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A review on the thermochemical reaction mechanisms for distiller pyrolysis process

Sheng-Lun Lin[1*], Hongjie Zhang[2], Wei-Hsin Chen[3,4,5], Yee-Lin Wu[1], Che-Wei Wu[1] and Shih-Wei Huang[6,7]

Abstract

Circular utilization of distillery byproducts is crucial, and pyrolysis has emerged as a viable technology for converting them into fuels and high-value chemicals. This review investigates the thermochemical reactions of byproducts generated during the grain fermentation process. We begin by discussing the physicochemical properties of these byproducts as they relate to their potential conversion into fuels. Subsequently, we explore various thermochemical processes for biomass-to-energy conversion, including the influence of reaction conditions and catalysts. The intricate interactions between cellulose, hemicellulose, lignin, and protein during pyrolysis are then examined. These interactions, particularly the Maillard reaction between proteins and carbohydrates and vapor–solid interactions, significantly impact the reaction pathways and ultimately the yield and quality of bio-oil, a key product of the pyrolysis process. Understanding these interactions, as evidenced by studies demonstrating the influence of levoglucosan, furfural, and hydroxyacetic acid on product yields, is essential for optimizing pyrolysis processes of distillery byproducts and maximizing the efficiency of biomass energy conversion. By elucidating the theoretical foundation and scientific basis for optimizing the energy conversion of distillery byproducts, this review aims to contribute to the development of sustainable and environmentally friendly practices within the brewing industry.

Keywords Distiller byproducts, Thermochemical processes, Cellulose, Hemicellulose, Lignin, Protein, Pyrolysis, Reaction mechanisms

1 Introduction

Low-carbon renewable fuel is globally considered as a potential cure for the energy crisis and environmental pollution caused by using fossil fuels [1]. Biomass has attracted much attention as a renewable energy source due to its abundance and CO_2 capture ability. In terms of energy supply, biomass is the world's fourth largest energy source after coal, oil, and natural gas, accounting for about 14% of the world's primary energy consumption [2]. In the biomass-to-energy conversion process, the net carbon emissions were reported almost zero in some cases [3, 4], supporting the importance of developing more practical and economical biomass energy refinery techniques.

Distiller grains with soluble (DGS) are the largest byproduct remaining after fermentation and production in industries such as Baijiu, vinegar, and bioethanol [5], containing crude fiber, protein, crude fat, and

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*Correspondence:
Sheng-Lun Lin
z11208011@ncku.edu.tw
[1] Department of Environmental Engineering, National Cheng Kung University, Tainan 701401, Taiwan
[2] School of Mechanical Engineering, Beijing Institute of Technology, Beijing 100081, China
[3] Department of Aeronautics and Astronautics, National Cheng Kung University, Tainan 701401, Taiwan
[4] Research Center for Smart Sustainable Circular Economy, Tunghai University, Taichung 407224, Taiwan
[5] Department of Mechanical Engineering, National Chin-Yi University of Technology, Taichung 411030, Taiwan
[6] Institute of Environmental Toxin and Emerging Contaminant, Cheng Shiu University, Kaohsiung 833301, Taiwan
[7] Center for Environmental Toxin and Emerging-Contaminant Research, Cheng Shiu University, Kaohsiung 833301, Taiwan

several trace components. The DGS production is huge that the Baijiu industry alone produces about 100 Mt of DGS each year in China [6]. According to a report by the Renewable Fuels Association, U.S., the ethanol producers generated 34.5 Mt of DGS, corn feed, and grain protein in 2021. DGS contains many unhydrolyzed and unfermented components and nutrients [7], and improper treatment can cause environmental pollution and waste of resources [8]. Currently, the main methods for processing DGS are feeding, agricultural application, bioenergy, genetic engineering, and microbiology [9] (as shown in Fig. 1). Currently, about 80% of DGS is consumed as feed for beef, dairy, pork, and other animals, but the huge differences in nutrient concentration and quality between different sources have always been a major obstacle to its use as animal feed [10], and agricultural application requires a longer period. At present, an excess of DGS emissions has been observed, so the treatment of DGS needs to be developed in some new fields [11]. Although genetic engineering and microbiological applications are emerging technologies, they are still in the early stages and are not suitable for processing large amounts of DGS. Therefore, converting DGS into bioenergy through biological and thermochemical processes is considered a very promising treatment method. DGS have a high energy content of 27 MJ kg^{-1} which is higher than other biomass, i.e., agricultural residues and wood have heating values ranged from 15–17 and 18–19 MJ kg^{-1}, respectively [12]. Thermochemical processes generally include gasification, pyrolysis, hydrothermal liquefaction, and hydrothermal carbonization (torrefaction) and can increase the energy density of DGS and convert them into valuable energy products in terms of biogas, biooil, and biochar. Among these processes, pyrolysis offers a simpler and more efficient approach compared to gasification, hydrothermal liquefaction, and hydrothermal carbonization (Table 1). Unlike gasification and hydrothermal methods, which require high temperatures, high pressures, and often an initial drying step, pyrolysis operates at lower pressures and eliminates the need for drying, thus reducing energy consumption and associated safety concerns. Furthermore, pyrolysis generates valuable byproducts, including biochar for soil amendment and bio-oil for further energy or chemical production. This versatility, coupled with its mature technology and ease of operation, makes pyrolysis a viable and ideal choice for DGS treatment.

Bio-oil is a product with high social and economic benefits and is also the main target product of pyrolysis which includes phenols, ketones, aldehydes, acids,

