Comparative Study on Slow Pyrolysis Products of Abandoned Furniture Materials

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Pyrolysis is an effective way to use abandoned furniture materials. This work dealt with solid wood, particle board, and medium density board obtained from dismantling discarded furniture as experimental materials. Slow pyrolysis was performed at a heating rate of 150 °C/h and pyrolysis temperatures of 400, 500, and 600 °C, and the products were analyzed. With the increase of pyrolysis temperature, the yield of solid products gradually decreased, while the yield of liquid products and non-condensing gases gradually increased. The carbon content in solid products reached 63.6 to 94.4%. The pyrolysis solution was acidic to weakly alkaline due to the different types and contents of adhesives in the three pyrolysis materials. Understanding the yield and characteristics of the pyrolysis products of waste furniture can provide more research directions for the recycling and utilization of these materials.

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INTRODUCTION

The service life of furniture products has gradually shortened, and the amount of discarded furniture is increasing progressively, especially for wood-based panel furniture (Wang *et al*. 2020; Xiong *et al*. 2020). China's annual waste of various types of wood products, mainly discarded furniture, is approximately 85 million cubic meters, comprising an important part of urban waste (Yang and Zhu 2021). Improper treatment of discarded wood-based panels causes environmental pollution. When wood-based panels are burned to generate heat, their adhesive and surface decorative layer produce NO, NO_2 HNCO, HCN, and other harmful gas precursors and release formaldehyde, which seriously affects air quality (Feng *et al.* 2012; Chen *et al.* 2015; Sun *et al.* 2019; Hu and Wan 2022). Simultaneously reducing waste and producing bioenergy through thermochemical technologies, such as pyrolysis, has been receiving increasing attention due to the depletion of reserve fossil fuels. Pyrolysis is a process for carrying out chemical reactions between gases at high temperature. This is a highly efficient biomass conversion technology that has broad application prospects in agricultural and forestry waste management (Lai *et al.* 2018; Liu *et al.* 2021b).

Pyrolysis is a thermochemical process that breaks down biomass/waste into products (such as biochar, bio-oil, and biogas) in an inert or anoxic environment (Foong *et al.* 2021). Pyrolysis transforms agricultural and forestry biomass with low energy density into gas, liquid, and solid phase products with high energy density and reduces energy material storage and transportation costs. Pyrolytic liquid can be used as a fuel to replace traditional energy and to extract chemical products with high added value, effectively recycling and reutilizing discarded furniture materials. Pyrolysis usually occurs in closed systems, thereby limiting hazardous air pollutants (HAPs), volatile organic chemicals (VOCs), and emissions of gases such as CO_2, NOX, and SO_2 to the atmosphere.

The overproduction of abandoned furniture with abundant lignocellulose content makes it suitable as a feedstock for pyrolysis to recover value-added products (Undri *et al.* 2015; Lai *et al.* 2018). Among pyrolysis products, biochar is used as a bio-fertilizer, dye adsorbent, and catalyst (Nam *et al.* 2017; Lam *et al.* 2018; Liew *et al.* 2018; Yek *et al.* 2019; Liu *et al.* 2020). The bio-oil produced can be upgraded to biofuel or used as a chemical additive, while biogas may replace fossil fuels and supply electricity (González-Arias *et al.* 2020; Ge *et al.* 2021).

