



Study on the Pyrolysis Behaviors of Urea-Formaldehyde Resin and Rice Straw Mixed Pellets

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In order to study the effect of biomass on the pyrolysis characteristics of urea-formaldehyde resin, the thermogravimetric experiments were carried out respectively using urea-formaldehyde resin (UF), rice straw (RS), and their mixed pellets with different proportions. The pyrolysis kinetics analysis was conducted. The results showed that the pyrolysis process of UF resin and mixed pellets could be divided into three stages: the drying and dehydration of the material, the rapid decomposition of volatile matter, and residue decomposition. The reaction order of UF resin and mixed pellets was discussed using the Coats–Redfern method, the activation energy of UF resin was 54.27 kJ/mol, and this value decreased with the addition of rice straw. As the mass ratio of UF resin to rice straw was 3:1, the activation energy achieved the lowest value, which means that the addition of rice straw was beneficial to the pyrolysis process of UF. In the process of pellet preparation, the falling strength and compressive strength of UF resin pellets can be improved by adding an appropriate proportion of rice straw. In this test, the yield of pyrolytic carbon reached the highest value of 23.93%, as the mass ratio of UF resin to rice straw was 3:2. When the mass ratio was 4:1, the highest liquid product yield of 43.21% was achieved.

Keywords: urea-formaldehyde resin, pyrolysis, rice straw, kinetics analysis, pellet strength

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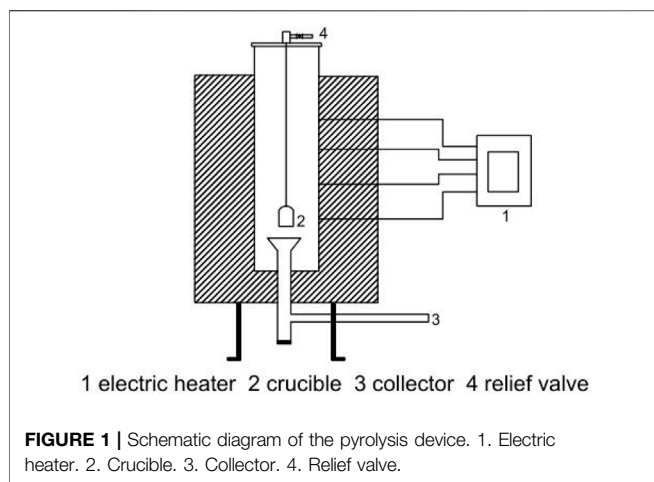
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1 INTRODUCTION

Because it is the main building material of wood products such as furniture, the production of the wood-based panel in China has reached 299.09 million m³ in 2018 (NFGA, 2019). Specifically, adhesives account for about 10% of wood substrates. These adhesives include urea-formaldehyde resin (UF), phenol-formaldehyde resin (PF), and melamine-formaldehyde resin (MF), among which UF resin is the most commonly used adhesive (Gu, 2015). Moreover, UF resin was listed as the 13th category of hazardous wastes according to the National Hazardous Waste List in 2016. Improper handling of UF resin can cause serious environmental pollution.

Pyrolysis technology can convert particleboard into value-added chemicals, such as improved biochar for fuel combustion (Ying et al., 2022). These studies provide a more valid basis for the recycling of urea-formaldehyde resin. In terms of practical engineering application, in order to reduce the difficulty of pretreatment, many researchers try to pyrolysis the mixture of UF resin and biomass to study the effect of UF resin on biomass pyrolysis. Feng et al. (2012) used TG and DTG analysis to evaluate the influence of UF resin on waste particleboards during the co-pyrolysis process and found that the thermal stability of particleboard was enhanced by UF resin, and the degradation was inhibited, especially for the second stage of pyrolysis. Zhang et al. (2014) analyzed the pyrolysis



characteristics of eucalyptus, eucalyptus added with 10 %UF resin, eucalyptus added with 10% MUF resin, UF resin, and MUF resin and found that UF resin and MUF resin can reduce the energy required for eucalyptus pyrolysis. Meanwhile, Zhang et al. (2016) studied the pyrolysis process and product characteristics of poplar, UF resin, and particleboard. The result showed that the effect of UF resin on particleboard cracking fluid was mainly reflected in nitrogen compounds. There are more nitrogen compounds in particleboard cracking fluid than poplar cracking fluid. Li et al. (2014) found that more nitrogen elements in UF resin were fixed by cellulose and into the solid products of cellulose pyrolysis. For lignin, UF resin combined with lignin during pyrolysis to generate thermally unstable compounds and continued pyrolysis to release large amounts of compounds, including nitrogen compounds and carbon oxides, which promoted the decomposition of lignin and directly affected the generation of products. However, there are some controversial statements about the effects of adhesives on wood pyrolysis (Xu et al., 2020).

