

Enhanced biofuel production by co-pyrolysis of distiller's grains and waste plastics: A quantitative appraisal of kinetic behaviors and product characteristics

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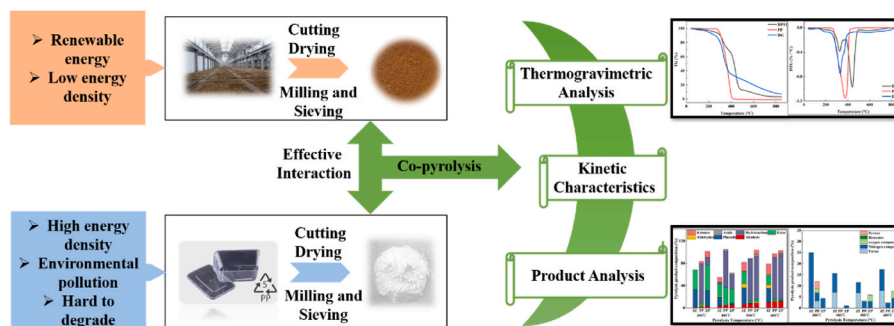
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HIGHLIGHTS

- Effects of co-pyrolysis of distiller's grains (DG) and polypropylene (PP) were positive.
- Co-pyrolysis delayed the conversion process with a low rate of mass loss.
- Interaction between DG and PP reduced the activation energy of the reaction.
- Less toxic by-products and better quality of pyrolysis products were obtained.
- Complex reaction mechanism for the co-pyrolysis of DG and PP was proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

Pyrolysis of biomass feedstocks can produce valuable biofuel, however, the final products may present excessive corrosion and poor stability due to the lack of hydrogen content. Co-pyrolysis with hydrogen-rich substances such as waste plastics may compensate for these shortcomings. In this study, the co-pyrolysis of a common biomass, i.e. distiller's grains (DG), and waste polypropylene plastic (PP) were investigated towards increasing the quantity and quality of the production of biofuel. Results from the thermogravimetric analyses showed that the reaction interval of individual pyrolysis of DG and PP was 124–471 °C and 260–461 °C, respectively. Conversely, an interaction effect between DG and PP was observed during co-pyrolysis, resulting in a slower rate of weight loss, a longer temperature range for the pyrolysis reaction, and an increase in the temperature difference between the evolution of products. Likewise, the Coats-Redfern model showed that the activation energies of DG, PP and an equal mixture of both were 42.90, 130.27 and 47.74 kJ mol⁻¹, respectively. It thus

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follows that co-pyrolysis of DG and PP can effectively reduce the activation energy of the reaction system and promote the degree of pyrolysis. Synergistic effects essentially promoted the free radical reaction of the PP during co-pyrolysis, thereby reducing the activation energy of the process. Moreover, due to this synergistic effect in the co-pyrolysis of DG and PP, the ratio of elements was effectively optimized, especially the content of oxygen-containing species was reduced, and the hydrocarbon content of products was increased. These results will not only advance our understanding of the characteristics of co-pyrolysis of DG and PP, but will also support further research toward improving an efficient co-pyrolysis reactor system and the pyrolysis process itself.

1. Introduction

With the continuous expansion in utilization of fossil fuel resources, energy shortages and environmental pollution have become global problems (Perera and Nadeau, 2022). Thus, finding clean, renewable energy sources to replace fossil fuels is vital. Pyrolysis is one of the important methods for the comprehensive utilization of biomass, and an important process from which to obtain renewable energy (Huang et al., 2022). The fuel energy conversion rate of biomass pyrolysis can reach 95.5%, which can maximize the conversion of biomass energy into energy products and make full use of such materials (Ding et al., 2021). Pyrolysis can also effectively convert raw materials into products such as biogas, biofuel and biochar under anaerobic or harsh pyrolysis conditions (Lee et al., 2020). Distiller's grains (DG), a by-product of the liquor and alcohol industry, are considered a carbon-neutral and sustainable biomass resource, which can be transformed into renewable energy via physiochemical technologies (e.g. anaerobic digestion and pyrolysis) (Tu et al., 2022). However, biofuel from the pyrolysis of DG has a high oxygen and nitrogen content, resulting from the lack of hydrogen present, which prevents the formation of hydrocarbons. As a result, the biofuel that is produced has high viscosity, low fluidity, low stability, and is highly corrosive (Sun et al., 2020; Li et al., 2022a,b,c). Therefore, it is necessary to develop a cost-effective strategy to overcome the drawbacks of this pyrolysis process.

Over the years, various approaches have been developed in order to optimize the biomass pyrolysis process, including such technologies as catalytic cleavage, emulsification, catalytic esterification, and co-pyrolysis (Kabir and Hameed, 2017; Lin et al., 2020; Li et al., 2022a,b,c). Due to benefits of easy operation, high efficiency, and potent synergy, co-pyrolysis has been widely employed in recent years to improve the quality of pyrolysis fuel. Previous research showed that, under the same conditions, co-pyrolysis of palm shell and recycled tires produced liquid biofuel with a yield that was up to 22% greater than that obtained from fast pyrolysis (Abnisa and Daud, 2015). Alvarez et al. (2019) demonstrated that pine sawdust and waste tire common pyrolysis process, biomass because of its oxygen-containing functional group instability release of some active free radicals, promote the rubber components in the waste tire occurs chain to release H radical, through hydrogen transfer effectively promote the conversion of oxygenic compounds to hydrocarbon products, improve the quality of biofuel. Thus, it can be presumed that, in the process of biomass pyrolysis, addition of hydrogen-rich substances, that can promote the formation of free radicals for co-pyrolysis, could extremely improve the yield and quality of biomass pyrolysis biofuel.

Plastics, as a type of hydrogen-rich organic polymer, are widely utilized in our everyday lives. Plastic packaging products were especially significantly used with the rise of takeaway food and internet shopping industries since the advent of COVID-19 pandemic in 2019 (Ngan and Khoi, 2022). Statistics show that the amount of plastic produced worldwide rose from 2 million tons in 1950 to 400 million tons in 2020 (Geyer et al., 2017; National Bureau of Statistics, 2021). Additionally, the widespread use of plastic products has also led to a significant increase in the production of plastic garbage. Usually, most of these waste plastics are burned or buried without being properly recycled, resulting in waste of resources and subsequent environmental pollution (Chen et al., 2021a,b). However, recent studies confirm that

plastics waste can be used as substrate for co-pyrolysis in order to enhance the performance of biomass pyrolysis processes (Ding et al., 2021). Alam et al. (2020) indicated that low-density polyethylene (LLDPE) promoted the production of aromatics and furthermore prevented the development of coke during the co-pyrolysis of bamboo sawdust with LLDPE. Likewise, co-pyrolysis of biomass and plastics can increase the H/C_{eff} ratio in the raw material system, promoting dehydration reactions of oxygen-containing compounds but inhibiting decarboxylation and dehydroxylation reactions, thereby contributing to the quality of biofuel (Alcazar-Ruiz et al., 2021).