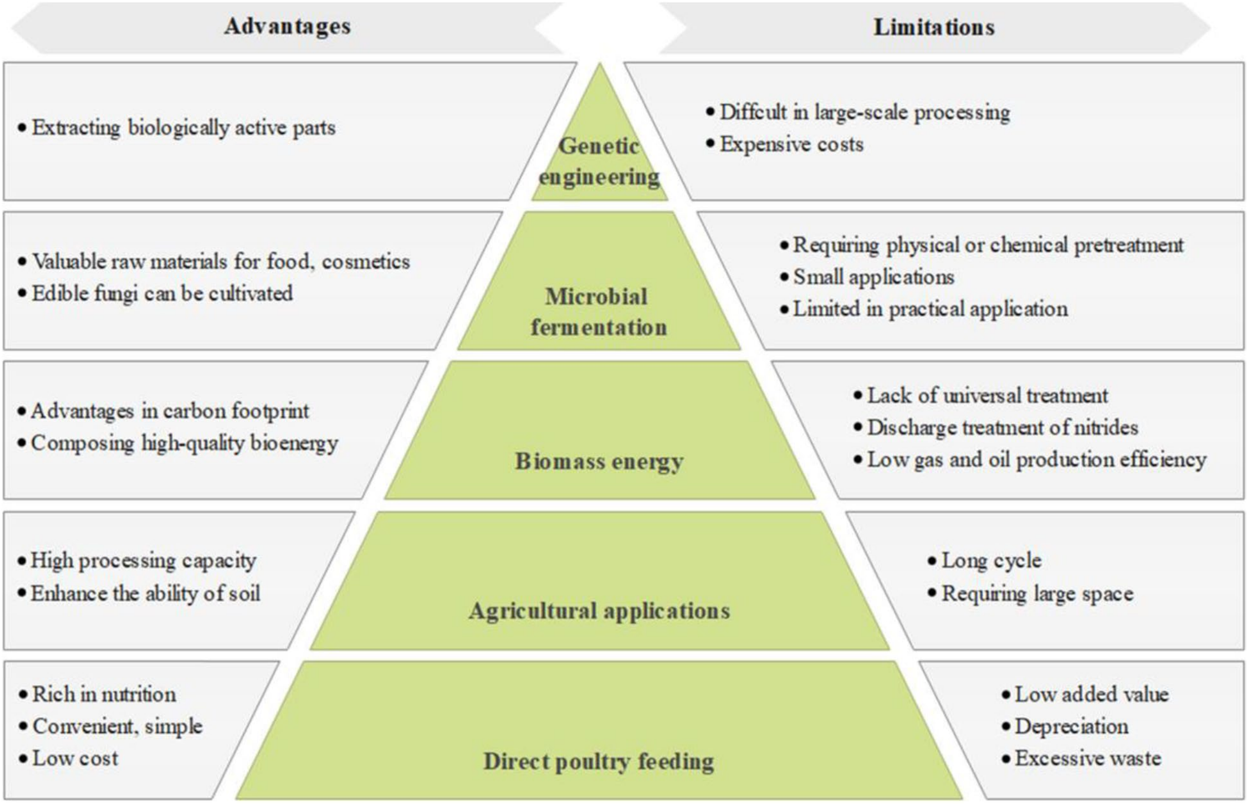

Fig. 1 Utilization status of waste distiller's grain

Table 1 Comparison of Various Thermochemical Treatment Technologies for DGS

Technology	Temperature (°C)	Pressure (kPa)	Main products	Ref
Gasification	900	101	H_2, syngas	[13]
Hydrothermal liquefaction	280–400	25,000	CO_2, H_2, CO, CH_4, C_2H_6	[14]
Hydrothermal liquefaction	240–280	101	biocrude oil	[15]
Hydrothermal carbonization	170–250	800–900	char	[16, 17]
Pyrolysis	400–700	101	acids, alcohols, esters, biochar. etc	[18]

and other organic compounds [19]. Bio-oil has various applications, including power generation, heating, and the production of high value-added chemicals, among which bio-oil with higher calorific value can be used as a transportation fuel. In addition, bio-oil generated from biomass pyrolysis has lower carbon emissions and air pollutant emissions compared to traditional fuels. The carbon in bio-oil mainly comes from plant biomass such as distiller's grains, and plants absorb carbon dioxide through photosynthesis during growth, thus forming a closed carbon cycle. Therefore, using bio-oil as a fuel can reduce greenhouse gas emissions and reduce the negative impact on climate change. The relative yield of each product depends on operating parameters, biomass type, and pyrolysis method. Typically, pyrolysis of wood biomass at temperatures ranging from 500 to 550 °C results in bio-oil production ranging from 60–80 wt%, biochar ranging from 20–30 wt%, and pyrolysis gas ranging from 20–25 wt% [20, 21]. Many researchers have also studied the effects of catalysts, particle size, heating rate, feed rate, and holding time on the pyrolysis process of different types of biomasses, in order to optimize the pyrolysis process and increase the production of bio-oil and other products [22]. From the perspective of process optimization, it is particularly important to have a better understanding of the pyrolysis reaction mechanism and kinetics of the basic components of biomass, and further develop biomass pyrolysis models.

Organic matter in DGS usually accounts for about 60–70% of the total mass, including carbohydrates, cellulose, hemicellulose, and a large amount of protein and fat. Due to the complexity of its composition, a series of complex chemical reactions are involved in its thermochemical conversion process. Although there have been many studies and reviews on pyrolysis experiments and reaction mechanisms of cellulose, hemicellulose and lignin, comprehensive comments on the interaction of multi-component mixing are lacking. Understanding the reaction mechanism and product composition involved in the pyrolysis process of DGS is crucial for optimizing the process and maximizing the required product yield, and the impact of the high protein content of DGS on pyrolysis cannot be ignored. In this review, we will explore in detail the reaction mechanisms involved in DGS pyrolysis, including its chemical composition, pyrolysis product composition, as well as the influencing factors and reaction mechanisms of the main components, and mainly focus on the mechanism of interaction between components.

2 Pyrolysis process for DGS

2.1 Analysis and characterization of DGS

As a biomass resource, DGS exhibits some differences in composition compared to other biomass. The carbon content with the highest contribution for DGS elemental analysis is the main cause of heat generation. The second contributive element is oxygen and followed by the hydrogen. The C/H ratio can affect the distribution of three-phase products during the pyrolysis of distiller's grains. When the C/H ratio is high, carbon elements will participate in more reactions during the pyrolysis process, resulting in more carbonaceous products such as olefins and aromatic hydrocarbons [17]. Moreover, there are over 3% of N elements and trace amounts of S elements in DGS, so toxic gases such as nitrogen oxides and sulfur dioxide will be generated during the pyrolysis process. The characterization of rice husk-based DGS and rice husks revealed that C/N ratio of rice husks was 49%, which was significantly higher compared to the 13% found in DGS. This difference could be attributed to the higher content of nitrogen-rich organic compounds, such as proteins and amino acids, present in the grains used for distillation [23, 24]. These are unfavorable elements that need to be noted during the DGS pyrolysis process and may have adverse effects on the environment. Generally, DGS has a higher content of carbohydrates and a lower content of recalcitrant components such as cellulose, hemicellulose, and lignin. The major components of DGS are carbohydrates (35–66%) [25], proteins (10–40%), cellulose (~ 15%), hemicellulose (5–10%), and lignin (~30%) (Table 2). These values represent a broad spectrum of possible compositions due to the inherent variability in DGS samples. Compared to other biomasses such as straw and wood, DGS has a higher protein content. The volatile matter with the highest content in DGS samples, accounting for about 70%, is also the main influencing factor in the pyrolysis process. Additionally, DGS typically has a high moisture content and requires drying prior to pyrolysis.

2.2 Thermogravimetric analysis and kinetic studies

Thermogravimetric analysis (TGA) is a powerful technique for investigating the thermal decomposition of materials by measuring mass loss characteristics and kinetic parameters [32]. The TGA curves of DGS typically exhibit several weight loss stages and most research divide the pyrolysis into three stages [5, 29, 30], each corresponding to a different thermal decomposition process. The first stage is dehydration stage (50–300 °C), the peak value of DGS is relatively small due to over-drying treatment. The second stage is the rapid decomposition and pyrolysis stage (300–600 °C), in which more than 40% of the mass loss occurs. It is mainly caused by the decomposition of hemicellulose, protein, cellulose, fat and amino acid, and generation a large amount of gas and condensable volatile components. The third stage is the slow decomposition stage (600–800 °C), in which lignin is carbonized to form coke and the reaction rate is slow. Compared with general lignocellulosic biomass, the initial decomposition temperature of DGS is lower, which may be due to the synergistic effect of protein and starch components, which can promote the decomposition of DGS [33].

