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Microwave Pyrolysis of Automotive Polypropylene Based on a Microwave Atmosphere Tube Furnace

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Abstract: *Plastics have light weight and excellent performance, which are widely used in all kinds of automobiles. Polypropylene (PP) and its reinforcing materials are used in automotive components, where the surfaces of bumpers and fenders are coated with paint. Traditional recycling can frequently generate various pollutants, such as paint sludge. Microwave pyrolysis is a more environmentally friendly pyrolysis method with a higher heating coefficient than traditional electric pyrolysis. This study first explores the elemental composition of two types of automotive PP plastics and uses thermo-gravimetric analysis and the Kissinger-Akahira-Sunose method to preliminarily calculate the activation energy of automotive PP. The calculation results show that the activation energy of PP containing paint ranges from 189.145 kJ/mol- 199.513 kJ/mol, with an average value of 193.903 kJ/mol. The activation energy of PP without paint is between 215.506 kJ/mol-265.794 kJ/mol, with an average value of 242.425kJ/mol. Then, pyrolysis experiments on PP for vehicles without paint are conducted using a microwave atmosphere tube furnace at different temperatures and microwave powers. The experimental results showed that, when the pyrolysis temperature increased from 500°C to 620°C, the total proportion of gas products rose from 0.75 wt.% to 4.81 wt.%, and the content of alkanes in the liquid products improved from 26.21 wt.% to 34.37 wt.%; when the microwave power increased from 900 W to 1100 W, the gas product rose to 20.77 wt.%, and the content of aromatic compounds in the liquid product improved to 17.78 wt.%. In addition, the pyrolysis experiment of automotive PP containing paint showed that paint had a relatively minor effect on the pyrolysis products of automotive PP. This study shows that using microwave pyrolysis to treat automotive PP and PP with paint is feasible, which provides a reference for the clean treatment of automotive polymers.*

Keywords*: polypropylene plastics, paint coating, microwave pyrolysis, pyrolysis kinetics, energy crisis*

1. Introduction

According to the International Energy Agency's World Energy Outlook, the world is facing the first energy crisis, the price of natural gas has reached unprecedented levels, the price of coal has reached a record high, and the price of oil has also shown an upward trend [1]. Non- renewable energy sources (such as oil, coal, and natural gas) are gradually consumed with the development of society and will eventually be exhausted in the future [2]. The automobile industry is gradually developing toward lightweight methods to reduce energy consumption and pollutant emissions. An important way to reduce vehicle weight is to use lightweight materials for reducing vehicle mass [3]. Plastics can meet the requirements of automotive lightweight technology due to the advantages of light weight, high strength, strong corrosion resistance, strong design flexibility, and strong fatigue resistance; thus, the application of plastics in the automotive industry is increasingly becoming extensive [4]. The landfill and incineration of plastic polymers can cause serious environmental pollution. Meanwhile, plastic waste and fossil fuels have similar performance, and using plastic waste to produce fuel can solve the growing energy demand and the problem of plastic waste treatment [5].

Ma et al. [6] studied the effect of polypropylene (PP) on the pyrolysis of high-impact polystyrene (HIPS). The pyrolysis of HIPS and the mixture of HIPS and PP were conducted in a fixed bed reactor at 410°C. The results showed that PP significantly influenced the pyrolysis efficiency of HIPS. Rodriguez

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et al. [7] studied the influences of a catalytic cracking catalyst and cracking temperature on the pyrolysis of high-density polyethylene (HDPE) wax to fuel. The experiment proved that the conversion rate of HDPE wax catalyzed by an industrial catalyst could reach 41.4-62.9 wt.%. Increasing acidity helps raise the yield of dry gas, liquefied petroleum gas, and coke. Syie et al. [8] used two catalysts, namely, HZSM-5 zeolite and FCC, to conduct catalytic pyrolysis of HDPE, LDPE, and PP by induction heating, and the experiment proved that induction heating could reduce the time required for the pyrolysis of plastic waste.

Microwave pyrolysis is a new pyrolysis method, the principle of which is to use microwaves as a heating source to heat solid materials [9]. Due to the heat and mass transferring limitation in the conventional heat method, the energy efficiency is low and the products fraction cannot be well controlled. The low heat conductivity of plastics makes the mass and heat transferring worse. Microwave-assisted pyrolysis has become a promising technology as it can realize fast, selective heating and is easy to control the reaction conditions [10]. Zhou et al. [11] conducted a catalytic pyrolysis study of plastic waste in a continuous microwave-assisted pyrolysis system, and the results showed that a higher pyrolysis temperature could promote the pyrolysis of wax, and the liquid yield could be increased to 48.9% when the pyrolysis temperature was 620°C. Liu et al. [12] conducted microwave-assisted pyrolysis of polyethylene terephthalate (PET) sheets of different sizes under different SiC loads and calculated that the optimal process conditions were achieved when the sheet size was 10×10 mm^2, the SiC load was 35 g, and the pyrolysis temperature was 550°C; the solid yield reached 35.67 wt.%, the gas yield reached 40.00 wt.%, and the recovery efficiency was 34.38%. Fan et al. [13] used microwave-assisted pyrolysis of different plastic wastes to produce aviation oil. The experimental results showed that the average heating rate of polystyrene (PS) was the lowest at 60°C/min, and the yield of aviation oil reached 98.78 wt.% at microwave power of 650 W, microwave absorption load was 60 g and the pyrolysis temperature was 460°C. Cui et al. [14] used a microwave-assisted fluidized bed reactor to study the gas production of PP plastics at different temperatures, fluidization speeds, and microwave powers. The study showed that the calorific value of the pyrolysis gas reached the highest value of 51.8 MJ/m^3 when the temperature was 900°C, the fluidization speed was 2.36×10^{-3} m/s, and the microwave power was 800 W.