In this article, thermogravimetric and kinetics analyses were performed using a thermogravimetric analyzer to analyze the activation energy. At the same time, the mixture of UF resin and biomass was pelletized to improve its strength and study the effect of mixing ratio on the pyrolysis characteristics and the distribution of pyrolysis products.

2 EXPERIMENTAL

2.1 Materials

The urea-formaldehyde resin (UF) was obtained from the waste wood-based panels produced by a building decoration company in Jinan city, Shandong province, China. Rice straw (RS) was obtained from Shanxi province, China. The original samples were crushed in a high-speed grinder and sieved to obtain a size fraction $<74\ \mu\text{m}$ and then dried in a drying oven at 105°C until the quality was constant. Then, UF resin and RS mixed ratios of 1:0, 5:1, 4:1, 3:1, and 3:2 were pelletized.

2.2 Experimental Method

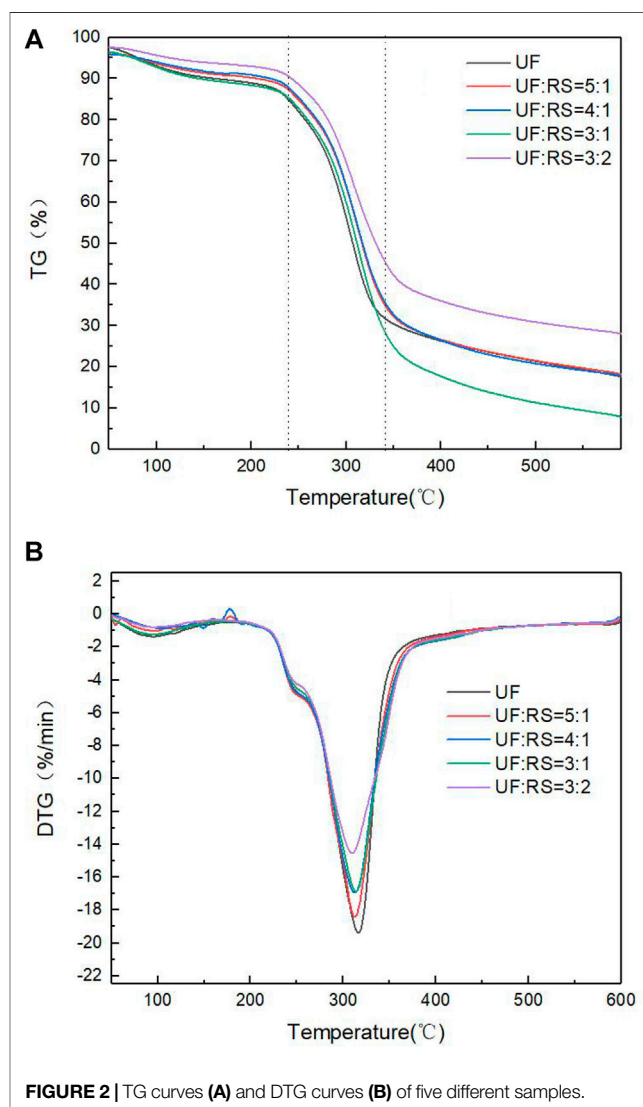
2.2.1 Thermogravimetric Test

Each mixed sample weighed 30 mg. The sample was thereafter placed in a microcomputer thermobalance (HTG-1) and heated up from 20°C to 600°C at a rate of $20^\circ\text{C}/\text{min}$ under a nitrogen atmosphere with a flow rate of $100\ \text{ml}/\text{min}$. TG data of the reaction process were recorded automatically by the data acquisition system.

2.2.2 Strength Test and Pyrolysis Experiment

Preparation of Urea-Formaldehyde Resin and Rice Straw Mixed Pellets

Take about 5 g of the mixed powder and put it into the designated ball mold. Keep it below 15 MPa for 10 min in the pelletizer machine to eliminate intermolecular pressure and strengthen molecular bonds (Wang et al., 2020). The diameter of the prepared pellet is between 10 and 12 mm.



Test Procedure of Falling Strength

The falling strength tester was used to test the falling strength of samples. The green pellets with a diameter of 10.0–12.5 mm were dropped freely on the steel plate from an altitude of 500 mm. This process was repeated several times until the pellets were broken. In the aspect of data processing, the maximum and the minimum values of falling times were deleted, and the arithmetic mean value was recorded as the falling strength index (times/pellet).