Table 2 Compositions of DGS used for pyrolysis

Unit (wt%)	Barley DGS [26–28]	Corn DGS [25, 29]	Sorghum DGS [5, 30]	Rice DGS [23, 25, 31]
Ultimate analysis				
C	45.5–49.0	49.0	44.2–50.7	39.0
H	6.3–0.7	6.3	4.6–7.1	6.3
O	33.6–39.8	33.6	38.5	25.2
N	4.5–8.1	4.5	4.8	3.0
S	0.4–0.7	0.4	0.3	0.4
Organic component				
Cellulose	15.0	16.0	15.0	15.8
Hemicellulose	5.4	42.1	5.4	11.3
Lignin	29.8	—	29.8	—
Protein	35.0–38.2	8.6–25	23.7	44.2–47.5
Proximate analysis				
Volatile	78.2	78.2	64.7–89.4	—
Fixed carbon	14.7	14.7	0.3–19.8	—
Water	7.1	7.1	0.3–7.7	8.9–15.7
Ash	4.0	2.2–8.9	7.0–7.8	2.6

Pyrolysis kinetics can study the pyrolysis mechanism of substances, and then predict their pyrolysis characteristics and optimize the pyrolysis process. The kinetic parameters of DGS pyrolysis usually include activation energy (Ea), reaction order (n), reaction rate constant (k), etc. These parameters can be obtained by fitting the TG (Thermogravimetric) and DTG (Differential Thermogravimetry) curves of pyrolysis experiments. The kinetic parameters of DGS pyrolysis can be determined by single reaction model, equal conversion non-reaction model, and lumped reaction model, such as Flynn–Wall–Ozawa method, Distributed Activation Energy Model, Kissinger Akahira Sunose method [23, 29, 30]. However, different biomass materials will have different behaviors due to their inherent physical and chemical properties [34], and the components of distiller's grains as a complex compound will change with time, so it is very difficult to find a satisfactory model to predict the whole decomposition process. The effective Ea of DGS pyrolysis varies greatly from 76 to 353 kJ mol^{-1} in the conversion range between 0.05 and 0.95 [35], reflecting the complexity of the kinetic mechanism of DGS pyrolysis.

2.3 Slow, rapid, microwave-assisted, co-pyrolysis of DGS

Slow pyrolysis is a pyrolysis process carried out at a relatively low heating rate (Table 3). It takes a long time and the tar yield is very low, but it can maximize the yield of solid products [36]. The slow pyrolysis of distiller's grains usually uses fixed bed or TG analyzer as the reactor, and the heating rate is less than 50 K min^{-1}. Inert gas (nitrogen or helium) is used as carrier gas to purge the reactor. In the process of DGS slow pyrolysis, the effects of temperature, heating rate and carrier gas on product yield are generally studied.

Rapid pyrolysis has great advantages in maximizing liquid production [45], with a pyrolysis temperature of approximately 500 °C for liquid production. The heating rate can be as high as 600 K min^{-1}, and the reactor is usually a fluidized bed or micro-reactor because they have higher heat and mass transfer rates and can reach high temperatures in a short period of time [46]. In the study of rapid pyrolysis of DGS, it was found that the bio-oil produced by DGS has a very high energy density (> 30 MJ kg^{-1}) higher than that of barley and wheat husks [40]. Wang et al. [18] also studied the influence of CaO catalyst in the rapid pyrolysis of distiller's grains. Adding the catalyst will produce more aliphatic, aromatic, and phenolic compounds, which are ideal substances for fuel production. The increase in their production may be due

Table 3 Studies on slow, rapid, microwave-assisted, co-pyrolysis of DGS

Feedstock	Catalyst	Reactor	Experimental details	Key Results	Ref
Slow pyrolysis					
DGS	None	Fixed bed	Mass: 3 g Reaction temperature and pressure: 400, 500, 600 °C and 100, 500, 1000 kPa Carrier and flow rate: N_2	The main component of bio-oil was fatty acid, and its yield decreased with the increase of pressure. At 500 °C and 100 kPa, the maximum yield was 36.4%	[11]
Rice husk DGS	None	TG analyzer	Mass: 10 ± 0.1 mg Reaction temperature and heating rate: 50–1000 °C and 10 °C min^{-1} Carrier gas: 60 mL-N_2 min^{-1}	The mass loss of RHDG of ~ 44% occurred at 250–400 °C. The volatiles released from pyrolysis had more diesel range organic compounds and H/C, O/C ratios. The activation energy of pyrolysis was ~ 240 kJ mol^{-1}	[23]
DGS	None	TG analyzer	Reaction temperature and heating rate: final temperature of 900 °C and 5, 10, 20, 30, 100 °C min^{-1} Carrier gas: 100 mL-He min^{-1}	The TG curve showed three main peaks at 280, 330 and 402 °C with a total weight loss of around 79%. NH_3 was the main N-compound released at low temperatures with a peak at 319 °C	[29]
DGS	None	TG analyzer	Mass: 5 ± 0.2 mg Reaction temperature and heating rate: 50–900 °C and 10, 20, 30, and 40 °C min^{-1}, the temperature rose from 50–900 °C Carrier gas: 150 mL-N_2 min^{-1}	The total mass loss was about 72%. Lignocellulose components such as protein and amino acid can promote the decomposition of DGS	[30]
Barley DGS	None	TG analyzer	Mass: 4.5 mg Reaction temperature and heating rate: final temperature of 773 and 900 K and 5, 10, 20 K min^{-1} Carrier gas: N_2 and air	DGS pyrolysis in air and nitrogen was similar, but oxidation environment would enhance degradation and reduced E_a. Degradation of multi-components in DGS and the catalysis of alkali compounds also reduced the activation energy	[27]
DGS	None	TG analyzer	Mass: 45% moisture of wet basis Reaction temperature and heating rate: final temperature of 650 °C, 850 °C and 10, 30, 50 °C min^{-1} Carrier gas: N_2 and air	The starting temperatures increased with the increase of heating rate and initial moisture content. The residual weights of DGS after oxidation in air were only 5.49% of the original dry mass	[37]
Moutai DGS	None	TG analyzer	Mass:5 mg Reaction temperature and heating rate: final temperature of 1223 K and 10, 20, 30, 40 K min^{-1} Carrier gas: 20 mL-N_2 min^{-1}	The effective activation energies of DDGs pyrolysis significantly varied with conversion (from 151.2 to 320.5 kJ mol^{-1} with the conversion range of 0.05–0.95)	[5]
Corn DGS	Zeolite	Microscale reactor	Mass: Catalyst mixed with DGS in a ratio of 20:1 with total mass of 5 mg Reaction temperature: 400, 500, 600, and 700 °C Carrier gas: 90 mL-He	Protein and lipid might enhance yield of aromatics and olefins. The highest carbon yields of aromatics and olefins (44.5 and 12.3%, respectively) occurred for a SiO_2/Al_2O_3 ratio of 30 at 600 °C	[38]
DGS	Ni–Al-MCM-41/(Me)-γ-Al_2O_3	Fixed bed	Mass: 5 g mixed with 5 mg catalyst Heating rate: 20 K min^{-1} for 1.5 h Carrier gas: 70 mL-N_2 min^{-1}	The average HHV of the bio-oil was 25,739 kJ/kg, which was about 61% of that of gasoline. Catalyst can promote the production of H_2, specially for Ni–Pd-γ-Al_2O_3, the volume percentage in pyrolysis gas reached to 55.6 vol.%	[39]