In the process of automobile production, plastics are usually used for external components such as air-inlet grilles, seals, wheel covers, and bumpers and internal components such as instrument panels, steering wheels, and seats [15]. In the use of various plastics, PP and its reinforcement materials are widely used in car bumpers, seats, fuel tanks and other locations due to their low price, good flexibility, and high compressive strength [16]. When PP material is used as a car bumper, it is usually painted on the surface of PP to prevent corrosion, reduce the noise of car operation, and increase aesthetics. Paint removal is usually required after the car is scrapped. Currently, the commonly used methods for paint removal mainly include high-pressure water injection, manual polishing, chemical solvent stripping, and other methods [17]. However, improper disposal of the residue after paint removal can produce automotive paint sludge (APS). Besides, automobile spray painting is the main source of VOCs, and improper treatment of paint sludge will cause serious environmental damage [18]. Automotive PP materials often contain talc powder and other substances to enhance the performance of PP plastics. At present, the pyrolysis of PP and other plastics involves mainly pure PP, and most of them are traditional electric heating pyrolysis, while the microwave pyrolysis of automotive PP is rarely studied. This study conducted microwave pyrolysis experiments on PP with and without paint recycled from ELV bodies. Moreover, the products of gas and liquid generated during the pyrolysis process were analyzed using GC–MS. The pyrolysis experiments of PP without paint were conducted at different powers and temperatures, and the pyrolysis products of PP with paint were compared to explore the possibility of direct pyrolysis of automotive PP.

2. Materials and methods

2.1. Materials

In this study, the door inner frame plastic and front bumper plastic of scrapped cars collected by a scrapped car recycling company in Kunming are used as raw materials. The plastic material of the door inner frame is PP-TD20, and the surface is not painted, while the plastic material of the front bumper is PP+EPDM-TD20, and the surface is painted red. The PQ-180-800 plastic crusher is used to crush the plastic sample into pieces of 3-5 mm. The samples before and after crushing are shown in Figure 1.

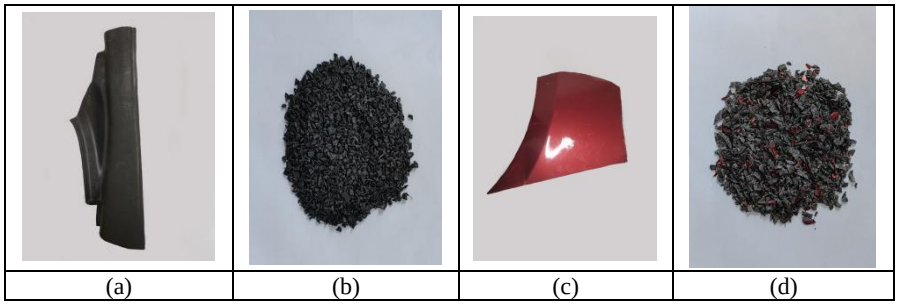


Figure 1. ELV plastic samples: (a) Plastic sample of ELV door inner frame before crushing (b) Plastic sample of ELV door inner frame after crushing (c) Plastic sample of ELV front bumper before crushing (d) Plastic sample of ELV front bumper after crushing

Certain microwave absorbers need to be used to enhance energy transfer during microwave pyrolysis due to the poor ability of plastics to absorb microwaves [19, 20]. The SiC crucible produced by Shandong Baide Ceramic Technology Co., Ltd. is used in the study as the absorbing medium material, with an average weight of 69.25 g.

2.2. Experimental system

An experimental system, as shown in Figure 2, is used to microwave heat PP particles.

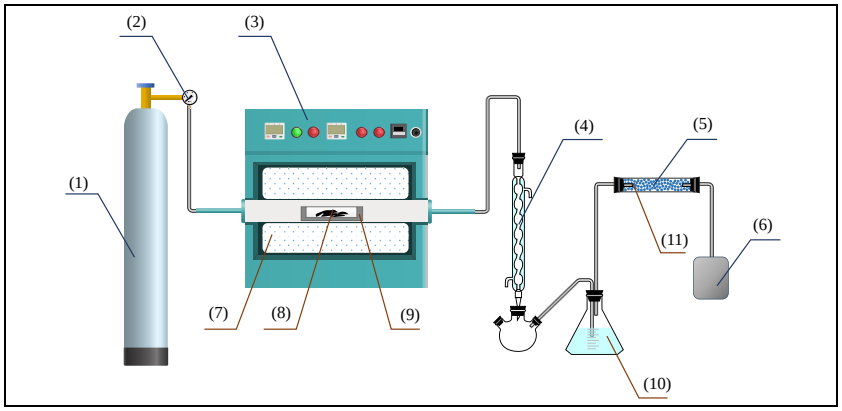


Figure 2. Microwave pyrolysis heating device: (1) Argon gas tank, (2) Gas flow meter, (3) Microwave atmosphere tube furnace, (4) Condenser tube, (5) Drying tube, (6) Gas collection bag, (7) Insulation materials, (8) Sample to be heated, (9) Crucible (SiC), (10) NaOH solution, (11) Color-changing silica gel