Moreover, previous studies demonstrated that addition of plastics can reduce the activation energy and improve the efficiency of pyrolysis conversion and product yield, due to the generation of hydrogen free radicals and small molecular free radicals from the plastics (Liu et al., 2017). Generally, the performance of co-pyrolysis of plastics and biomass was significantly correlated to the characteristics of the raw materials (Abbas-Abadi et al., 2021). In conclusion, the plastic has high H/C and low O/C properties, which can balance the variable content of hydrogen and oxygen in DG. In addition, it may also solve the problem that pyrolysis of plastic alone produces wax, which causes equipment clogging. Polypropylene (PP), the most prevalent type of "hydrogen rich, oxygen poor" plastic, is thought to be the finest hydrogen source for co-pyrolysis with biomass since it contains almost 14 wt percent of hydrogen (Uzoejinwa et al., 2018). Chen et al. (2020) investigated the co-pyrolysis of PP and six types of biomass, and observed that the monomers from PP reacted with biochar, reducing solid residue content and decreasing decomposition activation energy. Moreover, another study that conducted by Jiang et al. (2022) found that co-pyrolysis of PP and microalgae could provide a synergistic effect, boosting hydrocarbon generation while reducing harmful by-products like aromatic hydrocarbons and nitrogen-containing compounds. However, the optimizing co-pyrolysis process parameters and subsequent products were not studied. Moreover, information regarding the influence of PP as a hydrogen source additive on the performance of DG pyrolysis is insufficient, particularly in terms of reaction kinetics and product analysis during the co-pyrolysis of DG and PP. Furthermore, the interaction mechanism between DG and PP is currently unclear. Therefore, the current research on co-pyrolysis of DG and PP primarily focuses on these knowledge gaps and aims to provide a feasible way to recover the waste for renewable energy production with the unveiled mechanisms. Therefore, to fill this information gap, the kinetic, product characteristics and synergistic mechanisms of co-pyrolysis and individual pyrolysis of DG and polypropylene were conducted in this study. The major objectives of this study were i) to explore synergistic mechanisms of DG and PP pyrolysis and co-pyrolysis by analyzing the thermal weight loss behavior by thermogravimetric analysis; ii) to investigate the kinetics of DG and PP pyrolysis and co-pyrolysis by model fitting methods; iii) to determine the pyrolysis and co-pyrolysis products and their distribution at different reaction temperatures through pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS) analysis, and to define synergistic effects of co-pyrolysis of DG and PP from the perspective of product yield and quality.

2. Materials and methods

2.1. Samples preparation

DG and PP were collected from Wuliangye Group Co., Ltd (Sichuan, China) and a waste collection station in Fangshan District (Beijing, China), respectively. DG and PP were firstly dried in an oven (WDT-2C) at 105 °C for 24 h prior to conducting the thermogravimetric analysis. After that, DG and PP were crushed by multi-functional pulverizer and sieved through a 60-mesh screen to a consistent particle size of less than 250 μm. The DG and PP were combined in a vortex mixer at a 1:1 ratio, and the mixture agitated for 5 min in order to achieve uniformity. The mixed samples were stored in a desiccator and labeled as DP11.

2.2. Analysis of elemental composition

The main elemental compositions (C, H, N, and S) of the samples were determined by an elemental analyzer (Vario EL cube, Elementar, Germany). Relevant parameters, including the hydrogen/carbon ratio (H/C), hydrogen/carbon effective ratio (H/C_{eff}) and higher heating value (HHV), were obtained using the data collected through elemental composition analysis (Zhang et al., 2018), using the following equations:

$$H / C_{\text{eff}} = \frac{H - 2O - 3N - 2S}{C} \quad (1)$$

where the mole percentages of hydrogen, oxygen, nitrogen, sulfur, and carbon in the feedstock are H, O, N, S, and C, respectively.

The HHV of the biomass samples was calculated based on the following equations:

$$HHV(OLS) = 1.87C^2 - 144C - 2082H + 63.8C \times H + 129N + 20147 \quad (2)$$

$$HHV(PLS) = 5.22C^2 - 319C - 1674H + 38.6C \times H + 133N + 21028 \quad (3)$$

where the symbols C, H, and N in the formulae represent the amounts of elemental carbon, hydrogen, and nitrogen, respectively, in the samples. Equations (2) and (3) were obtained from regression analysis by calculating ordinary least squares (OLS) and partial least squares (PLS) values for the higher calorific values of the sample.

The average value of HHV (MJ/kg) was calculated according to equation (4):

$$HHV = \frac{HHV(OLS) + HHV(PLS)}{2} \\ = (3.55C^2 - 232C - 2230H + 51.2C \times H + 131N + 20600) \quad (4)$$

2.3. Thermogravimetric and thermodynamics model analysis

Thermal decomposition of DG, PP and DP11 at the three heating rates of 10, 20, 30 °C·min⁻¹ was explored using a thermogravimetric analyzer (TGA5500; SDT-Q600, TA Instruments, New Castle, USA). Before the experiment, the balance was calibrated, and three parallel experiments were conducted for each group of experiments to ensure the repeatability of the experiment. Briefly, 7 ± 1 mg of each sample was weighed and placed in the instruments HT Crucible. High-purity helium gas (He, 99.999%) was passed over the sample at a rate of 25 mL min⁻¹ and the temperature increased linearly from 40 to 850 °C at the pre-determined rate. Model fitting for the main reaction stage was then utilized in order to perform thermodynamic analysis of the samples. Pre-exponential factor (A) and activation energy (E) can be acquired from kinetic calculations based on thermal mass data (Coats and Redfern, 1964). Depending on the degree of the reaction, the rate of the solid reaction can typically be expressed by equation (5):

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (5)$$

The reaction rate constant k is represented by the Arrhenius equation as (Arrhenius, 1889):

$$k = A \exp\left(\frac{-E}{RT}\right) \quad (6)$$

where A (min⁻¹) denotes the pre-exponential factor, E (kJ·mol⁻¹) is the activation energy of the reaction, R is the gas constant, 8.314 J K⁻¹ mol⁻¹, and T (K) is the reaction's absolute temperature.

Additionally, α is the reaction conversion rate and calculated by the following equation:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f} \times 100\% \quad (7)$$

where m₀ is the initial mass (g) of the sample, m_t is the sample mass (g) at the time point of the reaction t, and m_f is the final mass (g) following the reaction.

β is the heating rate constant β = dT/dt. Therefore, it can be concluded:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(\frac{-E}{RT}\right) \cdot f(\alpha) \quad (8)$$

Analyzing formula (8) by integral method:

$$G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T e^{-\frac{E}{RT}} dT \quad (9)$$

The CR model was applied to kinetic analysis of samples including DG and PP as well as their mixture, DP11. In order to eliminate any possible effects induced by considering different heating rates, the kinetic parameters were calculated for the pyrolysis of the sample at a heating rate of 10 °C·min⁻¹ (Coats and Redfern, 1964).

When the series n is 1,

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E} \left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} \quad (10)$$

For most of the pyrolysis reactions, $\frac{2RT}{E} \ll 1$ equation (2.10) can be approximated by:

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\frac{AR}{\beta E} - \frac{E}{RT} \quad (11)$$

Since $\ln\left(\frac{AR}{\beta E}\right)$ is constant in equation (11), a straight line is drawn in $\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right]$ against $\frac{1}{T}$. The reaction activation energy E and the pre-exponential factor A are available from the slope $-\frac{E}{R}$ and intercept $\ln\left(\frac{AR}{\beta E}\right)$ of the straight line.

To investigate interaction between these materials, the theoretical thermal weight curves of DG and PP were calculated, and compared with the actual TG curves of DP11. The theoretical weight loss was calculated from equation (12):

$$W_{\text{Calculated}} = \sum x_i w_i \quad (12)$$

in the formula, x_i is the mass fraction and w_i is the weight of that fraction. The total mass loss of the material, as measured by equation (12) at a certain temperature, was the sum of the product of the weight loss of each component and its fraction.