Table 3 (continued)

Feedstock	Catalyst	Reactor	Experimental details	Key Results	Ref
Fast pyrolysis					
DGS	None	Heated foil reactor	Mass: 5–7 mg Heating rate: final temperature of 500–1300 °C and 600 °C min^{-1} Carrier gas: He	At 1,300 K, the final mass loss was 92wt%. High heating rate can change the protein decomposition mechanism from deamination to dehydration and promote the tar-N decomposition. CO was dominant at temperatures higher than 1,000 °C with increasing gaseous product	[40]
Barley DGS	None	Fluidized bed	Reaction temperature: ~500 °C	The potential yield of GS organic bio-oil was 48wt%. Bio-oil from DDGS had a very high energy content, ~80% of petroleum (dry basis) and was nearly pH-neutral, but will be more heterogeneous and viscous with time	[41]
DGS	CaO	Fixed bed	Reaction temperature: 490, 530, 570 °C Carrier gas: N_2	The oil composition was simple. When CaO was added to pyrolysis at 570 °C, more aliphatic and aromatic hydrocarbons were generated, and content of phenols was increased, while fatty acids and their esters was reduced	[18]
Microwave-assisted pyrolysis					
DGS	None	Microwave oven	Mass: 100 g Heating rate: 105, 130, 255, 500, and 570 °C min^{-1} at the power inputs of 600, 700, 800, 900, and 1000 W Carrier gas: N_2	The highest heating value of DDGS bio-oil was obtained at the 650 °C and 8 min, which was about 66.7% of the heating value of gasoline	[42]
Co-pyrolysis					
Oil-based drill cuttings + DGS	None	Fixed bed	Mass ratio of DGS: 10:0, 8:2, 7:3, 5:5, 3:7, 2:8, and 0:10 Reaction time: 250–500 °C	OBDC promoted the pyrolysis of DGS. Mass ratio of OBDC: DGS at 7:3, holding temperature at 350 °C, holding time for 60 min and heating rate at 10 °C min^{-1}	[43]
Waste plastic mulching films + DGS	ZSM-5/MCM-41	Microwave reactor	Mass: ~ 10 g Mass ratio of DGS: 0.25, 0.5, 1, 2 Reaction time: ~ 750 °C	Higher W/D ratio can promote bio-oil production and retard coke formation and synergy existed between them. Catalyst increased hydrocarbon yield in bio-oil	[44]

to the improvement of deoxygenation and dehydrogenation reactions on the catalyst.

Microwave-assisted pyrolysis is an inside-out dielectric heating method using electromagnetic wave with wavelength of 1 mm to 1 m, which is superior to traditional pyrolysis in terms of energy utilization, heating rate and selectivity [46]. Pyrolysis by microwave can effectively penetrate the DGS and directly transfer the energy to the inside, increase the rate of pyrolysis reaction, and reduce the pyrolysis temperature and time. Lei et al. [42] have tested the pyrolysis behavior in a batch microwave oven and the yield of bio-oil was 25–50%. Besides, it has found that the miscibility of hydrocarbon oil produced by microwave pyrolysis and gasoline was up to 1:1, and there was no phase separation, which was a good hydrocarbon source to replace gasoline. Zhang et al. [43] also discovered that microwave absorbers altered the composition of hydrocarbons in bio-oil, where the high heating rates provided can promote the formation of alkanes and aromatics. Due to the high moisture content and complex composition of distiller's grains, microwaves also serve as an ideal pretreatment technique. Utilizing microwave-assisted drying, the calorific value of sugarcane bagasse can be increased by 57% [47]. Compared to conventional methods, this approach also enhances the carbon content in the solid fraction while reducing the oxygen content. Li et al. [48] found that microwaves can disrupt the intact surface morphology and damage the molecular structure, thereby improving the efficiency of pyrolysis.

Co-pyrolysis usually involves two or more types of biomasses, which involves complex influencing factors such as the mixing ratio of different components, the type of catalyst, and the thermal effects between them, all of which can affect co-pyrolysis. DGS are usually hydrogen deficient in product composition, thus limiting the generation of hydrocarbons. Therefore, hydrogen rich substances can be considered in the co-pyrolysis process to promote hydrocarbon generation and improve the quality of bio-oil. Zhang et al. [43] conducted co pyrolysis of DGS with waste agricultural film mainly composed of polyethylene and found that the plastic was rich in hydrogen atoms. They found a clear synergistic effect between the two, and a 1:1 mixing ratio was the most favorable for the generation of hydrocarbons in bio-oil. Zhou and Zheng [6] also found a synergistic effect between DGS and oil-based drilling cuttings through co pyrolysis, resulting in a decrease in the production of harmful gases. This means that selecting the appropriate combination of co pyrolysis raw materials can gain advantages in terms of product composition and harmful gases generated. In addition, the type of catalyst also has a significant impact on the co-pyrolysis process. Researchers can regulate the pyrolysis products of biomass by selecting appropriate catalysts, for example, SiC and multi-stage ZSM-5/MCM-41 catalysts, which can significantly reduce the generation of by-products and improve the hydrocarbon yield in bio-oil during the co pyrolysis process of distiller's grains.

3 Pyrolysis mechanism of distiller's grains

3.1 Temperature dependence of Cellulose, Hemicellulose, Lignin, Protein

The pyrolysis of cellulose can be divided into three stages: initial pyrolysis stage (below 300 °C), rapid pyrolysis stage (300–600 °C) and slow pyrolysis stage (above 600 °C). In the initial pyrolysis stage, the main reactions are the cleavage of intermolecular and intramolecular hydrogen bonds and the dehydration reaction of hydroxyl groups. At the same time, the glycosyl molecules of cellulose will also undergo cleavage and rearrangement to produce some compounds containing double bonds and ring structures; In the fast pyrolysis stage, with the increase of temperature, the decomposition rate of cellulose will increase sharply and enter the fast pyrolysis stage. During this period, the breaking rate of cellulose molecular chain reached the peak, producing a large number of volatile gases, such as carbon monoxide, carbon dioxide, methane, and some liquid products, such as acetic acid, acetone, etc. When the temperature continues to rise, the decomposition rate of cellulose will gradually decrease and enter the slow pyrolysis stage. The solid products are mainly carbon and ash, and some liquid products, such as benzene and phenol, will also be produced.