The heating equipment used in this study is a microwave atmosphere tube furnace with a microwave power range of 100–1400 W. The microwave heating power and maximum heating temperature can be linearly adjusted. Quartz glass tubes are used as reactor walls inside the tubular furnace. Quartz glass is a microwave transparent medium that allows microwaves to pass through without losing energy [14, 21]. Quartz glass can withstand high temperatures of 1300°C and can be used for microwave heating of

PP plastics. The quartz glass tube is surrounded by an insulation material layer, which is composed of aluminum silicate ceramic. Aluminum silicate ceramic has a high electromagnetic wave transmittance and can be used as an insulation material in microwave heating to maintain the temperature of the heated sample inside the quartz tube [22]. During the heating process, argon gas is used to fill the interior of the quartz tube, which realizes an argon atmosphere environment. The flow rate of argon gas is controlled by a gas flow meter (YQB-731L, Zhejiang Taizhou Platinum Vacuum Reducer Factory). The PP sample to be heated is placed in a silicon carbide crucible and placed in the heating zone of the tube furnace. The heating product is treated with sodium hydroxide (NaOH) solution for tail gas treatment, and discolored silica gel is used for drying. The gas products are collected using gas collection bags. The liquid product condenses at both ends of the quartz tube, as shown in Figure 3. The product is dissolved in anhydrous ethanol and collected.

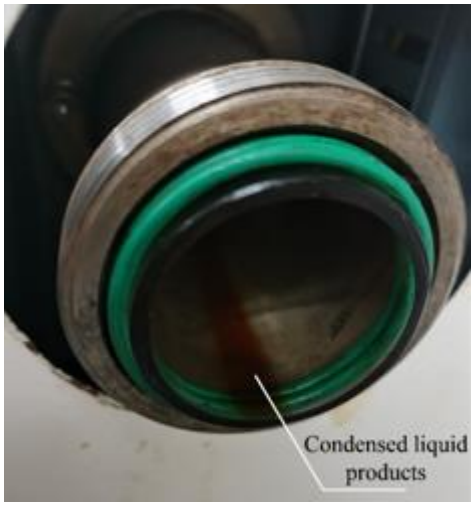


Figure 3. Liquid products condensed on the pipe wall

2.3. Preparation before the experiment

2.3.1. Characterization of raw materials

Technical analysis of two different PP particles was conducted in accordance with the national standard of the People's Republic of China GB/T212-2001 [23], and elemental analysis of the two PP particles was performed using an organic element analyzer (Elemantar: Vario UNICUBE) and inductively coupled plasma-mass spectrometry (ICP–MS: Agilent 7800). Two types of PP particles were analyzed using a thermogravimetric analyzer (TG 209, NETZSCH) in a high-purity nitrogen inert atmosphere with a maximum temperature of 600 ℃ at the heating rates of 5, 10, and 15ºC/min.

2.3.2. Experimental design

In this study, 7 g of broken PP particles without paint was weighed and subjected to three pyrolysis experiments under an argon atmosphere at different heating temperatures and microwave powers. The experimental samples of the three experiments were numbered 1, 2, and 3. Thereafter, under the experimental conditions of Sample 3, 7 g of PP containing paint was weighed and named Sample 4. Pyrolysis experiments were conducted on PP-containing paint under experimental conditions of 620ºC, 1100 W, and 20 min. The argon flow rate is 150ml/min. The experimental conditions for the four experiments are shown in Table 1.

Table 1. Test conditions for pyrolysis of PP

No.	Maximum heating temperature/℃	Heating microwave power/W	Residence time after heating/min	Paint
1	500	900	20	without
2	620	900	20	without
3	620	1100	20	without
4	620	1100	20	with

After microwave pyrolysis experiments were conducted, a gas chromatograph (GC 7820A, Agilent Technologies) was used to perform GC analysis on the collected gas products, and gas chromatography–mass spectrometry (TRACE1300-ISQ7000, Thermo Fisher Scientific Co., Ltd.) was conducted to perform GC-MS analysis on the collected liquid products for analyzing and comparing the pyrolysis products of automotive PP under three different conditions. After GC-MS analysis, the peak was compared with the standard spectrum, and the compound with the highest comprehensive probability was selected for analysis. After the experiment, all four samples were completely cracked, and the remaining portion in the crucible was composed of various ash fractions.

3. Results and discussions

3.1. Elemental and thermogravimetric analysis results

As shown in Table 2, the two types of PP used in this experiment both contain 20% talc powder, the main component of which is Mg_3 [Si_4O_{10}] (OH) $_2$. Therefore, in technical analysis, both contain 16.32% and 15.70% ash, respectively. In elemental analysis, Si and Mg account for a certain proportion. The chemical composition of paint is complex [24], and it contains a large amount of elements. In PP plastics containing paint, the nitrogen content significantly increases, while the carbon content significantly decreases.