2.4. Analysis of the pyrolysis products

Py-GC/MS was employed to identify the DG and PP pyrolysis products. The pyrolyzer (EGA/PY 3030i, Frontier Labs, Fukushima, Japan) served as inlet to the gas chromatography-mass spectrometer (7890A/5975C, Agilent Technologies Inc., Santa Clara, USA). Initially, in order to determine the ideal pyrolysis conditions, DG and PP were subjected to pyrolysis tests at various temperatures (300, 400, 500, and 600 °C). The

GC column was HP-5 (30 m × 0.25 mm × 0.25 μm). The sample inlet port was set as the program temperature increase, and the temperature was set at 250 °C. The sample was injected at 250 °C of inlet temperature using a manual sample inlet. The split ratio of the GC/MS was 150:1 with high purity helium (99.999%) as the carrier gas. Pyrolysis products were identified by comparison with data from the mass spectrometer spectral library (NIST11, NIST, Gaithersburg, USA).

2.5. Plotting and statistical analysis

Plotting and data analysis were performed using the Origin 2021 (OriginLab, Northampton, USA) and SPSS 19.0 (IBM Corporation, Armonk, USA) software suites. The data were examined for normality and homogeneity of variance prior to statistical analysis. Nonparametric tests were employed for the analysis if the variables were not normally distributed. Hence, a one-way analysis of variance (ANOVA) inherited by Tukey's HSD, Kruskal-Wallis, and Dunn post hoc tests were utilized in order to detect significant differences at the 0.05 significance level ($p < 0.05$) in the pyrolysis products from groups that were pyrolyzed using various samples. Each sample was checked three times when the experimental error of weightlessness measurement was less than ±3%.

3. Results and discussion

3.1. Characteristic of DG and PP

The elemental compositions of the DG and PP were analyzed in this study (Table 1). Results indicated that the C and H content of DG were lower than that of PP, whereas the O and N contents were opposite. Likewise, the lower H/C ratio and H/C_{eff} of DG was also observed in this study due to the oxygen-rich nature of this material. The ratios of H/C and H/C_{eff} were observed to be higher in PP. In fact, it was an excellent solution to the "hydrogen source" problem at the source of the reaction, which helped to improve the yield of hydrocarbons in the product, as well as the selectivity of olefins, aromatic hydrocarbons and other chemicals. Nearly half of the mass of DG (48.39 wt%) is composed of O, which hence accounts for enhanced production of oxygenated organics. The C (42.79 wt%) and H (6.42 wt%) in the structure can be converted into valuable renewable chemical intermediates. Whereas PP was rich in both C (81.40 wt%) and H (16.40 wt%). Moreover, contents of C and H are decisive for the HHV of a material. The HHVs of DG and PP were calculated to be 17.10 and 57.47 MJ kg⁻¹, respectively. When compared with other biomass (rice, raw microalgae), the lower contents of C and H in DG led to significantly lower HHVs (Huang et al., 2022; Ming et al., 2020). PVC has a lower carbon content due to the chlorine atoms replacing some of the hydrogen atoms during the polymerization of vinyl chloride (Chen et al., 2019). Larger HHV translates to higher energy density, which may act to accelerate the production of pyrolysis products (Schaum et al., 2016). From the above discussion, it can be inferred that blending DG with PP effectively synergistically complements the pyrolysis properties of each material so as to be more suitable for the process. Furthermore, it can be concluded that DG and PP co-pyrolysis may efficiently increase the elemental proportion of hydrogen in the pyrolysis reaction system, as well as enhance the economics of the exploitation of the DG resource. However, further studies

on the feasibility and effectiveness of co-pyrolysis of DG and PP are deemed necessary.

3.2. Thermogravimetric analysis

3.2.1. Individual pyrolysis behavior of DG and PP

Thermogravimetry (TG) and Differential Thermogravimetry (DTG) have previously been widely used to investigate and demonstrate the changes in weight of samples with temperature/time during pyrolysis (Li et al., 2022a,b,c; Bi et al., 2021). This study found that the two materials exhibited characteristics similar to those reported in earlier literature, in terms of their pyrolysis behavior (Aboulkas et al., 2008; Zhang et al., 2020). Fig. 1 illustrates the TG and DTG curves of DG and PP slow pyrolysis at different heating rates (10 °C·min⁻¹, 20 °C·min⁻¹ and 30 °C·min⁻¹). It can be concluded that the maximum rate of weight loss of DG and PP were similar at 10 °C·min⁻¹. It is evident from the DTG curves in Fig. 1 (d) and (e) that the maximum weight loss rates of DG and PP both happens under the heating rate of 10 °C·min⁻¹ (gray curves) compared with those under heating rates of 20 and 30 °C·min⁻¹.

Mass losses observed during the pyrolysis of DG are generally very similar at different heating rates. During the low temperature stage (40–450 °C), the three TG curves are almost identical, but at higher temperatures (450–850 °C), except for the curve recorded at a heating rate of 10 °C·min⁻¹, the curves deviate, indicating a slower loss of mass with temperature at heating rates of 20 °C·min⁻¹ and 30 °C·min⁻¹. This is due to the change in reaction kinetics caused by high temperature conditions (Liang et al., 2018). And because of a sample's inherent thermal resistance, as the heating rate is increased, the temperature differential between the sample's interior and exterior also rises. As a result, the weight loss of the sample is less when the heating rate is higher at the same temperature, and the TG curve shifts to the right. This is comparable to the co-pyrolysis procedure used to combine oil-based drilling cuttings with waste polyvinyl chloride, reported in the literature (Xia et al., 2021). As the heating rate increases, the gradually increasing temperature gradient will make the molecular bonds in the three components of DG biomass less stable and more susceptible to breakage (Li et al., 2018). This results in a corresponding reduction in the time required for DG to reach the final pyrolysis temperature, an increased absorption of thermal radiation by DG, and thus different weight loss under different heating rates. Similar results have been reported previously for the pyrolysis of *Chlorella vulgaris* under the temperatures of 50–550 °C (Azizi et al., 2017).

As shown in Fig. 1d, for DTG curves of DG, the thermal decomposition process of DG can be divided into three stages. For DG, the first phase was the dehydration stage, mainly occurring in the region of the thermal program starting at the initial temperature and progressing up to 124 °C. The sample weight loss in this region was small (2.42%), because the material was well dried prior to conducting the thermogravimetric analysis. Over the temperature range of 124 °C–471 °C, mass loss was much greater, indicating that this thermal region was the main breakdown stage, and it is at this step that the majority of the organic chemicals were released. The DTG curves show many peaks at this stage, which represent mass loss due the breakdown of protein, carbohydrate, and lipid (Xu et al., 2012). The third stage was the slow pyrolysis carbonization stage, within the temperature range from 471 to 850 °C.

Table 1
Sample composition and property parameters.

Samples	Elemental analysis (wt.%)					Property parameter			References
	C	H	O ^a	N	S	H/C	H/C_{eff}	HHV (MJ·kg ⁻¹)	
DG	42.79	6.42	48.39	1.35	0.10	1.79	0.01	17.10	This study
PP	81.40	16.64	1.20	0.00	0.31	2.44	2.42	57.47	This study
<i>Chlorella vulgaris</i>	48.30	7.15	35.04	9.01	0.50	–	–	21.58	Jiang et al. (2022)
PP	85.85	13.78	0.37	0	0	–	–	46.17	Jiang et al. (2022)

Note: '–' represents 'not reported', ^a By difference.