Aslan *et al*. (2018) used thermogravimetric analysis coupled with Fourier-transform-infrared spectroscopy (TG-FTIR) and pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS) to study the kinetic and gas products released by MDF pyrolysis. They showed that the gas components detected at the highest de-composition temperature (*i.e*., 800 °C) included alkenes, ketones, phenols, and cyclic compounds. Han *et al*. (2015) used TGA and Py-GC/MS to analyze the pyrolysis characteristics of medium density fibreboard (MDF) and particle board (PB), and showed that most of the oil was produced at 500 °C. The differences in the composition of the gaseous products can be attributed to the composition and content of lignocellulosic compounds in the wood, where a high lignin content favors the formation of phenols, whereas high hemicellulose content favors the formation of acids (Stas *et al.* 2020). Girods *et al*. (2008a) conducted TG tests on particleboard and composite flooring at low temperatures (523 to 573 K). The results showed that HCN was not detected in the gas products during low-temperature pyrolysis, and the temperature would affect the low caloric value of the pyrolysis residue. In addition, the pretreatment can remove part of the N element and purify the raw material (Girods *et al.* 2008a). Girods *et al*. (2008) examined the effect of urea-formaldehyde (UF) and melamine modified urea-formaldehyde resin (MUF) resins on the pyrolysis characteristics of eucalyptus wood at low temperature (250 to 300 °C) to remove nitrogen from the particle board containing UF resin adhesive. The results showed that there was selective pyrolysis between wood and UF. FTIR was used to analyze CO, CO_2, CH_4, and HNCO. The elemental and calorific value analyses of pyrolysis residual solids showed that the pyrolysis temperature did not affect N element content, and the increase in treatment temperature decreased the C, H, and O elements and calorific value (Girods *et al.* 2008b,c). Girods *et al*. (2009) produced activated carbon (WAC) through two-step thermochemical treatment of waste particleboard, including pyrolysis and vapor activation, with a specific surface area of 800 to 1300 m^2/g, close to commercial activated carbon (CAC) (Girods *et al.* 2009a,b). Although the phenol absorption capacity of WAC is slightly lower than that of CAC, the cost of WAC is lower, and the adsorption capacity is improved by increasing the dosage. Therefore, a reasonable design of the pyrolysis process should control the proportion and composition of solid, liquid, and product (Xiong *et al.* 2017).

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.

EXPERIMENTAL

Materials and Equipment

The pieces of furniture were severely damaged; they were obtained from the garbage recycling station of a residential area in Nanjing. After dismantling, there were three materials—solid wood (SW), particle board (PB), and medium density fiberboard (MDF)—with a moisture content of 14.3 to 15.6% (GB/T 1931 2009). All three types of materials (provided from the dismantling of different damaged furniture as cabinets, wardrobe, desk top plate, *etc*.) had different coatings layers on top. Tests were carried out in order to provide trustworthy information about the yield of products and the properties of solid and volatile liquid products obtained. The materials were dried at 103 °C for 24 h. The industrial and elemental results of these materials are shown in Table 1. The three types were cut into dimensions of 30 mm × 50 mm (thickness of 30 mm, 18 mm, and 21 mm) for further pyrolysis experiments.

Table 1. Analysis of Three Types of Materials

Material Type	Industrial Analysis (%)			Elemental Analysis (%)				
	Volatile Matter	Fixed Carbon	Ash	C	H	O	N	S
SW	80.09	18.57	1.34	47.68	5.45	46.53	0.15	0.01
PB	81.77	15.29	2.94	43.75	5.96	45.21	5.06	0.02
MDF	82.04	15.17	2.79	44.37	6.08	44.65	4.89	0.01

The fast pyrolysis was conducted in May 2021 in a laboratory-scale reactor (Fig. 1) 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.

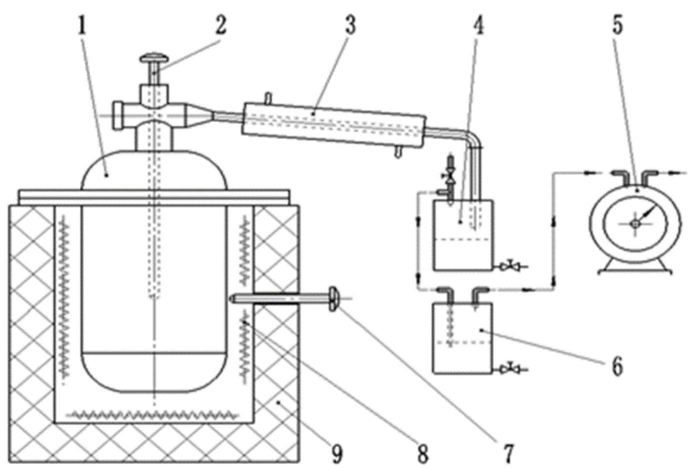

Fig. 1. Diagram of pyrolysis apparatus. (1) Furnace, (2) temperature transducer (within the furnace), (3) glass condenser, (4) gas and liquid separator, (5) flow meter, (6) tank, (7) temperature transducer (furnace exterior), (8) heaters, and (9) furnace stack

Pyrolysis Method

The experimental materials were pyrolyzed by piece-wise heating under the condition of anoxia. First, 1 kg of the material was heated from room temperature to 280 °C at the rate of 100 °C/h and held for 1 h, and then 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. After cooling for 24 h, volatile liquid and solid products were collected.