Table 2. Industrial analysis and elemental analysis results of PP without paint and PP with paint

Technical analysis (%)			Element analysis (%)		
	PP without paint	PP with paint		PP without paint	PP with paint
Moisture	0.12	0.62	C	71.33	65.84
Volatile matter	82.90	83.24	H	10.66	10.20
Ash	16.32	15.70	O	0.47	0.96
Fixed carbon	0.66	0.44	N	0	0.52
			Si	2.88	4.64
			Mg	2.19	1.89

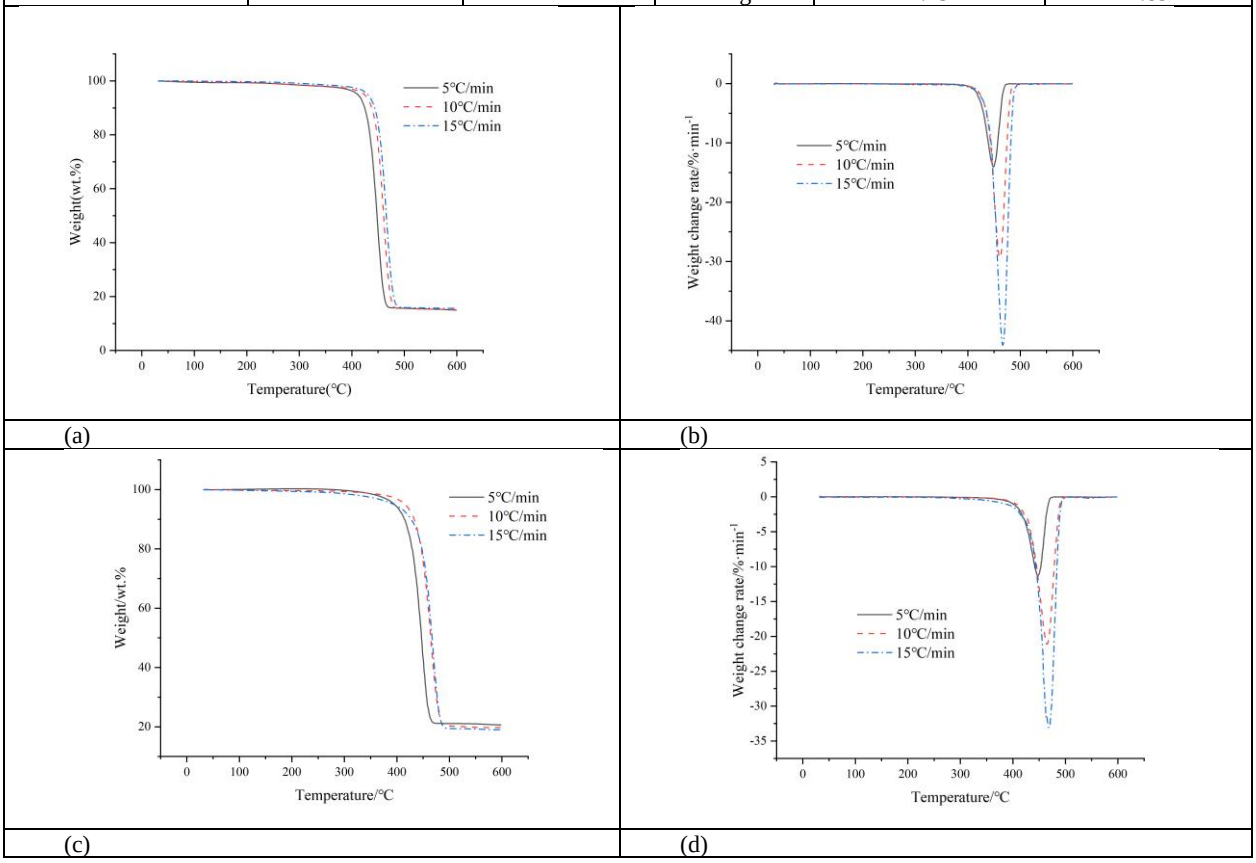


Figure 4. TGA and DTG curves: (a) DTG curve of PP without paint (b) TGA curve of PP without paint (c) DTG curve of PP with paint (d) TGA curve of PP with paint

The main parameters in pyrolysis are shown in Table 3. According to TGA analysis, there was no significant weight loss observed in the PP of the two paints before 200°C, indicating that the moisture content in the samples was relatively low. In the three experiments, the thermal decomposition of PP without paint occurred in the range of 379~496°C, and with the increase of heating rate, the initial temperature of decomposition, the temperature at which decomposition stopped, and the temperature at which weight loss rate was maximum shifted towards higher temperatures. This is because the reaction mechanism changed after the heating rate increased [25]. The thermal decomposition of PP containing paint occurs in the range of 279~500°C, and it can be observed that when the heating rate increases to 15°C /min, the initial reaction temperature decreases to 279°C. Therefore, it can be inferred that a higher heating rate will accelerate the volatilization of the volatile components contained in the paint. At the end of the reaction, the ash residue of PP without paint was 15 wt.% and that of PP with paint was 19 wt.%, and its ash residue was caused by the addition of talc and other additives to the PP plastics.

