

EFFECTS OF PYROLYSIS PROCESS ON PRODUCTS YIELD OF PLYWOOD FROM ABANDONED FURNITURE

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ABSTRACT

In this paper, the plywood obtained from dismantling discarded furniture was selected as pyrolysis experimental materials. Pyrolysis was performed at a heating rate of 100°C/h, 150°C/h and 200°C/h and pyrolysis temperatures of 400°C, 500°C, and 600°C to evaluate the effects of pyrolysis process on products yield and the products features. The results show that the yield of solid products gradually decreases with the increase of pyrolysis temperature and heating rate while liquid products and non-condensing gases' yield gradually increases. The carbon content in solid products reached 80.76 - 94.35%. Carbon content gradually decreases with pyrolysis temperature, but the proportion of C/H and C/N gradually increases. The pyrolysis solution is weakly acidic due to the adhesives in pyrolysis material.

KEYWORDS: Abandoned furniture, wood-based panel, pyrolysis process, pyrolysis products, elemental analysis.

INTRODUCTION

In recent decades, the rapid development of China's social economy has led to changes in people's lifestyle and consumption habits. The service life of furniture products is gradually shortened, and the number of discarded furniture is gradually increasing, among which wood-based panel furniture is the majority (Wang et al 2021, 2020). According to relevant reports, the annual waste of various wood products, mainly discarded furniture, is about 85 million m³ in China, which is an important part of urban waste (Xiong et al. 2020, Yang and Zhu 2021). The main treatment methods of these wastes are burial or combustion, which cause environmental pollution. Due to the adhesive and surface decoration layer in wood-based panels, harmful gases containing nitrogen such as NO, NO₂, HNCO and HCN will be generated during combustion, which will seriously affect the air quality (Feng et al. 2012, Chen et al.

2015, Hu and Wan 2022, Sun et al. 2019). As fossil fuel reserves are depleted, there is increasing interest in reducing waste and producing bioenergy through thermochemical techniques such as pyrolysis. Pyrolysis is an efficient biomass conversion technology developed in recent decades, which has a broad application prospect in the treatment of agricultural and forestry wastes (Lai et al. 2018, Liu et al. 2021).

Pyrolysis is an operative and auspicious technique for biomass decomposition, particularly for lignocellulose materials. Pyrolysis is a thermochemical process that breaks down biomass/waste into pyrolysis products (such as biochar, bio-oil, and biogas) in an inert or anoxic environment (Foong et al. 2021, Ge et al 2021). Pyrolysis can convert agricultural and forestry biomass with low energy density into gas, liquid and solid products with high energy density, and reduce the storage and transportation costs of energy materials (Nam et al. 2018). Pyrolytic fluid can be used as fuel to replace traditional energy and extract high value-added chemical products (Lam et al. 2018). Pyrolyzed biochar can be used as fuel, activated carbon making or soil amendment (Liew et al. 2018). Pyrolysis non-condensable gas can be used as combustible gas (Girods et al. 2008a).

Wood-based panels obtained from discarded furniture behave differently from wood during pyrolysis, due to the presence of adhesives, more nitrogenous products may be produced (Girods et al. 2008b). The pyrolysis behavior of urea-formaldehyde resin residue showed that the pyrolysis process could be divided into three stages: drying the sample, fast thermal decomposition and further cracking process (Chen et al. 2015). Isocyanic acid, which is the most essential nitrogen-containing product is caused at low temperature, while hydrocyanic acid is more produced at high temperature (Yek et al. 2019, Jiang et al. 2010, Girods et al. 2008c, 2009a,b). Therefore, a reasonable design of the pyrolysis process should control the proportion and composition of solid, liquid, and product. In this paper, the pyrolysis experiment was performed by segmental heating, and the yield of products and the properties of solid and liquid products were analyzed to provide technical support for rational and efficient utilization of discarded furniture (Xiong et al. 2017).