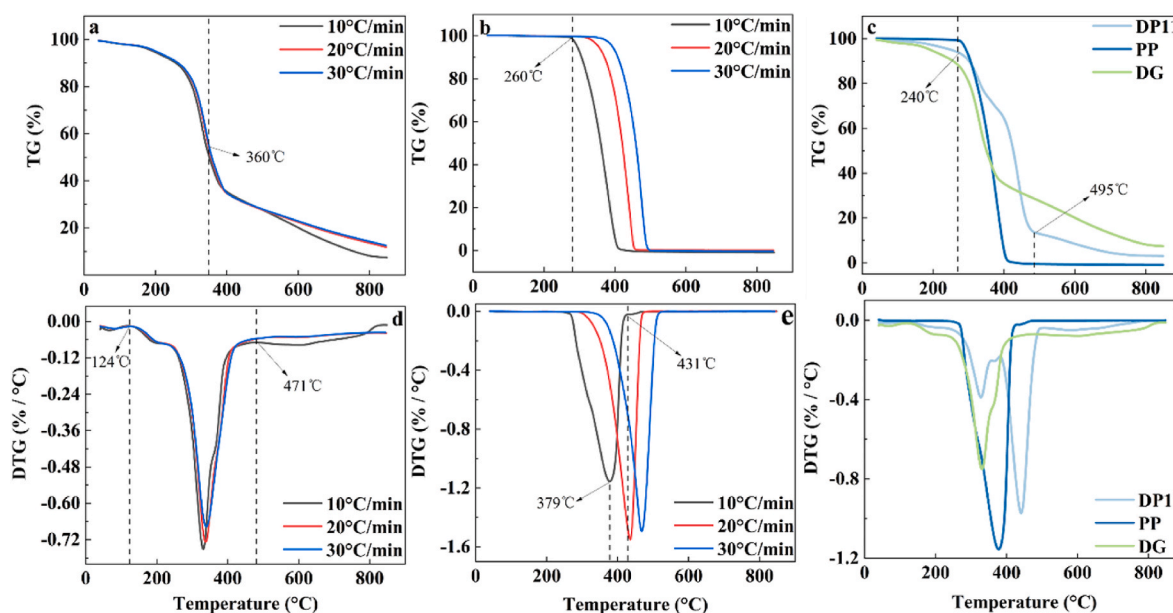


Fig. 1. TG-DTG curves of DG and PP pyrolysis at three different heating rates. a) TG curve of DG pyrolysis; b) TG curve of PP pyrolysis; c) TG curve of DG, PP and DP11 pyrolysis at $10^{\circ}\text{C}\cdot\text{min}^{-1}$ heating rate; d) DTG curve of DG pyrolysis; e) DTG curve of PP pyrolysis; f) DTG curve of DG, PP, and DP11 pyrolysis at $10^{\circ}\text{C}\cdot\text{min}^{-1}$ heating rate.

In this stage, lignin was mainly decomposed by carbonization, resulting in biochar and ash. The final DTG curve approaches 0, with 7.39% of the solid mass remaining.

The TG curves of DG and PP in Fig. 1a and b, respectively, present their significant different thermal decomposition behaviours. The thermal decomposition of DG can be divided into three steps, while the early and late stages of PP's thermal decomposition are represented by straight lines. Therefore, the overall thermal decomposition of PP can be considered as a one-step reaction, meanwhile, the DTG curve demonstrates that the thermal decomposition processes of DG and PP are influenced differently by the heating rate (Fig. 1 d and e). Here, the pyrolysis of PP occurred almost entirely in a single step, and only one peak was observed in the DTG curve. The TG curve demonstrates that thermal decomposition of PP began at around 260°C and ended at around 460°C . This research indicated that the mass loss of PP was about 99.98%, while the comparable mass loss for DG was about 72.61%. This phenomenon occurred because PP was a simple polymer, while the DG samples were biomaterials, consisting of many chemical compounds. Other reasons for the differences in final mass of the two materials include that the heat transfer inside the PP sample was more uniform, and some volatiles are produced by pyrolysis and were generated more rapidly, which made the ultimate mass loss more pronounced. Furthermore, DG undergoes intermediate gas pyrolysis, resulting in biomass as its final mass (Li et al., 2021a,b). This biomass is mainly composed of fixed carbon and residual ash, so the mass change before and after the reaction is small, and eventually contributing to the substantial mass difference observed between DG and PP.

3.2.2. Interaction between co-pyrolysis of DG with PP

The DG results showed that the temperatures corresponding to the maximum weight loss rate of DG and PP at a heating rate of $10^{\circ}\text{C}\cdot\text{min}^{-1}$ were 362°C and 370°C , respectively (Fig. 1d and e). Thus, the most promising condition of the heating rate of $10^{\circ}\text{C}\cdot\text{min}^{-1}$ was used to explore the separation of thermal effects and weight loss steps during the co-pyrolysis of DG and PP. The TG-DTG curves of DP11 heating from 40°C to 850°C at $10^{\circ}\text{C}\cdot\text{min}^{-1}$ in a He gas atmosphere are shown in Fig. 1c and f. Results showed that a slower rate of mass loss for DP11 (DG and PP with 1:1 ratio) was observed in this study (Fig. 1). As it can be seen from Fig. 1c, the TG curve of both DG and PP blends could be

divided into three stages. The first stage was from 40 to 240°C . This stage involved the evolution of volatile components, and, in addition, water evaporated during this phase. Because the sample was dried well during the preparation process, the reaction was not obvious. The second stage started at 240°C and completed at around 495°C . As the main reaction phase, two peaks of weightlessness were observed. This phenomenon could be explained as follows. The first maximum loss in weight was due to the decomposition of the weaker biomass components (protein and cellulose) in DP11, which accounted for a mass loss of about 20.64%. However, the second maximum weight loss occurred due to the continuous thermal decomposition of lignin, trace fat, and protein contained in the biomass component and the complete degradation of the plastic component, these decompositions led to a mass loss of about 54.41%. The final pyrolysis stage occurred over the temperature range 495°C – 850°C , in which the decomposition of lignin and the generation of biochar and ash were the main reactions.

Although the solid (e.g. ash and char) and gaseous products were not quantified in this study, previous studies supported that the pyrolysis liquid product was the main source of renewable biofuel via the co-pyrolysis of biomass and waste plastics. The pyrolysis liquid products contain high amount of aromatic hydrocarbons (Fig. 3) and the conversion rates to biofuels was much higher compared to the solid and gaseous products (Banu et al., 2020). Uzoejinwa et al. (2020) found through their study on the co-pyrolysis of seaweed and waste plastic (high-density polyethylene) at 500°C with a heating rate of $15^{\circ}\text{C}/\text{min}$ that the three-phase products generated during co-pyrolysis were composed of biofuel (75.9 wt%), biochar (14.6 wt%) and biogas (19.1 wt%). Finally, the pyrolysis behaviors of DG, PP, and DP11 was investigated by TG and DTG analyses. As illustrated in Fig. 1c and f, it can be clearly seen that there is an obvious interaction between DG and PP in the pyrolysis of the mixture of the two materials. In the separate pyrolysis process conducted by Chen et al. (2020) the activation energy obtained for PP was $302.04\text{ kJ mol}^{-1}$. This indicates that PP is difficult to react under separate pyrolysis conditions. However, in this study, when DG and PP were co-pyrolyzed, the activation energy obtained was 47.74 kJ mol^{-1} , which is significantly lower than the activation energy studied by Chen et al. (2020) ($302.04\text{ kJ mol}^{-1}$). This suggests that the presence of DG accelerates the pyrolysis reaction of PP. The lower activation energy of DP11 (47.74 kJ mol^{-1}) compared to other materials can be

attributed to the presence of small molecules and free radicals generated during the decomposition of DG. In simpler terms, the decomposition of DG had a significant impact on the decomposition of PP. The interaction between DG and PP resulted in a lower activation energy for the reaction, enhancing the overall decomposition process. And co-pyrolysis increases the temperature difference between the two maximal weight loss peaks observed in the DTG, corresponding to the pyrolysis of DG and PP, as well as the reaction temperature range of pyrolysis.