Table 3. Pyrolysis parameters of two types of PP particles

heating rate (°C/min)	PP without paint			PP with paint		
	Reaction initiation temperature (°C)	Temperature at maximum weight loss rate, (°C)	Reaction termination temperature (°C)	Reaction initiation temperature (°C)	Temperature at maximum weight loss rate, (°C)	Reaction termination temperature (°C)
5	379	449	487	366	446	479
10	388	461	493	377	465	494
15	397	466	496	279	470	500

3.2. Activation energy calculation results

The reaction kinetics equation used in the plastic pyrolysis process can be represented by the following equation [26]:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} exp\left(-\frac{E_\alpha}{RT}\right) f(\alpha), \quad (1)$$

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f}, \quad (2)$$

where α represents the mass conversion rate during the pyrolysis process, %; T is the pyrolysis temperature, K; A is the pre factor, min^{-1}; β is the heating rate, K/min; E_α is the activation energy of the reaction, kJ/mol; R is the gas constant, R=8.314 J/(mol·K); $f(\alpha)$ is the reaction mechanism function; m_0 is the initial mass, mg; m_t is the instantaneous mass at time t, mg; and m_f is the mass at the end of sample pyrolysis, mg.

The Kissinger-Akahira-Sunose (KAS) method is a commonly used method for calculating the activation energy during pyrolysis [27]. This method is based on the Coats-Redfern approximation, and its parameter equation expression is

$$ln\left(\frac{\beta}{T^2}\right) = -\frac{E_\alpha}{RT} + ln\left(\frac{AR}{E_\alpha g(\alpha)}\right), \quad (3)$$

where $g(\alpha)$ is the integral expression of the mechanism function model.

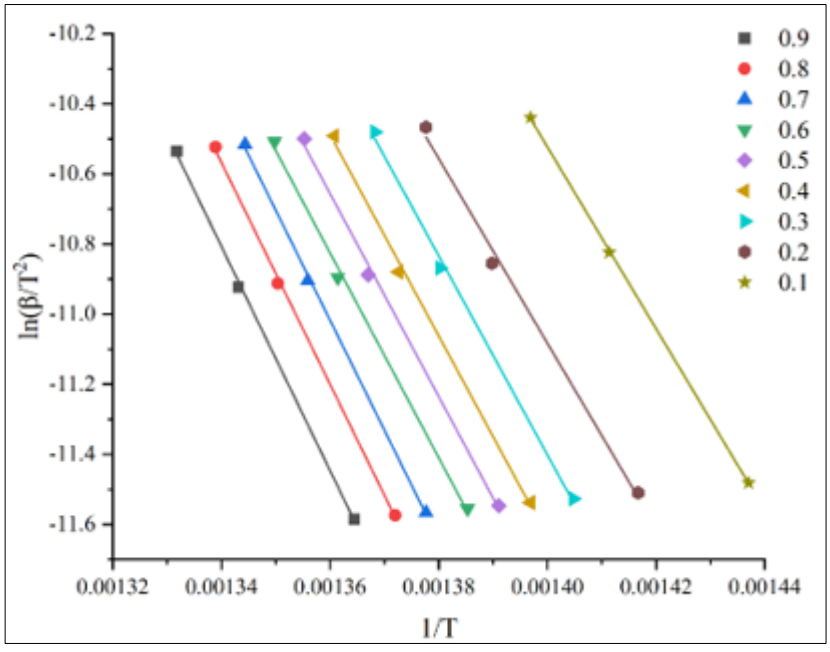
From (3), a linear fitting line between $ln\left(\frac{\beta}{T^2}\right)$ and $\frac{1}{T}$ can be obtained from the data of the thermogravimetric experiment when α is determined in the KAS method. The activation energy E_α can be calculated from the slope of the fitting line.

In this experiment, the activation energy of two types of PP particles was preliminarily calculated.

Linear fitting was performed on $ln\left(\frac{\beta}{T^2}\right)$ and $\frac{1}{T}$, and the activation energy was solved. The linear fitting curves of PP without paint and PP with paint are shown in Figure 5, and Table 4 shows the activation energy calculation table for the two types of PP particles. The calculation results show that the activation energy of PP containing paint ranges from 189.145 kJ/mol to 199.513 kJ/mol, with an average value of 193.903 kJ/mol. Moreover, the R^2 of the KAS method fitting the straight line is relatively low, suggesting that it is due to the complex composition of the paint; The activation energy of PP without paint is between 215.506 kJ/mol-265.794 kJ/mol, with an average value of 242.425 kJ/mol. The R^2 fitted using this method is relatively high. Compared with Chen's study [28] (249.65kJ/mol), the activation energy of PP containing paint was significantly reduced, while the activation energy of PP without paint showed little change.

