15% and 15% for training, validation and testing phase, respectively. Furthermore, the model performance can be evaluated by considering the mean square error (MSE) (Equation.3) and coefficient of determination (\(R^2\)) (Equation.4), where a lower MSE value and a higher \(R^2\) value indicate more optimized network architecture.

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

(3)

where \(\lambda_i\): experimental values; \(\beta_i\): and predicted values ; \(n\): the number of data points.

\[
R^2 = 1 - \frac{\sum (t_i - o_i)^2}{\sum (o_i)^2}
\]

(4)

where \(t\): the target; \(o\): output values.

Table 2. Summary of the ANN model properties.

| Parameters               | Value                          |
|--------------------------|--------------------------------|
| Input Data               | Heating rate (°C min\(^{-1}\)), Temperature (°C) |
| Target Data              | Mass Loss (%)                  |
| Training Function        | Levenberg Marquardt (LM)       |
| Transfer Function        | tansig                         |
| Performance Function     | MSE                            |
| Learning cycle           | 50 epochs                      |
| Validation checks        | 6                              |
| Error tolerance          | 0.001                          |
| Data division (%)        | 70-15-15                       |

### 3. Results and discussion

#### 3.1. Thermal oxidative decomposition process

Figure.1 and Figure.2 show the TG and DTG curves of soybean straw in air atmosphere at three different heating rates. In general, the entire thermal oxidative decomposition process could be roughly divided into three stages. The first stage (<180 °C) included a small amount of dehydration and the release of light volatiles, with a mass loss of 8.8-10.2% (depending on heating rates). The major mass loss of approximately 70 % occurs at the second stage (180 to 380 °C) due to
devolatilization of volatiles. The temperatures at the maximum mass loss rate were 289.15, 308.29 and 321.51 °C for heating rate of 10, 20 and 30 °C min⁻¹, respectively. With the increased heating rate, all curves shifted slightly toward a higher temperatures zone, while the pattern of thermal oxidative decomposition of soybean straw was basically unchanged. The reason for the temperature shifts, called thermal hysteresis, is that the heat transfer efficiency is lower at higher heating rates. The mass loss in last stage (>380 °C) was mainly related to chars oxidation. Overall observed combustion residuals were: 1.37%, 3.36% and 2.32% for heating rate sequence, indicating the insignificant effect of heating rate on the residual mass.

3.2. Model-free kinetics calculation

Activation energy, which is the energy required to initiate a reaction, can be used to find out the reactivity of any component. As the stages described in Section 3.1, the linear fitting of different model-free methods at various conversions is depicted in Figure.3. The calculated activation energies and their respective correlation factors using the KAS and OFW methods are presented in Table.3. In general, the activation energy calculated by the OFW method is slightly greater than the results from the KAS method and the coherence or reliability of the kinetic parameters are apparent from the high correlation factors ($R^2$). In stage 2, the activation energy presents a rising trend relative to the conversion rate. While in stage 3, the activation energy initially increases till the conversion rate of 0.5, and then a decrease is observed until conversion rate of 0.7. The reason maybe that the soybean straw is composed of cellulose hemicellulose and lignin with very different reactivity that arise from the difference in the chemical nature and physical structure. The multi-linear change indicated the complex thermal decomposition process for soybean straw which may be consisting of several reactions.

![Figure 1](image1.png)  
**Figure.1** TG curves for thermal oxidative decomposition of soybean straw

![Figure 2](image2.png)  
**Figure.2** DTG curves for thermal oxidative decomposition of soybean straw
Figure 3 Typical linear regression lines of model-free methods.

Table 3 Activation energy ($E$) and correlation factors ($R^2$) by KAS and OFW methods.

| $\alpha$ | Stage 2 | Stage 3 |
|---------|---------|---------|
|         | KAS     | OFW     | KAS     | OFW     |
|         | $E$ (KJ mol$^{-1}$) | $R^2$ | $E$ (KJ mol$^{-1}$) | $R^2$ | $E$ (KJ mol$^{-1}$) | $R^2$ | $E$ (KJ mol$^{-1}$) | $R^2$ |
| 0.2     | 87.57   | 0.94    | 92.01   | 0.95   | 202.7   | 0.97   | 203.46   | 0.97   |
| 0.3     | 90.75   | 0.95    | 95.19   | 0.96   | 305.59  | 0.99   | 301.46   | 0.99   |
| 0.4     | 93.92   | 0.95    | 98.34   | 0.96   | 522.72  | 0.99   | 508.06   | 0.99   |
| 0.5     | 98.18   | 0.97    | 102.49  | 0.97   | 586.05  | 0.98   | 568.39   | 0.98   |
| 0.6     | 104.08  | 0.98    | 108.21  | 0.98   | 462.82  | 0.96   | 451.32   | 0.96   |
| 0.7     | 114.23  | 0.98    | 117.99  | 0.99   | 410.06  | 0.91   | 401.30   | 0.92   |
| 0.8     | 131.01  | 0.99    | 134.09  | 0.99   | 514.77  | 0.94   | 501.05   | 0.94   |
| 0.9     | 160.73  | 0.99    | 162.59  | 0.99   | 819.24  | 0.94   | 790.85   | 0.94   |

3.3. Thermal decomposition prediction by the ANN model
For further understanding the thermal decomposition behavior of soybean straw, an ANN model was applied to simulate the predicted results with that of experimental data. Firstly, a multiple hidden layer model was selected to best fit the experimental data. In Figure 4, the error histogram is normally distributed across the zero error, which indicates insignificant errors between the targets (experimental) and the outputs (predicted). Figure 5 shows a high regression coefficient ($R^2 = 0.999$) between targets...
and outputs in training, validation and testing and it vindicates the robustness of the network. The results of the error histogram and the regression coefficient imply that the ANN model agrees well with the thermogravimetric experimental data. Therefore, the created ANN model can be applied to predict the thermal decomposition behavior with respect to the temperature for a new heating rate without laboratory experiments.

![Error Histogram with 20 Bins](image)

**Figure.4** Training, validation and test plots for ANN model

![Error Histogram Plot for ANN model](image)

**Figure.5** Error Histogram Plot for ANN model

4. Conclusions

In this study, the thermal analyse of soybean straw, a renewable energy source of biomaterial, was investigated via non-isothermal models along with ANN simulation. TG-DTG experiments revealed that the thermal oxidative decomposition of soybean straw could be divided into three stages and the second stage (180 to 380°C) would be the most suitable for thermal conversion of soybean straw into energy and chemicals. Kinetics analysis results showed that the activation energy calculated by the KAS and OFW methods presented a rising trend against conversion rate in stage 2, while a multilinear change in stage 3. As for ANN simulation, the good fitness between experimental and predict data ($R^2 = 0.999$) validated the accuracy of the model in predicting the mass loss of thermal oxidative decomposition process. The process variables presented in this study can provide design basis for the thermal conversion of soybean straw into high-value chemical and energy.

5. References

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