MATERIAL AND METHODS

Materials and equipment

The materials selected for this work are natural aged plywood dismantled from some pieces of abandoned furniture, which were severely damaged, were obtained from the garbage recycling station of a residential area in Nanjing. These plywood materials contained 11 layers of veneer and coated with decorative layer, glued by urea-formaldehyde resin adhesive. The initial moisture content of these material was 15.3 - 20.6% (measured in line with GB/T 1931 (2009) standard), and then dried at 103°C for 24 h. The industrial and elemental results of these materials are shown in Tab. 1. Due to the presence of urea-formaldehyde resin adhesive and decorative layer, the content of N element in the material is as high as 4.5%, much higher than the content of nitrogen in the wood (Liu et al 2022, Zhan et al 2019). In addition, the content of volatile matter is as high as 83.24%, which is also slightly higher than that in the wood. Finally, the size of these materials is 30 x 50 x (18-21) mm decomposed for further pyrolysis experiments.

Tab. 1: Industrial analysis and elemental analysis of experimental material.

Industrial analysis (%)			Elemental analysis (%)				
Volatile matter	Fixed carbon	Ash	C	H	O	N	S
83.24	15.82	0.94	44.94	6.86	43.65	4.54	0.01

The fast pyrolysis was conducted in May 2018 in a laboratory-scale reactor (Fig. 1) at Nanjing Forestry University (NFU), Jiangsu, China (32.08 °N, 118.81 °E). The device used for pyrolysis was a piece of fixed bed equipment for batch feeding. The reactor was 660 mm in diameter and 800 mm deep, and the power of the electric heater was 7.5 kW.

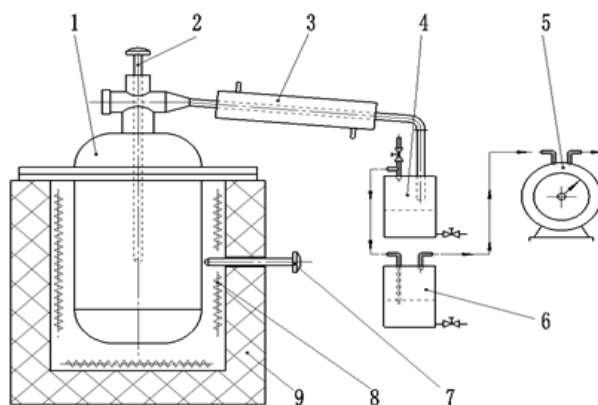


Fig. 1: Schematic diagram of pyrolysis apparatus. (1) furnace, (2) temperature transducer (within the furnace), (3) glass condenser, (4) gas and liquid separator, (5) flow meter, (6) tank, (7) temperature transducer (furnace exterior), (8) heaters, (9) furnace stack.

Methods

Pyrolysis method

In the pyrolysis test, the above experimental materials were pyrolyzed by piecewise heating under the condition of anoxia. 1000 g of the experimental material was raised from room temperature to 260°C at the rate of 100°C/h, 150°C/h and 200°C/h, then held for 1 h, finally, raised to the final pyrolysis temperature (400, 500, 600°C) at the rate of 150°C/h and held for 2 h. The non-condensing gas volume was detected during the experiment. After cooling for 24 h, liquid and solid products were collected for future analysis.

Solid products analysis

Elementar Vario EL type III elemental analysis system (Elementar Analysensysteme GmbH, Langensfeld, Germany) was used to analyze the pyrolysis solid products. The test conditions were as follows: oxygen was the combustion gas, the decomposition temperature was 1150°C, the separation device was an adsorption/desorption column, the detection device was a thermal conductivity detector (TCD), helium (He) was the carrier gas, and the sample weighed 2 to 4 mg.

The pH value of solid products was determined with an MP551 pH meter produced by Shanghai Sanxin Instrument Factory (Shanghai, China), following the national standard GB/T 12496.7 (1999).