Variation of $W_{\text{calculated}}$ and $W_{\text{experimental}}$ against temperature at $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ are presented in Fig. 2 for DP11 used in this study. Comparing the experimental thermal weight curve with the calculated thermal weight curve, it was evident that in the main phase of the pyrolysis reaction ($280\text{--}490\text{ }^{\circ}\text{C}$), the experimental value of the DP11 pyrolysis loss was lower than the calculated value, and the main interactions between DG and PP were inhibitory rather than synergistic. The inhibition of the pyrolysis process ended until around $490\text{ }^{\circ}\text{C}$. It's possible that this is the case since PP melts at low temperatures ($280\text{--}490\text{ }^{\circ}\text{C}$), preventing the volatilization of biomass materials. At high temperatures ($490\text{--}800\text{ }^{\circ}\text{C}$), after that, no significant interaction was observed at higher temperatures due to the complete decomposition of the plastic components in DP11.

3.2.3. Kinetics analysis

On each sample, a kinetic analysis was carried out. The kinetic analysis of DG, PP, and DP11, based on the primary reaction model, was mainly focused on the primary reaction phase. The frequency factor (A) and activation energy (E) of the pyrolysis process, which have been discussed in prior research, were calculated using the procedure given in Section 2.3 (Singh et al., 2021).

Table 2 lists the matching parameters for the $\ln(-\ln(1-x)/T^2)$ and $1/T$ fitting results. Each stage's correlation coefficient (R^2) was near to or higher than 0.9, showing that the fitting accurately captured how each stage's pyrolysis process worked. Additionally, it was discovered through a comparison of the data in Table 2 that PP decomposition has larger activation energy than biomass decomposition. This might be due to the stark differences in molecular structure between plastic and biomass (Zhou et al., 2006). The activation energy also varied greatly between the biomass components: the activation energy of the DG in this study was 42.90 kJ mol^{-1} . Among them, the activation energy of solid waste (SW) was close to that of DG, and that of *dunaliella salina* (DS) did not exceed 85 kJ mol^{-1} in each decomposition stage (Zhou et al., 2006; Chen et al., 2021a,b). In the study conducted by Chen et al. (2021a,b), it was found that the activation energies for DS and PP during separate

pyrolysis were high, measuring 83.5 kJ mol^{-1} and 289.4 kJ mol^{-1} , respectively. Similar results were also found in the study by Chen et al. (2020), where the activation energy for individual pyrolysis of PP, SP, and WS was determined to be 302.04 , 41.02 , and $167.59\text{ kJ mol}^{-1}$, respectively. Therefore, the activation energy obtained during the co-pyrolysis of DS-PVC, DS-PET, DS-PS, SP-PP, and WS-PP (as shown in Table 2) was found to be relatively lower compared to individual pyrolysis. This result is similar to the findings of the current study. In addition, a significant difference of the required activation energy of different plastics was observed during the thermal decomposition process. In this study, the activation energy for PP was found to be $130.27\text{ kJ mol}^{-1}$, which was lower than that PS (249.9 kJ mol^{-1}), PVC (185 kJ mol^{-1}), PET (280 kJ mol^{-1}), and PP ($302.04\text{ kJ mol}^{-1}$), respectively (Chen et al., 2020, 2021a,b). The reason for this difference may be that PP is a relatively simple linear polymer with a relatively simple chemical structure. In contrast, PS, PVC, and PET have more complex molecular structures, with a greater number of chemical bonds and functional groups, thus requiring more energy to break these bonds during the thermal decomposition process.

DG mostly affects the first step of breakdown, and the pyrolysis of PP occurs in the second stage. The results indicate that the addition of biomass DG in the pyrolysis of PP could reduce the activation energy of PP (about 63%), which has a strong engineering application value. Table 2 lists the reaction activation energies of the eight mixtures, and the activation energies in the high temperature region are: DS-PVC was 32.6 kJ mol^{-1} , DS-PET was 78.0 kJ mol^{-1} , DS-PS was 159.3 kJ mol^{-1} , SP-PP was $129.29\text{ kJ mol}^{-1}$. In the present study, the reaction activation energy of DP11 was 47.74 kJ mol^{-1} at a heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ over the temperature interval of $553\text{--}763\text{ }^{\circ}\text{C}$. Apart from being close to the activation energy of DS-PVC, DP11's activation energy was significantly lower compared to that of other mixtures, indicated a substantial advantage. Different activation energies indicated that the biomass-plastic mixtures exhibited different pyrolysis reactivities over different temperature ranges. Therefore, the foregoing results may indicate that the synergistic effect will significantly lower the activation energy during co-pyrolysis of biomass and plastics, which is appealing for engineering applications.

3.3. Product analysis

The heating rate and thermal parameters during pyrolysis had a significant impact on the pyrolysis products of DG and PP. The current study therefore concentrated on comparing the pyrolysis products from several samples (DG, PP, and DP11) and by varying the pyrolysis temperature (over the range $300\text{--}800\text{ }^{\circ}\text{C}$). Compounds including hydrocarbons, aromatic hydrocarbons, esters, in addition to other species were thought to be those with the most economic value out of all the pyrolysis byproducts observed.

3.3.1. Valuable pyrolysis products

The pyrolysis products of DG contained hydrocarbons, phenols, alcohols, esters, nitrogen compounds and other substances. As shown in Fig. 3, for the co-pyrolysis of DG and PP, in terms of the effective products, the relative amounts of hydrocarbons had gradually risen from 13.49% to 82.30% with increase in temperature, while esters and ketones gradually decreased, especially the relative content of esters, which rapidly reduced from 45.72% to 2.68%. Alcohols, however, showed a bimodal trend. At intermediate pyrolysis temperatures ($400\text{ }^{\circ}\text{C}$ and $500\text{ }^{\circ}\text{C}$) the formation of acids was observed to be enhanced. The main reason for this effect was that at these two temperatures the decomposition of esters was promoted, which in turn produced a certain amount of acids, but the energy barrier for further reaction of acids was not attained. Hence, when the temperature was increased to $600\text{ }^{\circ}\text{C}$, the acids reacted further, reducing the relative content of these compounds to zero. At lower temperatures ($300\text{ }^{\circ}\text{C}$), the pyrolysis products of DP11 were ethyl linoleate (22.18%) and ethyl palmitate (7.25%), which are

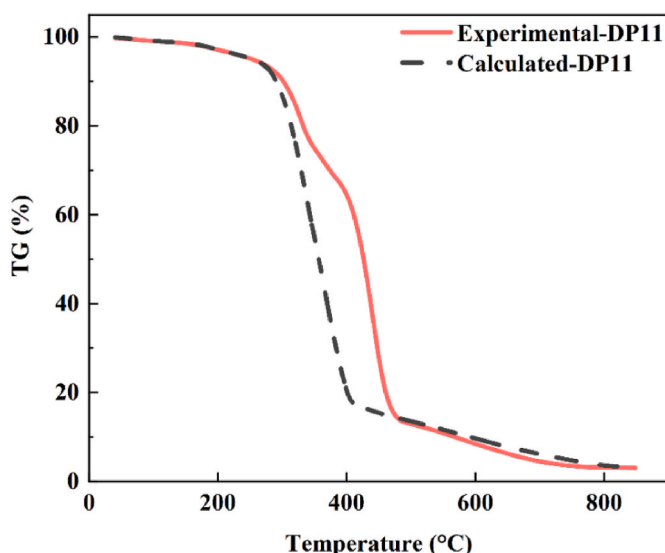


Fig. 2. Experimental and calculated TG curves of DP11.