Solid Products Analysis

An Elementar Vario EL type III elemental analysis system (Elementar Analysensys-teme GmbH, Langenselbold, 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 GB/T 12496.7 (1999) standard.

Volatile Liquid Products Analysis

The volatile liquid products of the pyrolyzed materials were analyzed by gas chromatography on a Turbo Matrix 650TD-CLARUS600 GC-MS device (Perkin Elmer, Waltham, MA, USA). The chromatography column was DB-5MS (30 m × 0.250 nm × 0.250 μm). The temperature was set as follows: the initial column temperature was 60 °C for 2 min, raised to 180 °C at 5 °C/min, then raised to 280 °C at 20 °C/min, 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 70 eV, the interface temperature 250 °C, the MS scanning range was 29 to 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 Statistics25 software (IBM, Armonk, NY, USA) 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, "material type" 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

During pyrolysis, the solid experimental materials are converted into the flue gas and a solid. The flue gas is divided into condensable liquid and non-condensable gas, and the final products can be divided into solid, liquid, and gas. The product yields of the pyrolytic materials at different pyrolysis temperatures are shown in Fig. 2 and Table 2. The proportion of solid products obtained from abandoned furniture through pyrolysis was 28.5 to 46.8%. Among the three materials, the order of solid product obtaining was particle board > middle-density fiberboard> solid wood. The liquid products' yield ranged from

30.6 to 48.4%, and the order of yield of liquid products was opposite to that of solid products. The non-condensing gas yield was 97.2 to 131.3 L/Kg. The solid products yield decreased with the increase in pyrolysis temperature, while the yield of liquid products and non-condensing gas increased.