To investigate physical structures of solid products, this work employed the environmental SEM (Quanta 200, FEI Company, Eindhoven, Netherlands) to observe the surface shapes of

biochar by measuring electrical conductivity. Samples were prepared by applying a sputter gold coating (2 nm) using Gold Palladium SEM Annular Sputtering by adopting the target 2" ID × 3" OD × 0.1 mm Anatech (SC502-314; Quorum Technologies, Ltd., Watford, UK). The bombarding volt-age used for SEM was 20.0 kV.

Liquid products analysis

The liquid products of the pyrolyzed materials were analyzed by gas chromatography. The gas chromatography-mass spectrometry instrument model was TueboMatrix 650TD-CLARUS600 GC-MS (PE-PerkinElmer, USA). The chromatography column was DB-5ms (30 m × 0.250 mm, 0.250 μm). The temperature was set as follows: the initial column temperature was 60°C for 2 min, then raised to 180°C at 5°C·min⁻¹, then raised to 280°C at 20°C·min⁻¹, and held for 5 min. The injection volume was 0.8 μl, He was the carrier gas, and the working temperature of the gasifier was 280°C. The ionization mode was electrospray ionization (EI), the source temperature was 220°C, the electron bombardment energy was 70eV, the interface temperature 250°C, the MS scanning range was 29 ~ 600U, and the scanning time was 0.2 s. The pyrolysis liquid products were measured with an MP551 pH meter (Shanghai Sanxin Instrument Factory, Shanghai, China).

Data statistical analysis

SPSS (IBM SPSS Statistics 25) was used for the analysis of variance at the 0.05 probability level. Homogeneity and normality of variance were tested by the Levene and Shapiro-Wilk tests, respectively. At the same time, "super-heating rate" and "pyrolysis temperature" were used as fixed factors to analyze the main effects and interactions.

RESULTS AND DISCUSSION

Analysis of yield of pyrolytic products of waste furniture materials

In the pyrolysis process, the experimental materials are decomposed into solid and flue gas, and the flue gas is condensed into liquid and non-condensable gas. The final product can be divided into solid product, liquid product and non-condensable gas. The product yields of the pyrolytic material under different pyrolysis process are shown in Tab. 2 and Tab. 3. The proportion of solid products from plywood through pyrolysis was 27.17 - 35.67%, that of liquid products and non-condensable gas were 39.64 - 51.32% and 86.44 - 147.69 L·kg⁻¹. The solid products yield decreased with the increase in pyrolysis temperature, while the yield of liquid products and non-condensing gas increased. Similarly, with increase of heating rate, the solid products content decreased, while the yield of liquid products and non-condensing gas increased. Comparing with the results of other authors (Aguirre et al. 2020), the proportions of solid, liquid and non-condensable are similar, which indicates that the adhesive and decorative layer have no obvious effect on the proportion of products in the three states.

Tab. 2: Yield of pyrolytic products of plywood from abandoned furniture under different process.

Pyrolysis temperature (°C)	Heating rate (°C/h)	Solid products (%)	Liquid products (%)	Non-condensable gas (L/Kg)
400	100	33.85 (2.72)	40.13 (1.41)	98.72 (2.73)
	150	31.82 (0.69)	41.02 (1.57)	102.76 (2.33)
	200	31.11 (0.59)	43.02 (1.86)	113.52 (6.76)
500	100	30.88 (3.04)	45.59 (7.53)	115.46 (7.73)
	150	30.04 (3.01)	46.51 (1.03)	124.83 (12.55)
	200	29.05 (1.59)	48.61 (3.12)	130.87 (11.69)
600	100	28.33 (2.11)	47.13 (5.04)	123.47 (6.53)
	150	27.99 (0.75)	47.93 (0.60)	131.74 (2.77)
	200	27.73 (0.38)	50.42 (1.07)	142.42 (4.31)

Note: Yields of pyrolytic products are presented by average values and (standard deviations).