Obtaining hemicellulose from natural biomass is challenging due to its complex structure, unclear definition, and inadequate separation methods [49]. It should be noted that even standard separation techniques can result in significant amounts of mineral residues in the hemicellulose, necessitating further purification. This increases the difficulty and confusion associated with the extraction process. Therefore, as an easily available hemicellulose polysaccharide, xylan is usually used as a representative of cellulose pyrolysis. Peng and Wu [50] divided the thermal decomposition of hemicellulose in the rapid pyrolysis process into four stages: water loss, the early pyrolysis stage of hemicellulose side chain dehydration and pyrolysis, the main pyrolysis stage, and the carbonization stage. Compared to the pyrolysis process of cellulose, hemicellulose begins to decompose more readily, mainly due to its random, amorphous structure that is rich in branches, making it easy to remove and degrade into volatiles from the main stem. Generally, hemicellulose pyrolysis produces a total product composition of 20–30% coke, 10–20% non-condensable gas and 40–60% bio-oil [51]. The initial dehydration stage predominantly involves the removal of water from the hemicellulose structure, followed by the dehydration and decomposition of side chains during the early pyrolysis stage. The main pyrolysis stage, which is the primary weight-loss thermal stage among the four stages, occurs at 220–315 °C. This stage is characterized by a significant increase in the rate of hemicellulose molecular chain breakage, leading to the release of a large volume of volatile gases (such as carbon monoxide, carbon dioxide, and methane) and liquid products like acetic acid and acetone. Finally, the carbonization stage primarily results in the formation of char.

Lignin is considered the most difficult part of biomass components to decompose because it has many ether bonds, hydroxyl groups, and methoxy groups [52]. In the study of the entire pyrolysis process of lignin, it was found that its pyrolysis occurs slowly, and the mass loss rate is very low [53, 54]. The pyrolysis process of lignin can be divided into three stages: initial weight loss stage, rapid pyrolysis stage, and carbonization stage, similar to the processes for cellulose and hemicellulose. The initial weight loss stage begins with the removal of external and internal moisture, leading to a slight decrease in mass. In the studies by Li et al. [55], it was found that lignin also undergoes complex initial reactions during this stage, where lignin bonds break, producing light gas molecules, and polymerization reactions occur, forming high molecular weight lignin fragments. Rapid pyrolysis occurs at higher temperatures (above 400 °C), mainly involving depolymerization, fragmentation, secondary reactions, and carbonization. Chen et al. [56] found that the rapid pyrolysis stage of lignin has a wide temperature range, low weight loss rate, and the highest residual mass, which may be due to the relatively stable chemical structure of lignin. When the temperature exceeds 600 °C, the carbonization stage begins, where the remaining lignin structure further decomposes to form more solid residues, namely char. The reaction rate at this stage is relatively slower, with less mass loss, primarily involving the transformation of the lignin structure into a more stable carbon structure.

Protein, composed of various amino acids linked by peptide bonds, undergoes a series of complex reactions during pyrolysis, breaking down into smaller molecules. The pyrolysis of protein is primarily divided into three stages [33]. The first stage, occurring between 50–200 °C, involves a slight weight loss mainly due to the cleavage of some side chains and the release of gaseous products like CO_2 and H_2O. The second stage, between 200–550 °C, is characterized by significant weight loss as protein decompose extensively, releasing volatiles. The main reactions during this stage include deoxygenation, dehydrogenation, and denitrification, producing small molecular gases such as NH_3 and HCN, along with nitrogenous liquid organic compounds. The third stage, after 550 °C, involves the further slow decomposition of residues, also leading to slight weight loss and the formation of more complex nitrogen-containing solid residues. Compared to other biomass components like cellulose, hemicellulose, and lignin, the nitrogenous nature of proteins makes their pyrolysis product composition unique. The formation of NH_3 primarily occurs during the decomposition of amino acid side chains in the first stage and the deamination of amine compounds formed in the second stage [57]. Bianchini et al. [58] has found that the catalytic pyrolysis of protein-rich Spirulina produces bio-oil with nitrogen content up to 16%, potentially leading to harmful NOx emissions during combustion. It is essential to focus on the nitrogen reaction pathways during pyrolysis to reduce nitrogen levels in bio-oil. This represents a significant challenge in industrializing bio-oil fuel production from nitrogen-rich biomass.

3.2 Detailed formation pathway of bio-based products

Pyrolysis oil is a liquid product rich in energy and easy to transport, generated during the pyrolysis process of biomass. It mainly consists of water and various organic components, including organic acids such as acetic acid, formic acid, and propionic acid; carbonyl and hydroxycarbonyl compounds such as aldehydes and ketones; sugars and anhydrosugars such as levoglucosan (LG), as well as some phenolic compounds [59]. Cellulose is the main source of carbohydrates, and wood xylan bio-oil is mainly composed of acids, ketones, aldehydes, and phenols, with phenols being the basis of lignin bio-oil [60]. LG, as a key primary product formed during the pyrolysis of cellulose, can be used as an intermediate or end product of the reaction. It can be directly converted into ethanol and butanol for biofuel production. In addition, due to its multifunctional hydroxyl and polysaccharide skeleton structure, it can be used for the production of nanomaterials, bioadsorbents, food additives, and the preparation of new materials [51, 52]. Among the furan products and derivatives generated during the pyrolysis of cellulose and hemicellulose, furfural and 5-hydroxymethylfurfural (5-HMF) are usually the two most abundant products, which are very valuable in energy and chemical products [61]. Furfural is a highly valuable chemical, considered one of the most promising bio-based products for sustainable production of fuels and chemicals in the twenty-first century [62]. Due to the presence of multiple oxygen atoms in the molecular structure of furfural, it can be converted to biodiesel by hydrogenation reaction and can also be used for the production of bio-based chemicals and bioplastics. Hydroxy acetaldehyde (HAA) is the most abundant linear carbonyl product in biomass pyrolysis. Phenolics are produced by the cleavage of C–C bonds in lignin, and are the only renewable source of lignin aromatics [63]. Its chemical structure and abundance suggest enormous potential as value-added chemical raw materials such as phenol, benzene, toluene, and xylene [64]. Therefore, understanding the formation mechanisms and pathways of these main products in depth is of great help for selective production, maximum industrialization, and energy utilization.

LG serves as a critical intermediate in the pyrolysis of cellulose, playing a pivotal role in the breakdown and transformation processes. The yield of LG varies between 5 and 80%, depending on the pyrolysis of different cellulose under different reactor formulations and test conditions [65]. Efforts have been made to understand the basic mechanism of LG formation and optimize the synthesis of LG to enhance the activity of its derivative products. However, the pyrolysis of cellulose involves a multifaceted network of chemical reactions, potentially encompassing hundreds of parallel or sequential reaction pathways, and the formation pathway of LG is not unique Previous research has extensively explored the reaction pathways for LG formation from cellulose through experimental methods. There are two main pathways for LG formation: one involves the initial partial depolymerization of cellulose, leading to shortened carbohydrate chains; the other involves the pyrolysis of any glucose-containing compound to form LG [59]. While these two pathways provide a fundamental framework for understanding how LG is formed from cellulose, in reality, the process may involve additional intermediate steps and molecular mechanisms. Yang et al. [66] using isotopic labeling experiments in simulated disaccharide model compounds, found that β-1–4 glycosidic bond can be homolytic at C1-O and C4-O positions, or heterolytic at the same position as homolytic cleavage to form two ions (Fig. 2). Density functional theory (DFT) was used to study the reaction mechanism of cellulose pyrolysis to form LG, including free radical mechanism, glucose intermediate mechanism, and the end of L-glucose chain mechanism [67]. The comparison of the three mechanisms indicates that the synergistic mechanism provides a lower energy path than the same or different splitting, with an energy barrier of only 223.7 kJ mol^{-1}. Wang et al. [68] compared the traditional synergistic reaction of disaccharides to form LG with other three new pathways involving H transfer to different hydroxyglycosidic bonds, which involved the transfer of H to glycosidic bond of different hydroxyl groups. It was found that H transfer to the nearest glycosidic bond was an effective competitive pathway for the synergistic reaction mechanism. Therefore, the mechanism of two transglycosylation steps occurring at the end of the LG chain was also the most reasonable pathway.