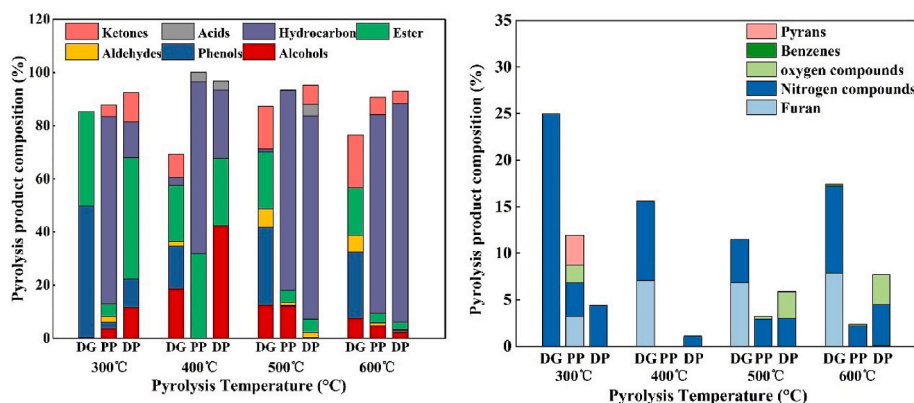


Fig. 3. Pyrolysis products of DP11, a) valuable compounds, b) toxic compounds.

Table 2

Kinetic parameters for pyrolysis of different plastics, biomass and mixtures.

Sample	Temperature range (°C)	Activation energy (E) (kJ·mol ⁻¹)	Frequency factor (A) (mol ⁻¹)	Correlation index (R ²)	Reference
PP	260–461	130.27	2.0×10^9	0.994	This study
DG	397–744	42.90	378.33	0.987	
DP11	553–763	47.74	3.11×10^3	0.981	
DS	215–298	53.5	1.8×10^{23}	0.994	
	298–336	83.5	8.3×10^8	0.968	Chen et al. (2021a,b)
	336–510	13.6	1.2×10^{13}	0.972	
PS	365–461	249.9	4.4×10^{18}	0.99	
PVC	285–308	185.0	5.0×10^{16}	0.95	
PET	380–490	280.0	1.2×10^{20}	0.98	
DS-PVC	230–340	71.8	9.5×10^5	0.97	
	405–515	32.6	7.0×10^1	0.95	
DS-PET	220–350	48.4	1.8×10^3	1.00	
	350–390	7.1	7.6×10^{-2}	0.96	
	390–490	78.0	2.7×10^5	0.97	
DS-PS	225–293	50.2	2.9×10^3	0.98	
	293–340	44.5	7.9×10^2	0.97	
	405–465	159.3	8.0×10^{11}	0.99	Chen et al. (2020)
PP	418–496	302.04	1.67×10^{21}	0.998	
SP	211–319	34.22	8.41×10^1	0.958	
	319–375	41.02	6.62×10^2	0.969	
WS	275–343	167.59	3.69×10^{14}	0.915	
SP-PP	250–348	60.44	1.43×10^4	0.988	
	440–520	129.29	5.68×10^8	0.919	
WS-PP	294–340	204.97	3.04×10^{17}	0.969	
	447–533	130.63	8.76×10^8	0.945	

Note: ‘-’ represents ‘not reported’; ‘PVC’ represents ‘Polyvinyl chloride’; ‘PET’ represents ‘Polyethylene terephthalate’; ‘DS’ represents ‘Dunaliella salina’; ‘SW’ represents ‘Solid waste’; ‘PS’ represents ‘polystyrene’; ‘SP’ represents ‘soy protein’; ‘WS’ represents ‘wheat starch’.

long-chain fatty acids (mainly C16–C18), but these compounds hardly appeared in the pyrolysis products of DG and PP alone. As economically-viable raw materials, ethyl linoleate is mainly used in the pharmaceutical industry, and ethyl palmitate can be used as a softener and lubricant, and could thus promote the development of a processing industry if easily available (Erb et al., 2016; Moura-Nickel et al., 2016). In addition, palmitic and oleic acids are also high-quality raw materials for biodiesel production.

3.3.2. Hazardous pyrolysis products

The nitrogen-containing compounds in the pyrolysis product and the pyrolysis temperature did not appear to be significantly correlated. Previous studies on the pyrolysis of both double-base propellant (Jin et al., 2023) and kitchen waste (Shen et al., 2023) have shown that NO_x can be released from the pyrolysis primarily exists in the form of NO, and NO₂ is primarily released during the pyrolysis process. The results can be used to explain that in biofuel (liquid products) obtained less N-containing product at high temperature of pyrolysis in this study (Fig. 3). Nevertheless, the content of nitrogen-containing compounds produced

by DP11 was 4.39% (at 300 °C), somewhat lower than that obtained from DG (14.68%), and closer to content from PP alone (3.64%), consistent with previous studies (Yang et al., 2019). Pyrans, benzenes, and oxygen compounds are generated during the pyrolysis process with relatively low content, which aligns with the previous pyrolysis study of cellulose, hemicellulose, and lignin (Ansari et al., 2019). In the co-pyrolysis process of DG and PP in this study, Furan and Benzene were generated at temperatures of 600 °C and 500 °C, respectively, with contents of only 0.105% and 0.116%, while oxygen-containing compounds were not produced during the co-pyrolysis process. Therefore, it is necessary to focus on other substances in greater detail.

In summary, a starting material formed from DP11 promoted the production of more valuable compounds (e.g., aliphatic hydrocarbons, alcohols, etc.), while reducing the levels of harmful products (e.g., nitrogen-containing compounds, furans, etc.). In terms of the latter species, a clear downward trend in production of nitrogen-containing oxides and furan substances emerged with increase in temperature. Co-pyrolysis apparently inhibited the generation of nitrogen-containing compounds at all pyrolysis temperatures, this effect being most

pronounced at 400 °C. The main reason for this was the more adequate decomposition of the PP component in the co-pyrolysis samples at higher temperatures. The proportion of hydrogen in the reaction system increased evidently, and the dehydration reaction took place with the oxygen in the product molecule, so as to realize the removal of hydroxyl and carboxyl groups, improve the yield of hydrocarbons, and visibly reduce the oxygen content in the product (Li et al., 2021a,b). Moreover, the synergistic effect was more distinct at higher temperatures, and the pyrolysis was more effective, producing more desirable products. At lower temperatures, the pyrolysis was not very efficient, which led to the generation of more harmful products. Accordingly, reasonable control of temperature range was one of the indispensable conditions through which to control the production of valuable materials and yet lessen the presence of harmful products.

3.3.3. Effects of temperature on pyrolysis product distributions

Compared with pyrolysis of individual materials, co-pyrolysis of biomass and polymer can further effectively improve the energy utilization, accelerate the reaction rate, reduce energy consumption and cost, and achieve efficient conversion of biomass and plastic pyrolysis products.