When "heating rate" was taken as the influencing factor, the P values of the solid product, liquid product, and non-condensing gas were all less than < 0.0001 , indicating that material type significantly impacts product yield. Taking "pyrolysis temperature" as the influencing factor, the P values of the three products are also less than 0.0001 , indicating that pyrolysis temperature significantly affects all the products' yields. The P values of "Heating rate \times pyrolysis temperature" were 0.014, 0.852 and 0.647, indicating no significant interaction between heating rate and pyrolysis temperature on all three kinds of products.

Tab. 3: Effects of material type and pyrolysis temperature on the yield of pyrolysis products.

Yield of pyrolytic products	Solid products (%)	Liquid products (%)	Non-condensable gas (L kg ⁻¹)
Heating rate			
100°C	31.02 ^a	44.28 ^c	112.55 ^c
150°C	29.95 ^b	45.15 ^b	119.78 ^b
200°C	29.29 ^c	47.35 ^a	128.94 ^a
Pyrolysis temperature			
400 °C	32.26 ^a	41.39 ^c	105.00 ^c
500 °C	29.99 ^b	46.90 ^b	123.72 ^b
600 °C	28.02 ^c	48.49 ^a	132.54 ^a
P values			
Heating rate	< 0.0001	< 0.0001	< 0.0001
Pyrolysis temperature	< 0.0001	< 0.0001	< 0.0001
Heating rate \times Pyrolysis temperature	0.014	0.852	0.647

Note: Mean values of pyrolysis products followed by the same small superscript letters (a–c) within a group are not significantly different based on Fisher's Protected LSD test at the 0.05 significance level.

Analysis of pyrolytic solid products

The main element of solid products obtained from pyrolysis of lignocellulose materials is carbon, also known as "biomass carbon", which can be used as fuel. It is often used as a soil amendment in agriculture because of its many internal voids and good adsorption capacity (Sohi et al. 2010). The elemental analysis and pH value of solid pyrolysis products are shown in Tab. 4. The main composition of solid pyrolysis products is carbon (80.76 - 88.89%). Comparing with solid products under different pyrolysis process, with increase of heating rate

and pyrolysis temperature, the carbon content increased, but nitrogen and hydrogen content decreased.

The pH value of solid products produced at different pyrolysis process ranges from 6.32 to 7.24, showing weak acidity to weak alkalinity. The pyrolysis temperature has little influence on the pH value, and the pH gradually decreases with the pyrolysis temperature, but the decrease is not significant.

Tab. 4: Element analysis and pH values of solid products.

Pyrolysis temperature (°C)	Heating rate (°C/h)	Element analysis						pH
		C	N	H	S	C/H	C/N	
400	100	80.76	5.44	3.68	0.19	21.95	14.85	7.24
	150	82.67	4.86	3.57	0.18	23.16	17.01	7.16
	200	82.19	3.77	3.26	0.21	25.21	21.80	7.01
500	100	83.26	3.98	3.19	0.17	26.10	20.92	6.43
	150	83.45	3.64	2.79	0.19	29.91	22.93	6.54
	200	84.87	3.17	2.68	0.18	31.67	26.77	6.77
600	100	87.26	3.25	2.81	0.22	31.05	26.85	6.41
	150	88.34	2.98	2.18	0.17	40.52	29.64	6.45
	200	88.89	2.37	2.06	0.19	43.15	37.51	6.32