Furfural can be produced during the rapid pyrolysis process of biomass, and appropriate catalysts can promote its selective production. Metal chlorides and inorganic acids are commonly used as catalysts for the production of furfural during pyrolysis. Previous studies have investigated the pathways for the formation of furfural using different cellulose units [69]. Using isotope labeling experiments with D-glucose, it was found that 5-HMF and furfuryl alcohol share the same precursor, and about three-quarters of furfural is produced by aldehyde C-1 of D-glucose. Wang et al. [70] used DFT calculations to study the carbon orientation of furfural in D-glucose and obtained consistent results, indicating that furfural mainly originates from C1 to C5 of D-glucose, where C1 is located on the aldehyde group. Through DFT calculations and rapid pyrolysis experiments, the formation pathways of furfural in glucose and mannose units were summarized, including two direct pathways and two pathways through 5-HMF (Fig. 2b). The results showed that the favorable pathway for furfural was through the intermediate of dihydroxyacetone and 3-deoxyglucosinone, while 5-HMF was almost not formed through secondary decomposition [71] (Fig. 2c). Taking xylose units as an example, it was found that the formation of furfural involves a series of reactions, including ring opening, dehydration, enol ketone tautomerism, cyclization, and dehydration. The rate determining step is the 4,5-dehydration reaction, with an energy barrier of approximately 300 kJ mol^{-1}.

As an important product of cellulose and hemicellulose pyrolysis, HAA yield can be as high as 12% [72]. In order to clarify the production mechanism and reaction pathway of HAA more clearly, extensive research has been conducted both from isotope labeling experiments and DFT theoretical calculations. Many researchers believe that HAA may originate from the decomposition of C1-C2 and C5-C6 fragments during the direct pyrolysis process of cellulose [73, 74], as well as from the secondary decomposition of LG [75]. But the two pathways compete in parallel, and LG decomposition only forms a very small amount of HAA [76]. In the study of different mechanisms for the pyrolysis of monosaccharides to generate HAA, three types of mechanisms were proposed [77], namely the C-O bond breaking mechanism, the C–C bond breaking priority mechanism, and the dehydration priority mechanism (Fig. 2d). As can be seen, β-D-glucose is mainly formed through ring opening and bridging dehydration to form LG and D-glucose, while HAA is mainly produced through the decomposition of D-glucose, while LG is unlikely to produce HAA through secondary decomposition under non catalytic action due to its high energy barrier (303 kJ mol^{-1}).

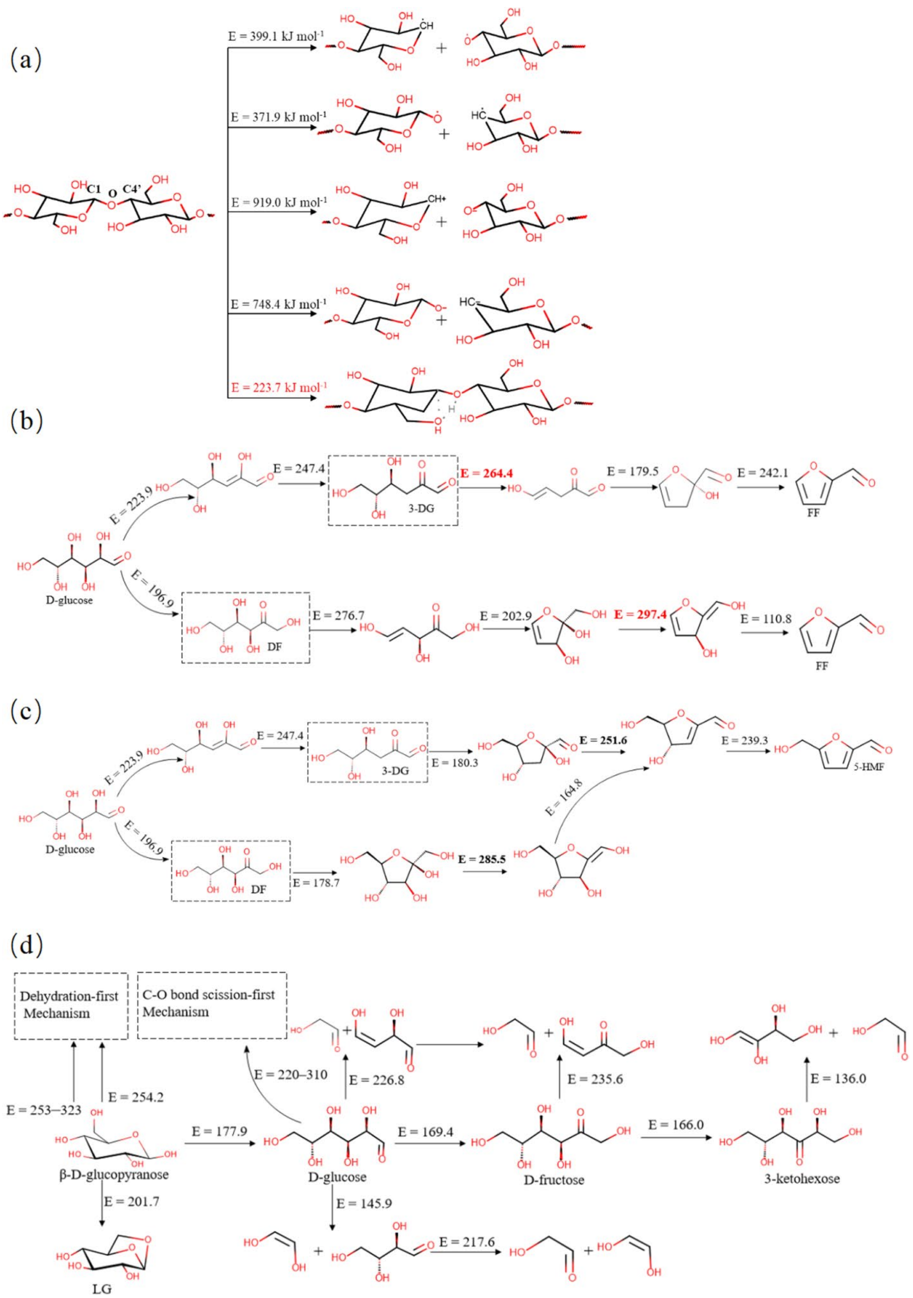

Fig. 2 Generation pathways and reaction energy barriers of main pyrolysis products: (**a**) LG, **b** FF, **c** 5-HMF, and **d** Phenols

Phenols are the main components in lignin pyrolysis bio oil, and their relative content can reach a maximum of over 70% at 600 °C [56]. Lignin pyrolysis produces phenolic compounds through the cleavage of ether and C–C bonds [78]. In Py-GC/MS experiments and DFT theoretical studies on the pyrolysis of β-O-4 type lignin [79], it was found that both homogeneous decomposition at low temperature and homogeneous decomposition and synergistic decomposition at medium temperature are the main reactions for the formation of phenolic substances.