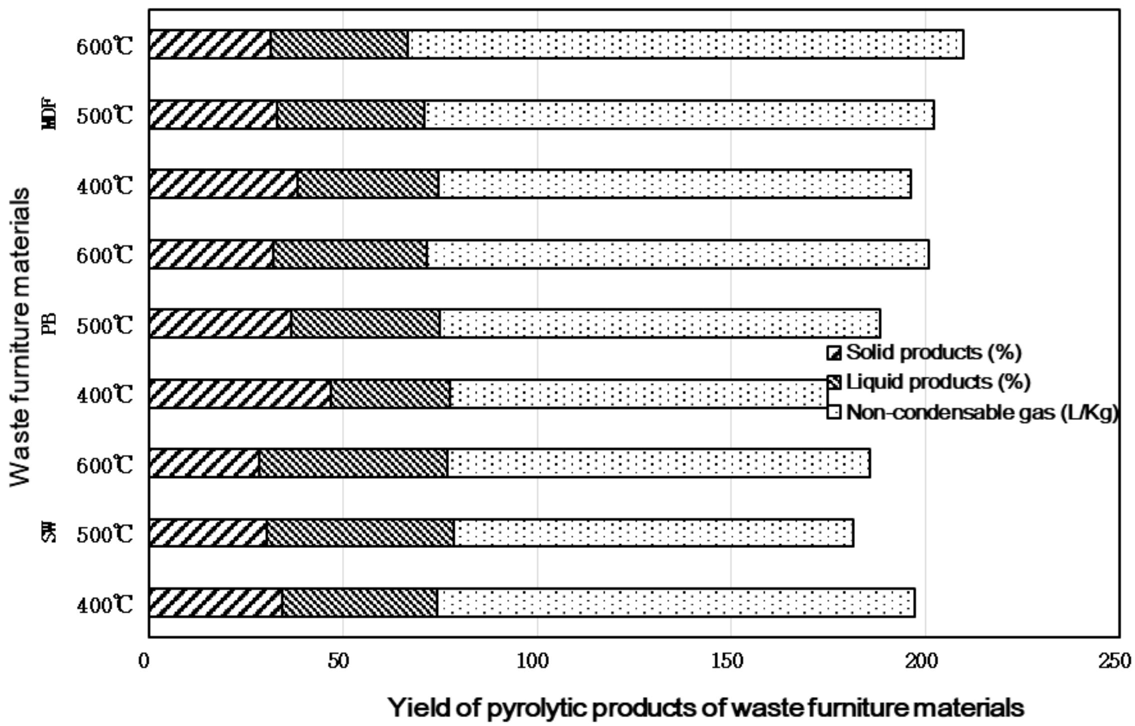

Fig. 2. Yield of pyrolysis products of the three materials at different temperatures

Table 2. Effects of Material Type and Temperature on the Pyrolysis Yield

Yield of Pyrolysis Products	Solid Products (%)	Liquid Products (%)	Non-condensable Gas (L/Kg)
Material type			
SW	31.11c	45.42a	111.61b
PB	38.45a	113.18b	36.63b
MDF	36.28b	34.16b	131.95a
Pyrolysis temperature			
400 °C	39.67a	35.66b	113.98b
500 °C	33.34b	41.16a	115.81b
600 °C	30.61c	41.51a	126.95a
	P values		
Material type	< 0.0001	< 0.0001	< 0.0001
Pyrolysis temperature	< 0.0001	< 0.0001	< 0.0001
Material type × Pyrolysis temperature	0.009	0.012	< 0.0001

When "material type" was taken as the influencing factor, the P-values of the solid product, liquid product, and non-condensing gas were 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 "material type × pyrolysis temperature" were 0.009, 0.012, and < 0.0001, indicating a significant interaction between material type and pyrolysis temperature only on the non-condensable gas.

Analysis of Pyrolytic Solid Products

After pyrolysis, the solid product of abandoned furniture is mainly carbon, also known as "biomass carbon", which can be used as fuel. Because of its loose texture and many internal voids, it is often used as a soil amendment in agriculture (Yerrayya *et al.* 2020). The elemental analysis and pH value of solid pyrolysis products are shown in Table 3. The main component of solid pyrolysis products was carbon (63.6 to 94.4%). The carbon content of solid wood was higher than that of particle board and medium-density fiberboard. In contrast, particle and medium-density fiber boards' nitrogen content is higher than that of solid wood, possibly due to the different contents of adhesives and decorative layers. Comparing the different pyrolysis temperatures, there is a common trend in the elemental changes of the three solid products. With the pyrolysis temperature, the carbon content in solid products increases, while the nitrogen gradually decreases, and the carbon to nitrogen ratio gradually increases. One of the most striking observations is also the very high content of nitrogen in the particleboard and medium density fiberboard. This high percent of nitrogen is undoubtedly coming mainly from urea formaldehyde resins. The pH value of solid products produced by all materials at different pyrolysis temperatures ranged from 6.44 to 9.04, showing weak acidity to weak alkalinity. The material type had little influence on the pH value, and the pH gradually increases with the pyrolysis temperature, but the increase was not significant

Table 3. Element Analysis and pH Values of Three Types of Solid Products

Material Type	Pyrolysis Temperature	Elemental Analysis (%)						pH
		C	N	H	S	C:H	C:N	
SW	400 °C	84.88	0.13	3.78	0.22	22.46	652.92	6.44
	500 °C	87.52	0.16	2.73	0.23	32.06	547.00	7.13
	600 °C	94.35	0.15	1.69	0.25	55.83	629.00	7.99
PB	400 °C	80.73	5.88	2.86	0.24	28.23	13.73	8.17
	500 °C	83.38	5.31	2.65	0.22	31.46	15.70	8.57
	600 °C	88.49	4.72	2.01	0.21	44.02	18.75	8.98
MDF	400 °C	63.64	3.26	2.39	0.22	26.63	19.52	8.31
	500 °C	68.72	2.68	1.83	0.19	37.55	25.64	8.73
	600 °C	72.18	2.35	1.64	0.18	44.01	30.71	9.04