As shown in Fig. 3, the optimum pyrolysis temperature of DP11 is 600 °C. The hydrocarbon substances (13.49%) and other valuable products, including Alcohols (11.66%), Ester (45.72%), and Ketones (10.89%), were generated under the pyrolysis temperature of 300 °C (Fig. 3a). Notably, hydrocarbon substances are widely recognized as the primary source of biofuel obtained through biomass pyrolysis treatment (Yu et al., 2020). Along with the increased pyrolysis temperature to 400 °C and 500 °C, the generated hydrocarbon substances increased to 25.73% and 76.45%, respectively. Under the pyrolysis temperature of 600 °C, a significantly higher yield of hydrocarbon substances (82.30%) were obtained, which was around 6 times higher than that of 300 °C. Furthermore, as shown in Fig. 3b, harmful by-products represented by nitrogen compounds are the lowest at 600 °C (4.37%) compared to the productions (4.5%–4.7%) under other temperatures. Therefore, it is determined that 600 °C is the optimal pyrolysis temperature for the co-pyrolysis of DG and PP. At a pyrolysis temperature of 600 °C, the relative content of hydrocarbons can reach 82.30%. At 300 °C, the relative content of esters can reach 45.72%, and at 400 °C, the relative content of alcohols can reach 42.22%. This is mainly because the PP component in the co-pyrolysis samples is decomposed more fully at a higher temperature, the hydrogen content in the reaction system increases significantly, and dehydration reactions occur via the oxygen in the product molecules, achieving the removal of hydroxyl and carboxyl groups, improving the yield of hydrocarbons, and significantly reducing the oxygen content of the product (Chen et al., 2020). Hydrocarbons are natural components of fossil fuels and are of high value in the preparation of biofuels (Li et al., 2020).

The C5 and C6 alcohols account for the largest proportion, and their main component is furfuryl alcohol, which is an important organic raw material (Zhao et al., 2021). Esters can be used to prepare lubricants, softeners and other industrial chemicals (Kanter et al., 2022). Thus, the co-pyrolysis of DG and PP shows obvious synergism. Through co-pyrolysis, the ratio of hydrogen and oxygen in the reaction system can be effectively adjusted, the oxygen content of the product can be significantly reduced, the yield of hydrocarbons can be increased, and the potential of resource utilization and energy application of DG and PP can be improved. The main substances generated by pyrolysis show good selectivity relative to the pyrolysis temperature. At different temperatures, yields of the products are different, thus different temperatures can be selected for co-pyrolysis, so as to achieve the selective preparation of the particular products required.

4. Co-pyrolysis mechanism analysis

The co-pyrolysis of DG and PP involves a complicated reaction

pathway, as shown in Fig. 4. Both random scission of polymer links and chain-end cleavage processes were discovered during the general thermal decomposition of PP. PP decomposes into different lengths of alkenes, alkanes, and many hydrogen radicals under high temperature. Some alkenes and alkanes undergo their own aromatization and cyclization reactions to generate cycloalkanes and aromatic hydrocarbons (Yang et al., 2022). PP generates alkyl and alkenyl groups that combine with the benzene ring, replacing hydrogen atoms on the benzene ring. The observation of the reaction routes, which also showed that intermediate PP products occasionally create propylene continuously multiple times, served as evidence for this (Guo et al., 2022). The carbohydrates in DG and the smaller organic groups in the olefin formed by the pyrolysis of PP (mainly furan) form aromatic hydrocarbons through the Diels-Alder and dehydration reactions (Qi et al., 2018). Alkenes generated by PP pyrolysis are transformed into aromatic hydrocarbons by cyclization, aromatization and oligomerization (Hasan et al., 2022). The addition of PP inhibited the Maillard reaction between amino acids and reduced sugars in proteins, resulting in a decrease in nitrogen-containing molecules and an increase in the synthesis of aliphatic hydrocarbons (Wu et al., 2017). Throughout the hydrogen pool evolved by PP pyrolysis, lipids and esters potentially interact with H free radicals to generate substantial amounts of long chain hydrocarbons and long chain alcohols. While free radicals generated by PP react with furans, aldehydes, and ketones to form alcohols and hydrocarbons, PP prevented the Diels-Alder reaction between alkenes and the production of phenols and aromatics (Zhang et al., 2021).

Furthermore, previous studies have demonstrated that the presence of nitrogen (N) in pyrolysis volatiles primarily originates from the proteins present in biomass. However, it is important to note that excessive nitrogen content can negatively impact the quality and stability of the resulting biofuel (Xiong et al., 2023). Yang et al. (2022) have utilized density functional theory to reveal that the co-pyrolysis process of *Enteromorpha prolifera* and waste plastics (polyethylene) is beneficial in reducing the types and quantities of nitrogen-containing compounds, resulting in a decrease in the relative content of nitrogen-containing compounds from 7.91% to 3.53%. Amino acids can be used to explain the transformation and evolution of nitrogen during the pyrolysis process and the pyrolysis process involves the direct decomposition of amino acids into smaller molecular products by eliminating H₂O, CO₂, R, or NH₂ groups (Chen et al., 2022). Subsequently, 2,5-diketopiperazine can be formed by the dehydration condensation between two amino acid molecules (Xu et al., 2020). Based on the above information and experimental result, Fig. 4 summarizes the mechanism and pathways of nitrogen migration during the co-pyrolysis process of DG and PP. It can be concluded that during the co-pyrolysis process, nitrogen molecules can migrate through interactions and reactions between reactants. Nitrogen gas is released in the form of gas, resulting in a reduction of nitrogen-containing harmful substances. Moreover, different reaction conditions can lead to different paths and rates of nitrogen compound formation, thereby achieving a reduction in nitrogen-containing compounds.

5. Potentials for implementation

Large amounts of waste cause great pressure on the environment, and a method for the effective harmless reduction, and treatment of valuable resources, is particularly important. Co-pyrolysis has a strong potential for further development. While realizing rapid and significant reduction in waste volumes, it makes full use of the organic components in the waste to generate biofuel, biochar and biogas. Therefore, developing co-pyrolysis technologies is an important way to recover high calorific value gas and oil, recover and utilize resources, and effectively control secondary pollution.

According to this study, supplemented by other literature, biomass and plastic co-pyrolysis will not only reduce the amount of material waste produced, but can also recycle important chemicals and