3.3 Interactions of main components during pyrolysis

The interaction between the basic components of biomass (Fig. 3) can be divided into three groups: cellulose lignin, cellulose hemicellulose, and lignin hemicellulose. Pay attention to the generation of volatile substances (CO_2, CO, etc.), tar, and coke. In the interaction between

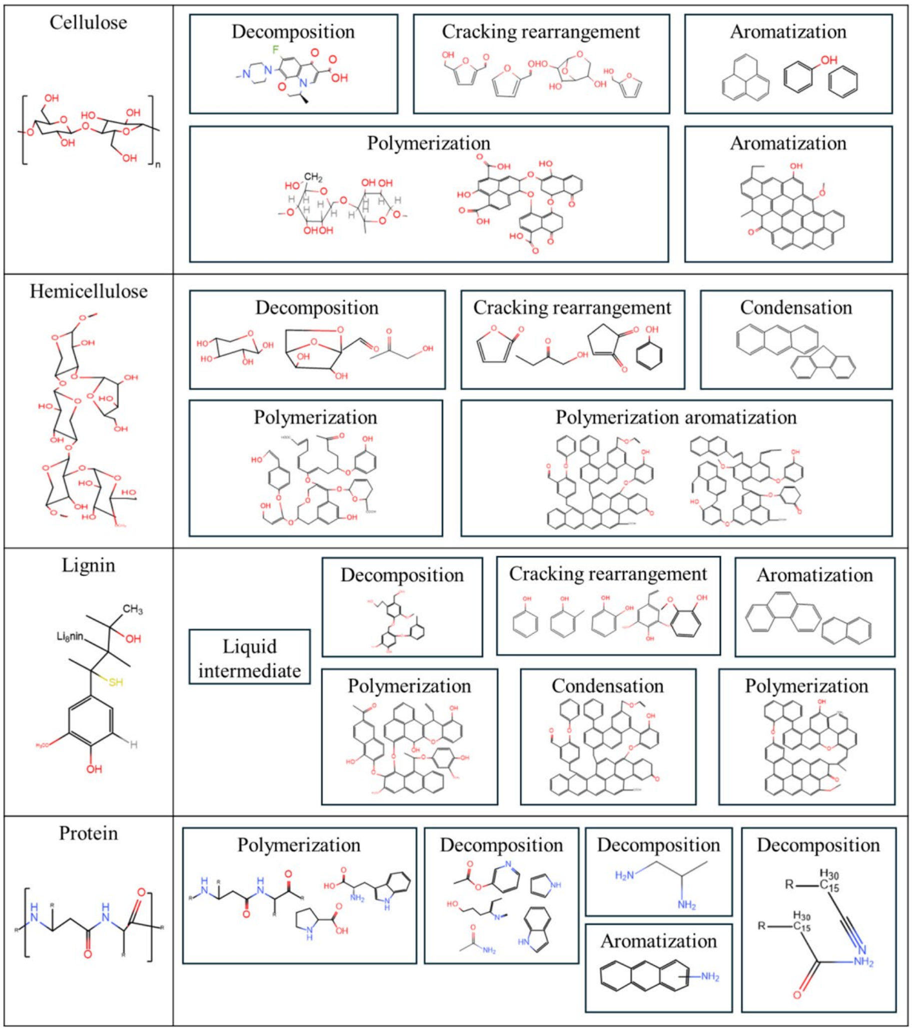

Fig. 3 Pyrolysis mechanism of single component

cellulose and lignin, Giudicianni et al. [80] and others believe that lignin can promote the cracking of primary volatiles of cellulose and promote the formation of coke. Others [81, 82] also found the same conclusion that the interaction between cellulose and lignin leads to an increase in coke production and a decrease in tar production. In the study [83], it was shown that in addition to the inhibition of tar formation, the generation of volatile substances is also inhibited. However, there are different conclusions in the study of Zhang et al. [82], they found the interaction between the two could promote the generation of volatile substances. Hilbers et al. [84] has found that the interaction between cellulose and lignin had no effect on the yield of coke. These conflicting results underscore the complexity of cellulose-lignin interactions during pyrolysis, which could be attributed to various primary processes. The influence of these interactions on the formation of liquid and gaseous products warrants further investigation to uncover more comprehensive mechanisms. In the pyrolysis products of natural corn straw cellulose and lignin, it was found that the interaction between the two would inhibit the formation of LG but enhance the formation of low molecular weight compounds and furan, while the generation of lignin derived phenols would slightly increase [85]. From a chemical perspective, not only are there hydrogen bonds between cellulose and lignin, but there are also more stable covalent bonds, particularly ether bonds [86]. This close structural connection may influence the distribution of pyrolysis products during the mixed pyrolysis of cellulose and lignin. In previous discussions, we mentioned that the pyrolysis of cellulose involves the breaking of glycosidic bonds, a process that produces a molecule of LG and a LG end-group [87]. The second set of reactions can produce low-molecular-weight substances. It is evident that the interaction between cellulose and lignin tends to enhance this second set of reactions, leading to an increased yield of compounds such as furans.

In the lignin–hemicellulose interaction, the active free radical fragments produced by hemicellulose pyrolysis may promote the ring opening reaction of phenolic components generated by lignin pyrolysis through gas phase interaction [88]. In the study of Wang et al. [89], it was found that lignin can inhibit the formation of acetic acid and 2-furfural derived from hemicellulose, but hemicellulose can promote the formation of lignin derived phenol. This may be because the compounds in lignin interact with the intermediate products produced by hemicellulose pyrolysis, changing the reaction rate. The secondary reactions occurring during pyrolysis, including those induced by interactions between the vapor–solid phases, might explain the interactions between components [90]. In another study, the steam generated from hemicellulose acted as a catalyst, facilitating the conversion of lignin's guaiacol and O-containing groups, thereby reducing the oxygen content in lignin. Similarly, the interaction between hemicellulose and lignin charcoal also catalyzes the decomposition of hemicellulose to produce more small molecule substances [91].