Test Procedure of Compressive Strength

The compressive strength was tested using the compressive strength tester. In the aspect of data processing, the maximum and the minimum values of falling times were deleted, and the arithmetic mean value was recorded as the falling strength index (N/pellet).

Pyrolysis Process

Tests were performed at atmospheric pressure, and the pyrolysis reactor was surrounded by an electric furnace. The schematic lab-scale configuration is illustrated in **Figure 1**. The effective height of the pyrolysis reactor was 800 mm. Samples were fed into the furnace through the top of the pyrolysis reactor. A thermocouple was used to monitor the temperature profile in the middle of the pyrolysis reactor.

Initially, 5 g of sample was put into the center of the reactor, and the electric heater was turned on. Under vacuum, the mixture was heated up to 550°C and kept for 60 min. Then, the reaction mixture was cooled to room temperature. The gas products were collected by a sampling bag and measured by the water drainage method. The liquid products were collected by syringe, and the pyrolysis char was retained in the crucible.

3 EXPERIMENTAL RESULTS AND DISCUSSION

3.1 Pyrolysis Characteristics

Figures 2A,B, respectively, show the TG curves and the DTG curves of five samples.

As shown in **Figure 2**, the pyrolysis process can be divided into three stages, which have similar pyrolysis rules but have their own characteristics. This is consistent with the research of GIRODS P (Girods et al., 2008a; Girods et al., 2008b; Girods et al., 2009).

The first stage (20°C–239°C) is the drying and dehydration stage of the material. It is mainly caused by the evaporation of water in the material and the release of free formaldehyde in UF; the reduction of polymerization degree caused by chain break of macromolecular compounds in straw; and the formation of hydroxyl group, carbonyl group, and hydrogen peroxide group (Lowell and Zhengtian, 1988; Feng et al., 2012; Thao and Yuh, 2021).

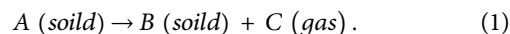
The second stage (239°C–340°C) is the main pyrolysis stage, which is the pyrolysis of volatiles in UF resin and decomposition and volatilization of cellulose, hemicellulose, and lignin in RS. In particular, cellulose is massively pyrolyzed in the process (Zhang et al., 2021). After the addition of RS, the TG curve of UF resin

shifted to high temperature region and the maximum weight loss rate decreased obviously. Therefore, it is speculated that the addition of straw improves the thermal stability and inhibits the rapid pyrolysis process of UF resin.

The third stage (340°C–600°C) is residue decomposition. The mass of samples is no longer changed, and the pyrolytic char is eventually formed. The content of RS affects the yield of pyrolytic charcoal, which is mainly affected by the high thermal stability of lignin (Ma et al., 2015). When the mass ratio is 3:2, the yield of pyrolytic char reaches a maximum.

3.2 Kinetic Analysis

Generally, the thermal degradation of the solid materials may be assumed to occur after following **Eq. 1**:



The reaction rate can be expressed as **Eq. 2**, (Hu and Shi, 2008):

$$\frac{d\alpha}{dt} = kf(\alpha), \quad (2)$$

where k is the reaction rate constant; t is the reaction time, s; and α is weightlessness rate, %:

$$\alpha = \frac{w_0 - w}{w_0 - w_\infty}, \quad (3)$$

where w_0 is the initial mass of sample, mg; w is the mass of sample at time t during thermal degradation, mg; w_∞ is the final mass of sample, mg.

The relationship between reaction rate constant K and reaction temperature T can be expressed by the Arrhenius equation:

$$k = Ae^{-\frac{E}{RT}}, \quad (4)$$

where A is the pre-exponential factor, 1/s; E is the apparent activation energy, kJ/mol; R is the gas constant value, 8.314 J/(mol K); T is the absolute temperature of reaction, K.

For non-isothermal heating at a constant heating rate, the reaction rate β is

$$\beta = \frac{dT}{dt}, \quad (5)$$

Equation 6 can be obtained:

$$\frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T e^{-\frac{E}{RT}} dT, \quad (6)$$

where $f(\alpha)$ is a mechanism function of kinetic research. The mechanism function of urea-formaldehyde resin pyrolysis is usually assumed as