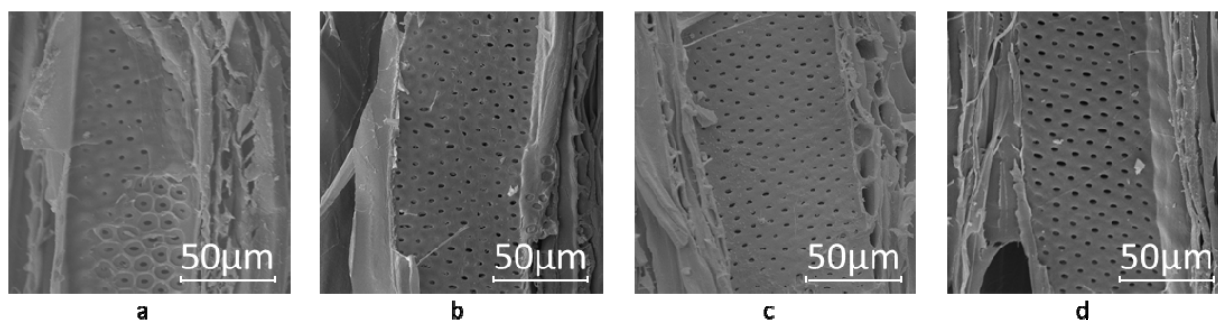


Fig. 2: SEM micrographs of plywood and solid product pyrolysis under different temperature: a) before pyrolysis; b) 400°C; c) 500°C; d) 600°C.

In order to assess the potential changes in the physical structure of solid pyrolytic product under 400°C, 500°C and 600°C. SEM microscopic pictures are present in Fig. 3. Under the condition of high temperature, the main components in the plywood decompose and the microstructure becomes more flat, but the basic shape remains unchanged. The pits on the cell wall became larger obviously after pyrolysis, and the pyrolysis temperature had little effect on the microstructure.

Analysis of pyrolytic liquid products

Pyrolytic liquid product of biomass material is usually is a translucent brown liquid with a sour taste, acidic, often called wood vinegar liquid, widely used in agriculture, forestry, and animal husbandry. In this study, the condensed liquid sat for two weeks, and filters out the tar on the surface.

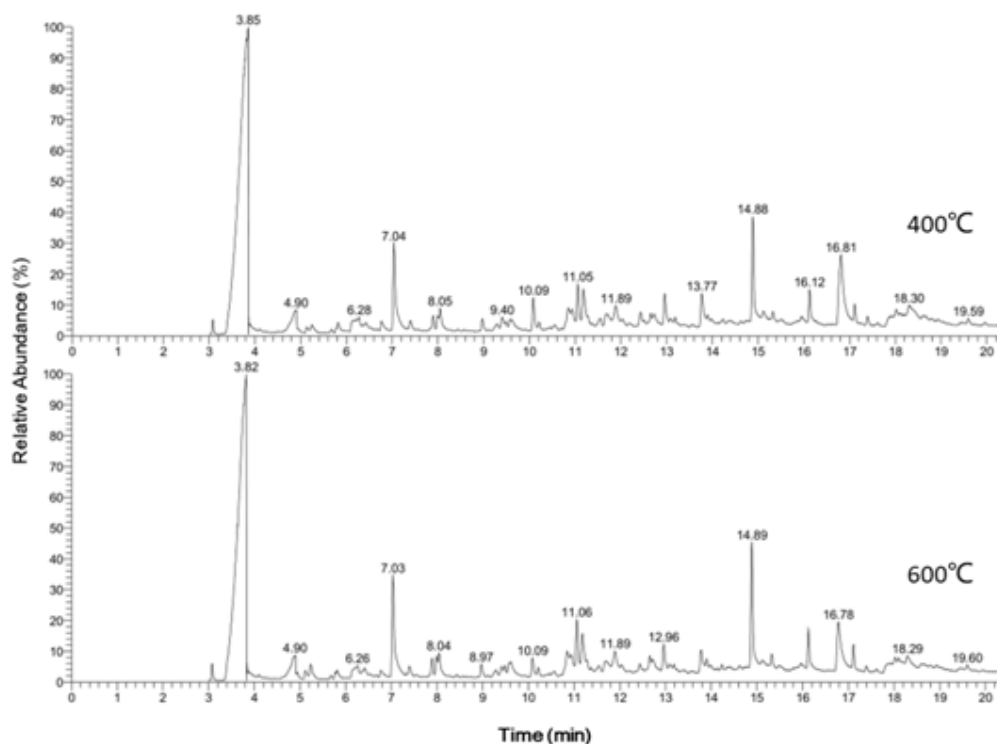


Fig. 3: Chromatogram of the liquid pyrolysis products.