In the cellulose hemicellulose interaction, Zhang et al. [85] found that there was almost no interaction between physical mixture and natural mixture. In other studies, weak interactions were observed between the two, but the generation of volatile substances during cellulose pyrolysis was inhibited [89, 92]. Cellulose hemicellulose interaction can significantly promote the formation of hemicellulose derivatives, furans and CO_2, while inhibiting the formation of some cellulose derivatives, especially L-glucose. In the study conducted by Ding et al. [93], it was found that the co-pyrolysis of the two did not generate new pyrolysis products, indicating that no new reaction pathways were formed, but rather the product distribution was affected. The glycosidic bond formation process during cellulose pyrolysis can provide hemicellulose with hydrogen donors (-H) and hydroxyl donors (-OH), promoting the ring-opening of C5 in hemicellulose and subsequently facilitating the formation of typical hemicellulose intermediates such as ethyl-1-propenyl ether and furfural [94]. Meanwhile, the filled hemicellulose may melt and wrap around the cellulose skeleton at low temperatures, increasing the reaction energy barrier of glucose molecules [92], which could explain the suppression of L-glucose formation.

In order to study the nitrogen conversion in biomass, the interactions between protein and cellulose, hemicellulose and lignin have also been studied in the past. There are very complex types of amino acids in proteins, and Ren et al. [95] found that the strength of interaction between amino acids and cellulose, hemicellulose and lignin depends on the type and structure of amino acids. It is worth noting that Qi et al. [30] studied the interaction between non lignocellulose components (mainly protein and amino acid) and cellulose, hemicellulose and lignin in distillers' grains, and found that the interaction of amino acid will increase the reaction rate and activity in the pyrolysis process, thus improving the decomposition process. Wei et al. [33] discovered that the Maillard reaction creates a reductive environment that facilitates the combination of nitrogen-containing products with carbonyl groups, leading to the formation of cyclic ketones, including five- and six-membered O-heterocyclic compounds. Given the nitrogenous nature of proteins, it is crucial to pay special attention to the reaction pathways of N-substances when examining the interactions between components, with the aim of minimizing their environmental impact. However, research into the specific promotive or antagonistic effects of proteins in co-pyrolysis on particular products remains insufficiently explored. This necessitates a more in-depth investigation to clarify the role of proteins in influencing the product distribution and to devise strategies that mitigate any adverse environmental effects.

In the pyrolysis process, interactions among intermediate products also play a significant role. Lu et al. [96] studied the interaction reaction mechanism between pyrolysis product carboxylic acid and LG at the micro level, and compared the energy barriers of esterification reaction, organic redox reaction, and catalytic interaction between the two. They found that acetic acid tends to form a catalyst during the secondary decomposition process, and LG can also serve as a catalyst. Therefore, LG is a common intermediate for studying the interactions between pyrolysis materials. It can not only decompose into various small molecules during fiber pyrolysis, but also participate in other reactions as a reaction intermediate to generate different products.

3.4 Potential emissions of DGS pyrolysis products.

When DGS undergo pyrolysis treatment, it involves complex chemical reaction processes that occur under anaerobic or almost anaerobic conditions, causing the organic matter in the distiller's grains to decompose into smaller molecules. Pyrolysis not only effectively converts biomass waste such as distiller's grains, but also recovers energy. However, it also generates various gaseous emissions and by-products, which may have an impact on the environment and human health.

During the pyrolysis process, the large organic molecules in the distiller's grains are first decomposed into smaller organic molecules. The main gaseous substances produced in this process include small molecule gases such as H_2, CO, CO_2, and CH_4. These small molecule gases are the basic products of the pyrolysis process of organic matter, among which H_2 and CH_4 are valuable energy gases. However, the emissions of CO and CO_2 need to be strictly controlled because they have adverse effects on the environment, especially CO_2, which is one of the main greenhouse gases causing global warming. For some unconventional emissions, Madsenet al. [14] detected sulfur compounds including methanethiol, dimethyl sulfide, and propanethiol, among other sulfur-containing compounds in GC/MS analysis of DGS. Moreover, the concentration of methanethiol was already above its odor threshold of 0.9–8.5 ppbv. Besides, cellulose biomass, characterized by its porous and microstructured composition, undergoes a transient liquid-phase intermediate formation under pyrolysis conditions, further decomposing into volatiles and permanent gases while releasing aerosols. Thus, aerosol emissions during the pyrolysis process are inevitable [97].

From the perspective of composition, DGS, as a nitrogen-containing substance, can yield a certain amount of gaseous N-pollutants when processed through pyrolysis technology. On the other hand, the pyrolysis oil retains and transforms part of the nitrogen content from the raw material. Research indicates that the main gaseous nitrogen pollutants during the biomass pyrolysis process are $NH_{3,}$ HCN, and HNCO [98]. HNCO easily decomposes into HCN at high temperatures. Nitrogenous substances in pyrolysis oil, when combusted, are also released in the form of NOx (nitrogen oxides), which can have detrimental effects on the environment. Therefore, although pyrolysis technology can effectively convert DGS and dry particles and recover energy, its accompanying various gas emissions and by-products also need to be carefully managed to reduce potential impacts on the environment and human health.

4 Conclusions

This work reviews the research on biomass pyrolysis guided by distiller's grains. The reasons why distiller's grains are worth paying attention to, the differences in chemical composition compared to other biomass, and the thermochemical behavior and pyrolysis characteristics exhibited during the pyrolysis process were discussed. The pyrolysis mechanism of distiller's grains components, the generation mechanism of some biobased products, and the reaction mechanism of interaction between components were mainly discussed. Some main research viewpoints are summarized as follows.

(1) The main components of distiller's grains also include protein components that cannot be ignored, in addition to cellulose, hemicellulose and lignin similar to general agricultural wastes, which may have a great impact on the pyrolysis behavior of distiller's grains.
(2) Interactions exist not only among the fundamental components but also between the gas phase and gas–solid phase. However, these interactions do not generate new substances; instead, they primarily affect the distribution of the products, indicating that the reaction pathways have not been altered or that no new pathways have been created.
(3) The formation pathways of pyrolysis products like LG, furfural, and HAA may be parallel or competitive. Understanding the pathways and mechanisms of biobased product formation can guide the conversion of specific fuel products to higher yields and better select biomass and necessary conditions.

Currently, the research on explaining and verifying the interactions among the compositions of biomass during pyrolysis needs to be strengthened, which may have important value for the resource utilization of biomass, and this is the decisive choice to make the thermochemical process more competitive.

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Authors' contributions
Sheng-Lun Lin: Conceptualization, Formal analysis, Data collection, Methodology, Validation, Visualization, Investigation, Funding acquisition, Project administration, Resources, Writing—original draft, review, and editing. Hongjie Zhang: Formal analysis, Data collection, Investigation, Validation, Writing—original draft. Wei-Hsin Chen: Data collection, Data analysis, Investigation, Validation. Che-Wei Wu: Data collection, Data analysis, Investigation, Validation. Yee-Lin Wu: Funding acquisition, Data analysis, Validation. Shih-Wei Huang: Conceptualization, Funding acquisition, Investigation, Project administration, Resources, Supervision, Writing—review & editing. All authors read and approved the final manuscript.

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Availability of data and materials
The authors declare that the data supporting the findings of this study are available within the paper and its Supplementary Information files. Should any raw data files be needed in another format they are available from the corresponding author upon reasonable request.

Declarations

Competing interests
The authors declare they have no competing interests.

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