Analysis of Pyrolytic Solid Products

The liquid condensed by pyrolysis of wooden materials was allowed to stand still for 2 weeks, and the tar on the surface was filtered out. It was a translucent brown liquid with a sour taste, acidic, and often called wood vinegar liquid. It is widely used in agriculture, forestry, and animal husbandry. Figure 3 shows the chromatogram of three types of liquid pyrolysis products at 600 °C. The main components of the liquid pyrolysis products of the examined materials were similar, with the maximum peak value between 3.65 and 3.85 min. The corresponding component is acetic acid, which is the same as the pyrolysis products of other lignocellulosic materials (Aguirre *et al.* 2020).

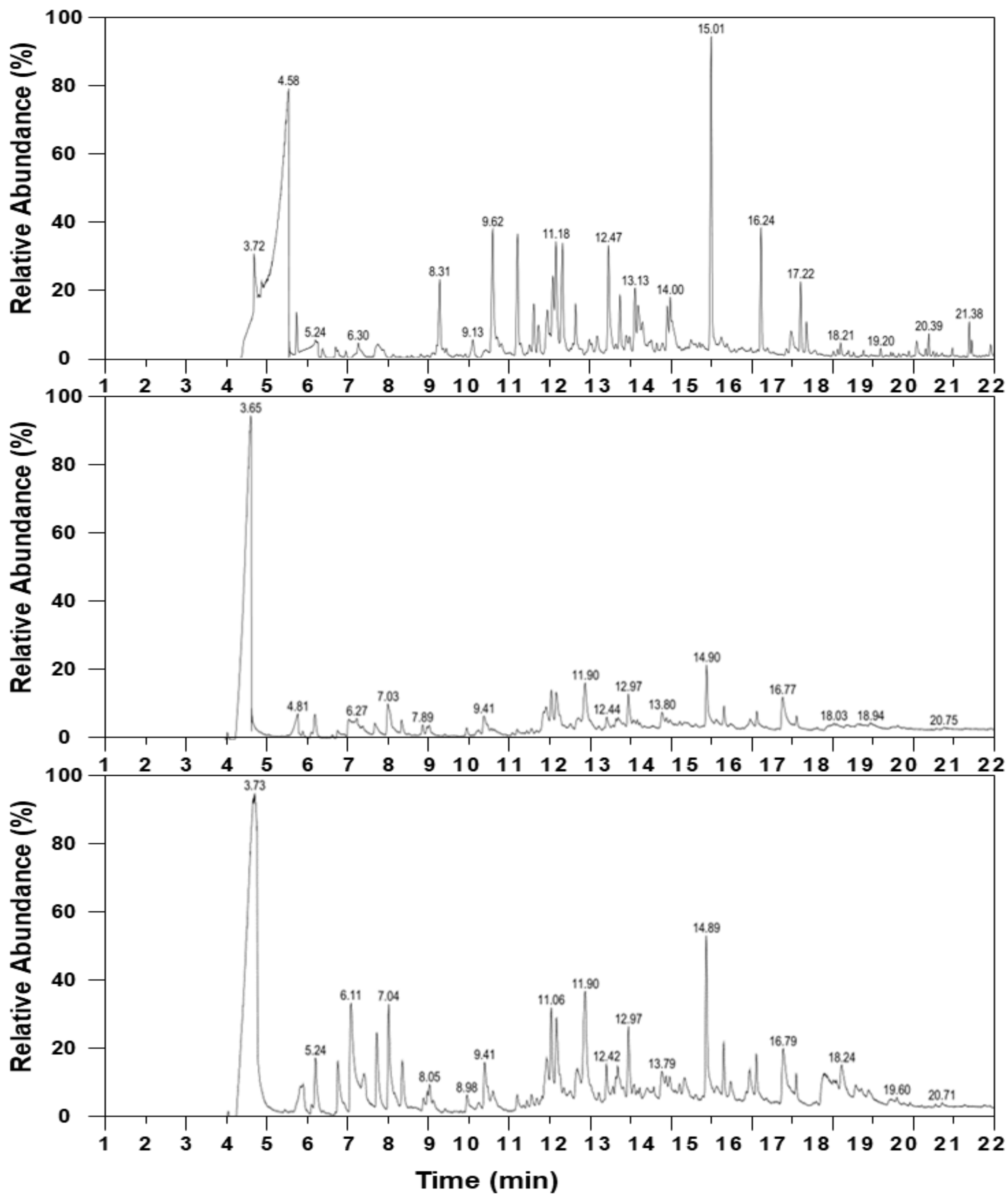

Fig. 3. Chromatogram of the three types of liquid pyrolysis products at 600 °C

The chemical compositions corresponding to the pyrolysis liquid products of three different materials are shown in Table 4. The composition of the pyrolysis liquid products shown in Table 4 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) accounted for 21.9 to 49.1%. Pyrrole, N,N-dimethylformamide, acetamide, ethylenediamine, n-methylacetamide, N,N-dimethyl-acetamide, 5-aminimidazole-4-formamide-1-β-d-furan riboside 5-phosphate, 3-hydroxypyridine, homoserine, 2-methylL-5-(1-propenyl), and (E)-nitrogenous compounds such as pyrazine and melamine are mainly derived from the pyrolysis of adhesives or veneers in wood-based panels. The furan derivatives mainly come from polycellulose, the six-membered fragment of cellulose after ring opening or the intermediate product levodextrose. The furan ring structure is obtained in the hemiacetal process after the ketonation of enol.

Table 4. Major Compounds Identified in the Pyrolysis Liquid Products for all Tree Conditions

No.	Compound Name	Chemical Formula	Area (%)		
			SW	PB	MDF