Fig. 3 shows the chromatogram of liquid pyrolysis products at 400°C and 600°C with heating rate of 200°C/h. According to the chromatogram, the main components of the liquid pyrolysis products are organic acid, with the maximum peak value between 3.65 and 3.85 min. The corresponding component is acetic acid, the same as the pyrolysis products of other lignocellulosic materials (Mengfan et al. 2022). Compared with liquid products from two different pyrolysis process, chromatogram shapes are very similar, revealing that pyrolysis temperature has little effect on the composition of liquid products.

Tab. 5: Chemical formula and chromatographic area of major compounds identified in the pyrolysis liquid products.

No.	Compound name	Chemical formula	Area (%)	
			400°C	600°C
1	2-Butanone	C ₄ H ₈ O	0.86	-
2	Acetic acid	C ₂ H ₄ O ₂	39.32	45.33
3	Propanoic acid	C ₃ H ₆ O ₂	2.44	2.63
4	Pyrrole	C ₄ H ₅ N	1.29	-
5	Formamide, N,N-dimethyl-	C ₃ H ₇ NO	0.88	0.76
6	Acetamide	C ₂ H ₅ NO	-	1.3
7	Ethylenediamine	C ₂ H ₈ N ₂	1.6	0.72
8	Acetamide, N-methyl-	C ₃ H ₇ NO	-	0.72
9	2-Furanmethanol	C ₅ H ₆ O ₂	7.42	5.52
10	N,N-Dimethylacetamide	C ₄ H ₉ NO	-	0.71
11	2-Cyclopenten-1-one, 2-methyl-	C ₆ H ₈ O	1.02	0.77
12	Furafylline	C ₁₂ H ₁₂ N ₄ O ₃	0.94	-
13	Butyrolactone	C ₄ H ₆ O ₂	1.41	1.79
14	2-Cyclopenten-1-one, 3-methyl	C ₆ H ₈ O	0.99	0.82
15	Phenol	C ₆ H ₆ O	-	0.75
16	Pyridine, 3-methoxy-	C ₆ H ₇ NO	1.34	0.8

17	1,2-Cyclopentanedione, 3-methyl-	C ₆ H ₈ O ₂	1.51	2.24
18	Pantolactone	C ₆ H ₁₀ O ₃	2.11	1.64
19	Butanoic acid, 3-methylphenyl ester	C ₁₁ H ₁₄ O ₂	1.12	1.00
20	Phenol, 2-methoxy-	C ₇ H ₈ O ₂	3.17	1.91
21	Cyclopropyl carbinol	C ₄ H ₈ O	3.72	2.71
22	3-Pyridinol	C ₅ H ₅ NO	1.11	1.09
23	O-Succinyl-L-homoserine	C ₈ H ₁₃ NO ₆	1.6	1.34
24	Benzoic acid	C ₇ H ₆ O ₂	-	1.12
25	5,6,7,8-Tetrahydroquinoxaline	C ₈ H ₁₀ N ₂	0.91	-
26	1,4:3,6-Dianhydro- α -D-glucopyranose	C ₆ H ₈ O ₄	2.1	2.22
27	1,2-Benzenediol, 3-methoxy	C ₇ H ₈ O ₃	2.15	2.79
28	Phenol, 2-methoxy-4-methyl-	C ₉ H ₁₂ O ₂	0.94	-
29	Phenol, 2,6-dimethoxy-	C ₈ H ₁₀ O ₃	8.21	5.88
30	1,3,5-Triazine-2,4,6-(1H,3H,5H)-trione, 1,3,5-trimethyl-	C ₆ H ₉ N ₃ O ₃	0.91	-
31	1-Naphthaldehyde	C ₁₁ H ₈ O	0.82	-
32	3,5-Dimethoxy-4-hydroxytoluene	C ₉ H ₁₂ O ₃	2.48	1.81
33	α -D-Glucopyranose, 1,6-anhydro-	C ₆ H ₁₀ O ₅	5.1	7
34	Benzene, 1,2,3-trimethoxy-5-methyl-	C ₁₀ H ₁₄ O ₃	1.43	0.83
35	1,3,5-Triazine-2,4,6-triamine	C ₃ H ₆ N ₆	-	1.02
36	Methyl gallate	C ₈ H ₈ O ₅	-	1.04
37	1,2,4-Cyclopentanetrione, 3-butyl-	C ₉ H ₁₂ O ₃	1.09	1.75