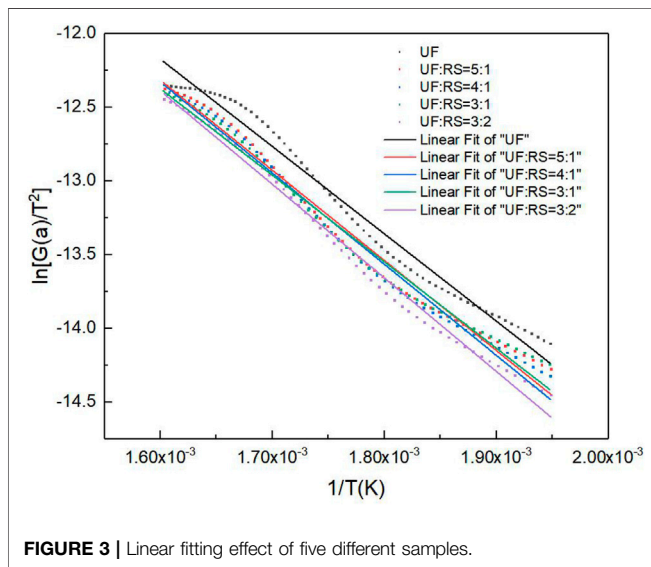
$f(\alpha) = (1 - \alpha)^n$, where n is the reaction order.

Collating **Eqs 2–6**, we can get

$$\ln \left[\frac{G(\alpha)}{T^2} \right] = \ln \left[\left(\frac{AR}{\beta E} \right) \left(1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT}, \quad (7)$$

TABLE 1 | Kinetic parameters of pyrolysis reaction of five different samples.

Samples	Fitting temperature T/K	Activation energy E/(kJ mol ⁻¹)	Frequency factor A/s ⁻¹	Correlation coefficient	Sum of squares of residuals
UF	513–624	54.27	147.8899	0.9813	2.7450
UF:RS = 5:1	513–624	50.84	162.1216	0.9834	1.9219
UF:RS = 4:1	513–624	51.40	180.3949	0.9857	1.6942
UF:RS = 3:1	513–624	48.80	99.1369	0.9829	1.8441
UF:RS = 3:2	513–624	52.76	226.6777	0.9908	1.1624

**FIGURE 3** | Linear fitting effect of five different samples.

where $G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)}$ for the general temperature range and for most of the E values $\frac{E}{RT} > 1$; therefore, $1 - \frac{2RT}{E} \approx 1$.

Equation 7 can be simplified as

$$n \neq 1, \ln\left(\frac{1 - (1 - \alpha)^{1-n}}{(1 - n)T^2}\right) = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT}, \quad (8)$$

$$n = 1, \ln\left(-\frac{\ln(1 - \alpha)}{T^2}\right) = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT}. \quad (9)$$

$\ln(G(\alpha)/T^2)$ is plotted against $1/T$, and a straight line is fitted with slope $-E/R$. The higher the linear correlation is, the more correct the mechanism function $f(\alpha)$ is selected. It is considered that the pyrolysis process of high-temperature samples is dominated by the velocity of heat conduction rather than the kinetics of chemical reaction (Lowell and Zhengtian, 1988). Therefore, the second stage of the TG curve is performed as linear fitting. The reaction order N is determined by comparing the correlation coefficient in the range from 0 to 2 with the step size of 0.2. Then, the activation energy E and frequency factor A of the UF resin cracking reaction can be calculated according to the intercept and slope of the straight line.

Through calculation and comprehensive consideration of the kinetic correlation coefficients of five samples, the best fitting is obtained using the first-order reaction kinetic model in this study. Therefore, the selected mechanism function form is $f(\alpha) = 1 - \alpha$.

The obtained dynamic factors are shown in **Table 1**, and the linear fitting effect is shown in **Figure 3**.

As can be seen from **Table 1**, the activation energy of UF resin is the highest, and the activation energy is the lowest when the mass ratio is 3:1. The activation energy of samples with added biomass was lower than that of UF resin. Because RS has the characteristics of low density and loose structure, it is found that the surface structure of blended power is looser after adding RS, which facilitates the occurrence of pyrolysis reaction and reduces the activation energy.

3.3 The Falling Strength and Compressive Strength of Pellet

By testing the falling strength and compressive strength of the pellets, the falling strength is 6.6, 9.3, 28.1, 27.8, and 10.3, and the compressive strength (N/pellet) is 47.0, 151.6, 174.7, 204.4, and 430.9, respectively corresponding to the following five mixing ratio pellets, UF:RS = 1:0, UF:RS = 5:1, UF:RS = 4:1, UF:RS = 3:1, and UF:RS = 3:2. It can be seen that the drop strength and compressive strength of UF resin were minimum when it was pelleted alone. With the addition of RS, the falling intensity of mixed pellets increased first and then decreased. When the mass ratio of UF to RS varied from 5:1 to 3:1, the falling intensity increased significantly. However, when the mass ratio of UF to RS continued to increase to 3:2, the falling intensity of the pellet decreased sharply. Therefore, the increase of RS ratio could not increase the pellet falling intensity continuously. As the ratio of RS increased, the compressive strength continued to increase.