1	Acetic acid	$C_2H_4O_2$	20.66	46.83	33.27
2	Propanoic acid	$C_3H_6O_2$	1.24	2.2	2.53
3	Pyrrole	C_4H_5N	-	2.27	2.45
4	Formamide, N,N-dimethyl-	C_3H_7NO	-	0.94	2.1
5	Acetamide	C_2H_5NO	-	3.11	5.27
6	Ethylenediamine	$C_2H_8N_2$	-	1.16	1.17
7	2-Furanol, tetrahydro	$C_4H_8O_2$	1.18	-	-
8	Acetamide, N-methyl-	C_3H_7NO	-	1.22	3.01
9	Furfural	$C_5H_4O_2$	1.51	-	-
10	2-Furanmethanol	$C_5H_6O_2$	-	3.46	3.98
11	N,N-Dimethylacetamide	C_4H_9NO	-	1.09	1.92
12	Butyrolactone	$C_4H_6O_2$	3.53	1.02	1.62
13	2-Cyclopenten-1-one, 3-methyl-	C_6H_8O	1.01	0.69	0.87
14	Phenol	C_6H_6O	6.6	2.12	2.25
15	1,2-Cyclopentanedione, 3-methyl-	$C_6H_8O_2$	7.69	-	-
16	Butanoic acid, 3-methylphenyl ester	$C_{11}H_{14}O_2$	1.84	2.84	1.98
17	Phenol, 2-methoxy-	$C_7H_8O_2$	7.8	1.98	2.62
18	Cyclopropyl carbinol	C_4H_8O	4.68	3.24	3.18
19	3-Pyridinol	C_5H_5NO	-	0.98	1.44
20	O-Succinyl-L-homoserine	$C_8H_{13}NO_6$	-	4.21	4.97
21	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	$C_7H_{10}O_2$	2.15	-	-
22	5-Hepten-2-one, 5,6-dimethyl-	$C_9H_{16}O$	1.03	-	-
23	Benzoic acid	$C_7H_6O_2$	-	1.14	1.22
24	Pyrazine, 2-methyl-5-(1-propenyl)-, (E)-	$C_8H_{10}N_2$	-	0.76	1.84
25	Phenol, 4-ethyl-	$C_8H_{10}O$	4.62	-	-
26	Phenol, 2-methoxy-4-methyl-	$C_8H_{10}O_2$	2.01	-	-
27	1,4:3,6-Dianhydro-à-d-glucopyranose	$C_6H_8O_4$	2.5	2.92	2.8
28	1,2-Benzenediol	$C_6H_6O_2$	2.56	-	-
29	Hydroquinone	$C_6H_6O_2$	1.22	-	-
30	1,2-Benzenediol, 3-methoxy-	$C_7H_8O_3$	1.62	3.2	1.27
31	Phenol, 4-ethyl-2-methoxy-	$C_9H_{12}O_2$	3.18	-	-
32	Phenol, 2,6-dimethoxy-	$C_8H_{10}O_3$	12.03	4.38	6.45
33	3,5-Dimethoxy-4-hydroxytoluene	$C_9H_{12}O_3$	4.28	3.43	5.19
34	á-D-Glucopyranose, 1,6-anhydro-	$C_6H_{10}O_5$	1.57	3.44	2.78
35	Benzene, 1,2,3-trimethoxy-5-methyl-	$C_{10}H_{14}O_3$	2.35	-	-
36	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-	$C_{10}H_{14}O_3$	1.14	-	-
37	1,3,5-Triazine-2,4,6-triamine	$C_3H_6N_6$	-	0.7	2.49
38	Methyl gallate	$C_8H_8O_5$	-	0.67	1.33