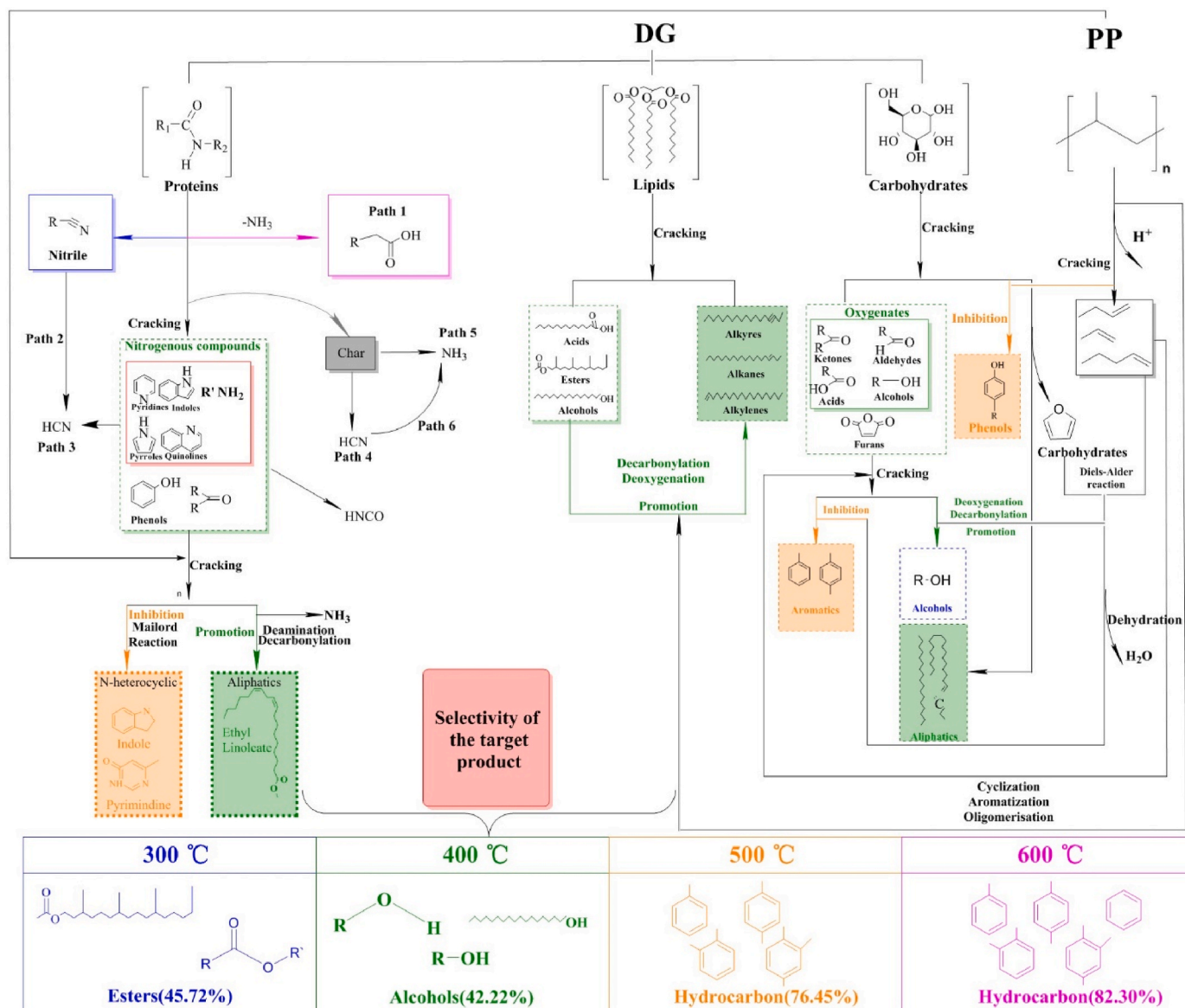


Fig. 4. Simplified reaction mechanism proposed for the co-pyrolysis of DG and PP.

alternative fossil fuels. Moreover, co-pyrolysis technology can provide a driving force to find a feasible way to an optimized combination of fossil energy and new energy. The quality of pyrolysis can be improved; minerals in biomass can not only promote pyrolysis, produce more hydrocarbons, but also slow the radical polymerization and improve the condensation of thick ring compounds in the co-pyrolysis system. Future research will focus on the study of biomass ash content to obtain information regarding its impact on the distribution and reaction of pyrolysis products. Various minerals and metals present in the ash can either act as catalysts or inhibitors, influencing reaction pathways and product yields. Higher ash content in DG has multiple effects on pyrolysis production and distribution (Huang et al., 2023). Firstly, ash presence promotes char formation, reducing volatile gas production and increasing solid residue yield. The ash composition, particularly alkali and alkaline earth metal concentrations, can catalyze secondary reactions, leading to the generation of undesirable by-products like tars, phenolics, and polycyclic aromatic hydrocarbons (PAHs). These by-products can compromise the quality of biofuel or syngas derived from pyrolysis (Zhu et al., 2018). In addition, with the increase of the content of N and O in the raw materials, harmful substances produced in the pyrolysis process will also increase, such as nitrogen-containing

compounds and furans (Uzoejinwa et al., 2018). Therefore, the technology should be further optimized in order to avoid this increase of harmful substances and thus enhance the quality of biofuel. Thus, extra process optimization should be utilized in order to eliminate such toxics in the end products, for example, by using zeolite as a catalyst, and therefore regulate the creation of N-containing compounds, which gives a view of possible improvement (Li et al., 2019). Additionally, increasing the heating rate during the co-pyrolysis of biomass and plastic process (e.g., 20, 30, 50 °C·min⁻¹) may also be an effective way to enhance the production of valuable products and reduce the formation of harmful by-products. However, in order to improve the overall process design, it is also very important to properly understand the reaction mechanism. Here, we propose the reaction mechanism for co-pyrolysis of DG and PP, through which the theoretical foundation for future applications is presented.

In addition, by targeting specific desired products, the composition and distribution of the products can be controlled during co-pyrolysis. Depending on the desired chemical or energy products, the pyrolysis conditions such as temperature can be adjusted to achieve high selectivity in the synthesis of specific products. Hydrocarbons are natural components of fossil fuels, which are of high value in the process of

preparing biofuel fuels. With the increase of temperature, the relative content of hydrocarbons increased rapidly from 13.49% (300 °C) to 82.30% (600 °C). Furthermore, at 600 °C, the relative content of hydrocarbon substances continues to increase, along with an increase in the variety of substances. The carbon chain length still predominantly consists of C9, with the main hydrocarbon substances being C9 olefin (2,4-dimethyl-1-heptene) and C9 cycloalkane (1,2,4-trimethylcyclohexane). The carbon chain lengths of the remaining hydrocarbon substances are mainly concentrated between C6 and C10. In conclusion, considering factors such as the acidity of biofuel and the content of hydrocarbon substances, the optimal pyrolysis temperature for co-pyrolysis of DG and PP at 600 °C is recommended. This temperature provides the best conditions for producing high-quality substances. Furthermore, according to Fig. 3, it can be observed that at a temperature of 600 °C, there is a significant decrease in the relative content of oxygen-containing compounds such as esters, phenols, ketones, alcohols, as well as other nitrogen-containing compounds. The synergistic effect is most apparent under these conditions. Therefore, this study demonstrated the high potential of biofuel generation and identified the optimal operational strategies for the co-pyrolysis of biomass and waste plastics. At different temperatures, the predominant product components vary. Depending on the target products, different temperatures can be selected for co-pyrolysis of DG and PP, thereby further enhancing the potential of DG and PP pyrolysis applications. In addition to analyzing and studying the liquid products mentioned above, in the future, it is also worthwhile to further investigate the gas and solid products. This can help optimize the pyrolysis process, improve the design of pyrolysis reactors, and effectively utilize and efficiently recover gas and solid products.

6. Conclusions

In light of the escalating accumulation of biomass and plastic waste, the exploration of efficient strategies for waste utilization has emerged as a pivotal focus of research. In this study, a co-pyrolysis approach was employed to investigate the simultaneous decomposition of DG and PP. Compared to the co-pyrolysis of biomass and other common plastics like polyethylene (PE), the co-pyrolysis of DG and PP exhibited enhanced production of valuable compounds, particularly hydrocarbon substances (82.30%). Notably, the co-pyrolysis process exhibited a significantly reduced activation energy (by 63%) compared to the individual pyrolysis of PP. This indicates that co-pyrolysis facilitates a more energy-efficient reaction system, thus favoring the reaction kinetics. Additionally, the optimal temperature for co-pyrolysis was determined to be 600 °C, as it yielded the highest quantity of valuable products (such as hydrocarbons) while minimizing the formation of detrimental byproducts (e.g., nitrogen compounds). These findings contribute to the ongoing efforts in developing sustainable approaches for waste management and resource recovery. These research findings hold significant importance in the development of sustainable waste management and resource recovery methods, while also providing support for further investigations into improving efficient co-pyrolysis reactor systems and the pyrolysis process itself.

Credit author statement

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

the work reported in this paper.

Data availability

Data will be made available on request.

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