The pellet quality has a significant impact on subsequent processes, which is mainly manifested in the dropping of raw pellets during transportation and blasting during oxidizing roasting. The proper compressive strength is conducive to the pyrolysis of pellets. The pellets tend to be pulverized when the compressive strength is low. The high compressive strength is not conducive to the complete progress of the reaction (Kaikai et al., 2017). According to relevant literature, the quality requirements of green balls are as follows: falling strength >7 times/piece and compressive strength >12 N/piece (Lv, 2018). It can be seen from the experimental data that the proper addition of RS is beneficial in increasing the compressive strength and falling strength of the blend pellet.

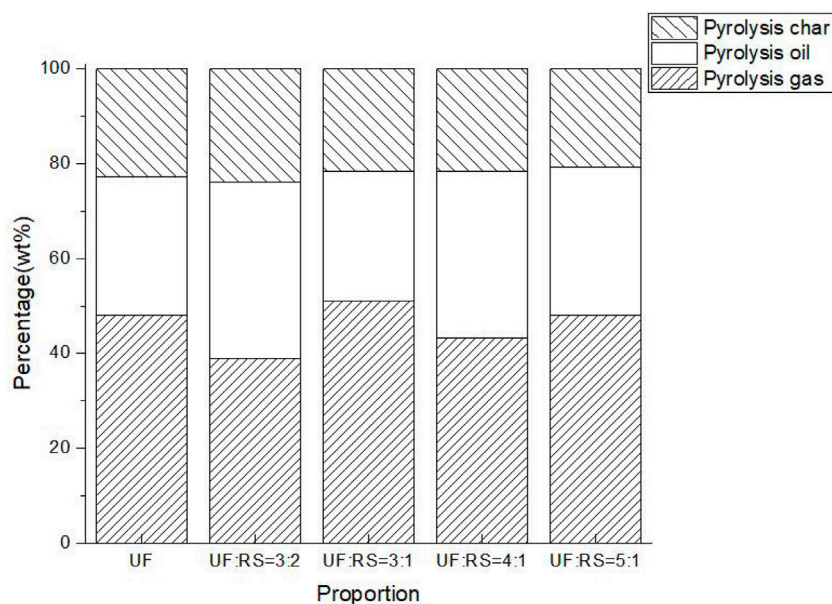


FIGURE 4 | Distribution of three-phase products of samples at 550°C with different proportions.

3.4 The Pyrolysis Product Distribution of Pellet

The pyrolysis products distribution of mixed pellets is shown in **Figure 4**.

As shown from **Figure 4**, the yields of pyrolysis products of mixed pellets are significantly different. The liquid yield is the lowest during the pyrolysis process of UF resin pellets. When the mass ratio of UF resin to RS is 4:1, the mass fraction of pyrolysis oil is the highest (43.21%). When the mass ratio of UF resin to RS is 3:1, the mass fraction of pyrolysis gas was the highest, which is 50.97%. When the mass ratio of UF resin to RS is 3:2, the mass fraction of pyrolytic char is 23.93%. The cellulose in the biomass promotes the retention of nitrogen during the pyrolysis of the UF resin (Zongyuan et al., 2018) and exerts a positive effect on reducing the release of nitrogen-containing compounds. The mass ratios of UF to RS have a great influence on product distribution. Therefore, the doping ratio of biomass can be modulated according to the actual needing for the various phase products.

4 CONCLUSION

The TG method was used to study the co-pyrolysis of UF and RS. The conclusion was obtained that incorporating RS greatly improved the thermal stability of UF in the main pyrolysis. Further kinetic analysis showed that the reaction is of first order. After RS is added, the activation energy required for the UF resin reaction is reduced. In the process of pellet preparation, the falling strength and compressive strength of UF resin pellets

can be improved by adding an appropriate proportion of RS. During the co-pyrolysis process of UF resin and RS, the ratio of RS has a significant effect on the distribution of three-phase products. The mass fraction of pyrolytic carbon is the highest (23.93%) when the mass ratio of UF resin to RS is 3:2. When the ratio of UF resin to RS is 4:1, the liquid product yield reaches the maximum value, which is 43.21%.

DATA AVAILABILITY STATEMENT

The raw data supporting the conclusion of this article will be made available by the authors without undue reservation.

AUTHOR CONTRIBUTIONS

SL and ZZ proposed research concepts and experimental design. XL contributed to the analysis of data and articles. HB conducted experiments. WZ and DR made constructive comments on the revision of the article.

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