The 4-O-methyl-D-glucuronic acid unit on the branch chain of xylan in hemicellulose decomposes, undergoes demethylation, dehydration, and CO_2 release, and produces furan ring structure. 3-methyl-2-cyclopentene-1-ketone and 3-methylcyclo-pentane-1, 2-diketone cyclopentenones are mainly derived from the breakdown of hemicellulose. Aromatic compounds such as phenol, guaiacol, 3-methoxy-catechol, syringol, and 2, 6-dimethoxy-4-methylphenol are mainly derived from lignin pyrolysis.

The main product of volatile liquid pyrolysis of solid wood is an organic acid with an acidic pH of 4.21 to 5.23, which can be used directly as an herbicide (Liu *et al.* 2021a), and also used as a liquid fertilizer after being diluted with water (Wang *et al.* 2022). The pH value of the wood-based panel pyrolysis liquid product was 5.64 to 8.56, showing weak acidity to weak alkalinity, due to integration of the nitrogen into structure of liquid compounds adhesives and decorative layers (Mu *et al.* 2011). The nitrogen in the liquid from PB and MDF pyrolysis, mainly was present as amine-N and heterocyclic-N, which showed excellent anti-bacterial performance, thus could be used for wood preservation (Mu *et al.* 2011). 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 is shown in Table 5. The pyrolysis liquid of the MDF was weakly alkaline. In contrast, the pyrolysis liquid of particle board was weakly acidic, mainly because the types and contents of adhesives were different. With the pyrolysis temperature, the pH values of all pyrolysis liquids showed an increasing trend, but the values were not significant.

Table 5. pH Values of Volatile Liquid Products During Pyrolysis

Material Type	Pyrolysis Temperature		
	400 °C	500 °C	600 °C
SW	4.21	4.78	5.23
PB	5.64	5.78	5.69
MDF	7.08	7.98	8.56

CONCLUSIONS

1. The yield and characteristics of discarded furniture materials' pyrolysis products are very different from ordinary wood materials because they contain adhesive and decorative materials.
2. The materials' pyrolysis solid product yields were in the order particle board > medium density fiberboard > solid wood. However, the liquid product yield order was solid wood > particle board > medium density fiberboard.
3. The solid product yield gradually decreased with the increase in pyrolysis temperature. In contrast, the yield of liquid products and non-condensing gas gradually increased. The main component of solid pyrolysis products was carbon, the carbon content of solid wood was higher than that of particle board and medium-density fiberboard.
4. The liquid products were weak acid to weak alkaline, and the pH of the three pyrolysis liquids increased slightly with the pyrolysis temperature.
5. 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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