The chemical composition corresponding to the pyrolysis liquid products under two different temperature is shown in Tab. 5. The composition of the pyrolysis liquid products in Tab. 5 is very complex, mainly including acids, alcohols, ketones, aldehydes, amides, furan derivatives, sugars, and other substances, among which organic acids (mainly acetic acid and propionic acid) account for 41.76% - 47.96%. Nitrogenous compounds such as pyrrole, formamide, acetamide, ethylenediamine, furafylline, pyridine, pyridinol, are mainly derived from the pyrolysis of adhesives in plywood (Xu et al 2020, Zhan et al 2019).

The furan derivatives mainly come from polycellulose, the six-membered fragment of cellulose after ring opening or the intermediate product levodextrose (Michael et al. 1991, Yang et al. 2020). The furan ring structure is obtained in the hemiacetal process after the ketonation of enol. The 4-O-methyl-D-glucuronic acid unit on the branch chain of xylan in hemicellulose decomposes, undergoes demethylation, dehydration, and CO₂ release, and produces furan ring structure. 3-methyl-2-cyclopentene-1-ketone and 3-methylcyclopentane-1, 2-diketone cyclopentenones are mainly derived from the breakdown of hemicellulose. Aromatic compounds are mainly derived from lignin pyrolysis (Li et al. 2001).

According to some literatures, the main product of liquid pyrolysis of solid wood is an organic acid, which pH value can be less than 4 (Jale et al. 2007). Due to adhesives and decorative layers, the pH value of the plywood pyrolysis liquid product is 5.68 - 6.34, showing weak acid. Pyrrole, pyridine, pyrazine, and other compounds are five- and six-membered N-heterocyclic compounds, which are alkaline and neutralize the organic acids produced during the pyrolysis of cellulose and lignin. The pH value of the pyrolysis liquid produced at different temperatures and different heating rates is shown in Tab. 6. With the pyrolysis temperature and heating rate increasing, the pH values of pyrolysis liquids showed a decreasing trend, but the values were not significant.

Tab. 6: pH values of liquid products during pyrolysis.

Heating rate (°C/h)	Pyrolysis temperature (°C)		
	400	500	600
100	6.34	6.21	5.86
150	6.13	6.08	5.79
200	5.96	5.84	5.68

CONCLUSIONS

Pyrolysis is an effective technology for treating discarded plywood of waste furniture. Pyrolysis temperature and heating rate have important effects on product yield and product characteristics. The pyrolysis of discarded furniture plywood can obtain 27.17 - 35.67% solid product, 39.64 - 51.32% liquid product and 86.44 - 147.69 L·kg⁻¹ non-condensing gas. With increasing pyrolysis temperature and heating rate, solid products content decreased, while liquid products and non-condensing gas content increased. The carbon content of solid products decreased with the pyrolysis temperature, but the C/H and C/N ratios increased gradually. The liquid products were weak acid, which pH values decreased with increasing of pyrolysis temperature and heating rate. A comprehensive understanding of the product yield and characteristics of wood-based furniture waste in different pyrolysis processes can provide scientific guidance for their rational and effective disposal.

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