Table 4. Activation energy of two types of PP particles calculated by KAS method

	PP without paint		PP with paint	
α	E_α(kJ/mol)	Correlation coefficient R^2	E_α(kJ/mol)	Correlation coefficient R^2
0.1	215.506	0.9999	189.145	0.8295
0.2	218.936	0.9954	196.203	0.8611
0.3	235.963	0.9977	194.423	0.8942
0.4	238.654	0.9977	199.513	0.9285
0.5	240.686	0.9977	196.161	0.9069
0.6	242.729	0.9977	192.195	0.9103
0.7	260.690	0.9993	190.570	0.8965
0.8	262.871	0.9993	196.251	0.8838
0.9	265.794	0.9993	190.662	0.8794



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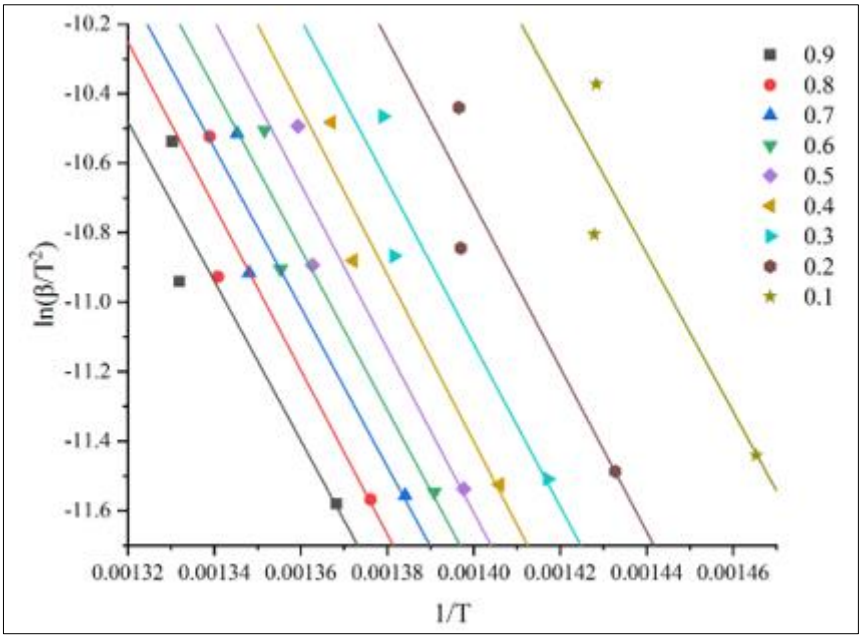
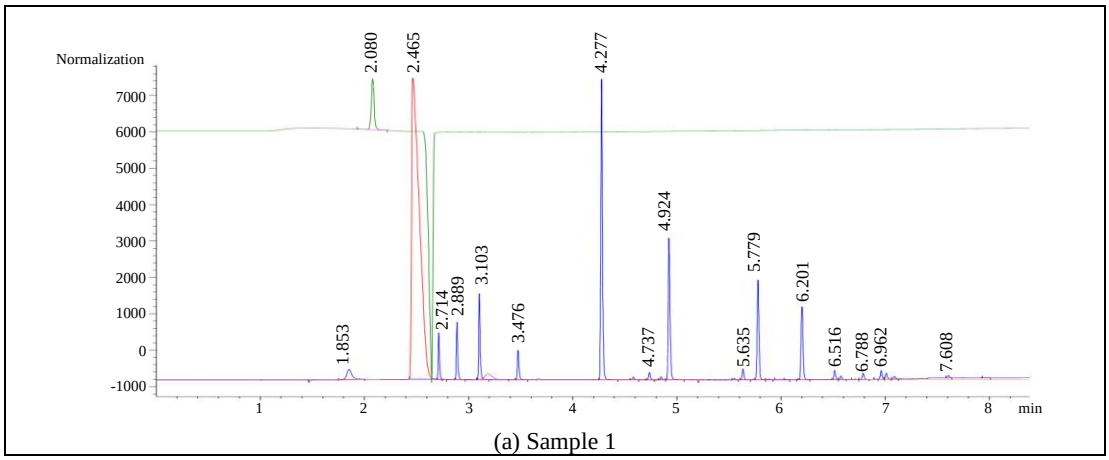


b

Figure 5. Linear fitting curves (a)PP linear fitting curve without paint (b)PP linear fitting curve with paint

3.3. GC and GC-MS analysis

As shown in Figure 6, the GC analysis results of four sample gas products were obtained using a normalized quantitative method during gas chromatography experiments. In the GC analysis diagrams of the four samples, the blue line represents the front signal, which mainly analyzes the composition of various organic compounds in the gas product; the red line represents the rear signal, which mainly analyzes carbon oxides; and the green line is the auxiliary signal, and its main analysis object is hydrogen gas.



(a) Sample 1

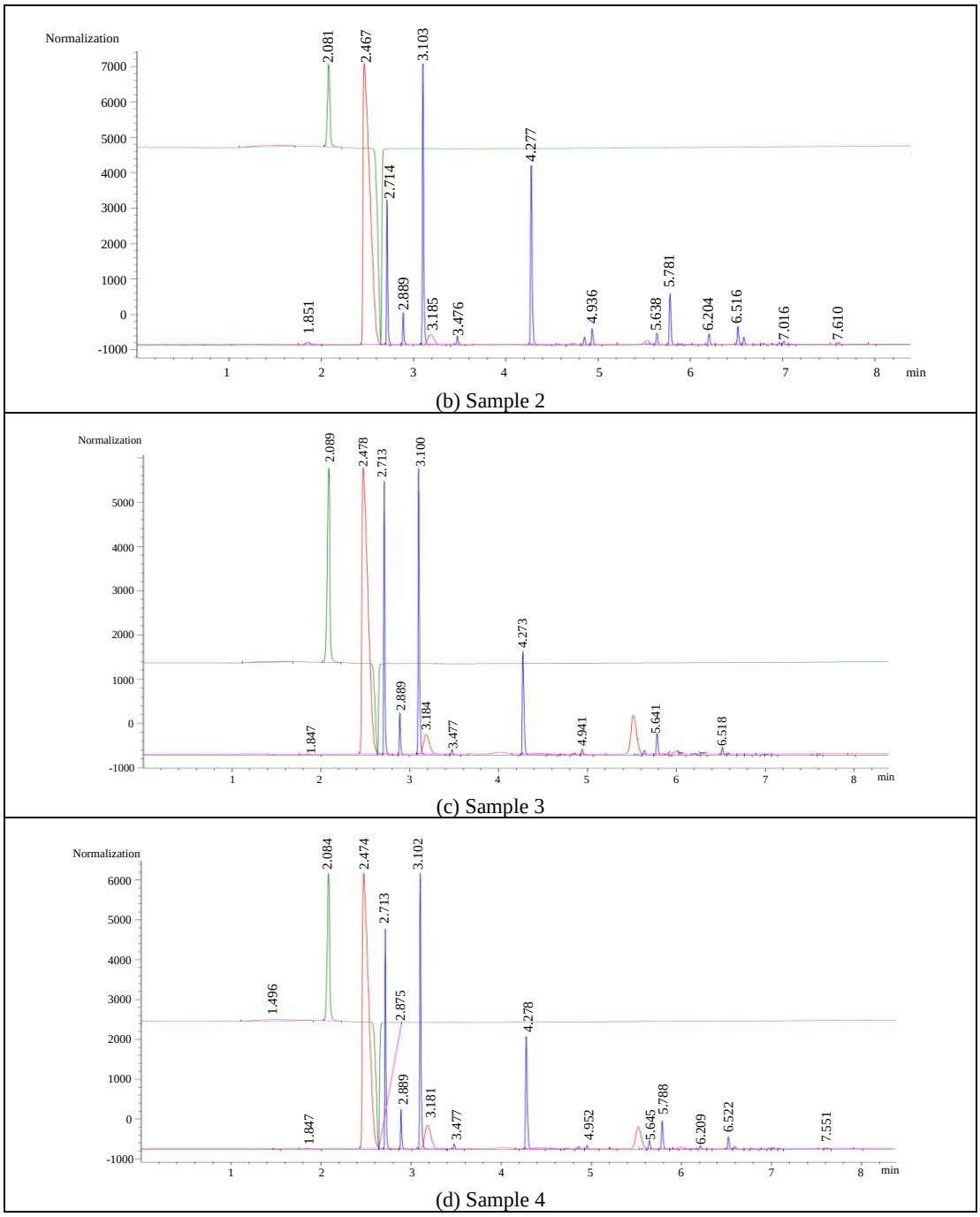


Figure 6. GC analysis diagrams for four samples

The GC-MS (chromatographic column: HP-5MS, 30 m×0.25 mm i.d.×0.25 μm thickness) analysis results of the liquid products of the four samples are presented in Figure 7. The initial temperature of the column temperature box was 50°C, which was increased to 280°C at 15°C/min and maintained for 10 min. The temperature of the gasification chamber and transmission line was 280°C. Helium was used as the carrier gas with a flow rate of 1 mL/min.

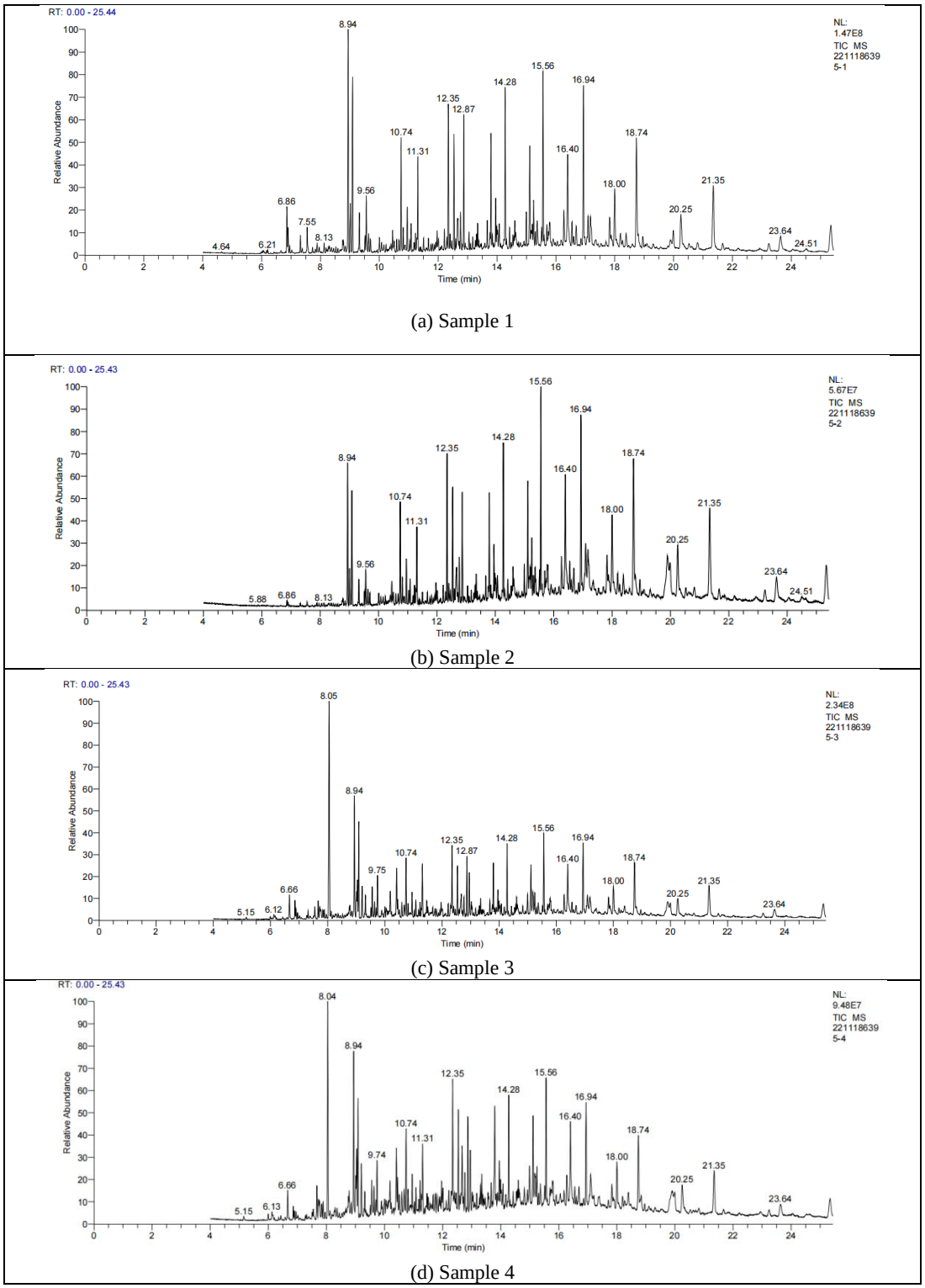


Figure 7. GC-MS analysis diagrams for four samples

The main component of automotive PP is polypropylene, with the chemical formula $(C_3H_6)_n$. After heating and cracking, the carbon–carbon single bond in the PP polymer molecule will break, and the gas produced is mainly composed of various low-carbon hydrocarbons. With the recombination and random binding of carbon-carbon single bonds, the alkanes and olefins in the product undergo aromatization reactions, which results in the formation of organic compounds with different carbon atom numbers, such as alkanes, olefins, alkynes, aromatics, and cyclohydrocarbons, in the liquid oil [29].

3.4. Result comparison

3.4.1. Effect of temperature on products

The gas products of Samples 1 and 2 are compared in Figure 8. Given the use of an argon gas atmosphere during the experiment and the small mass of the heated samples, more than 95% of the gas collected in the gas products of each group of samples is argon gas. As shown in the diagram, less leakage of gas substances occurs at lower temperatures. The high temperature promotes the fracture of carbon–carbon single bonds in PP as the temperature increases, which leads to a significant rise in the production of gaseous substances. The proportion of gas products in the total collected gas increases from 0.75 wt.% to 4.81 wt.%.

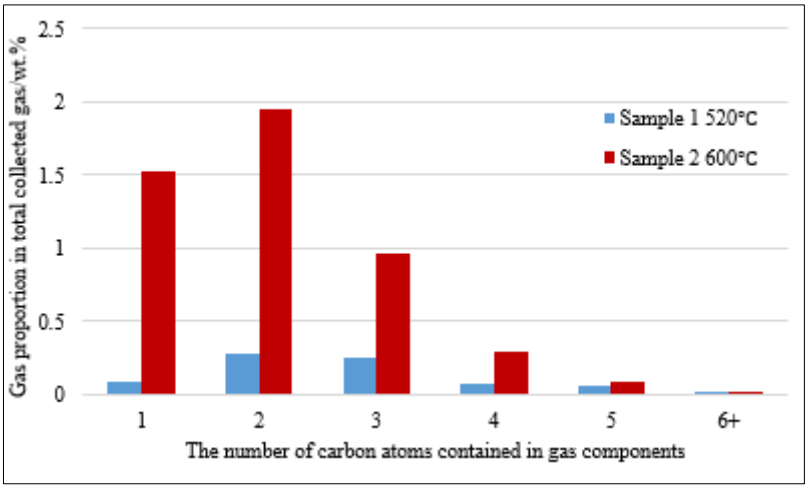


Figure 8. Comparison of gas product composition between Samples 1 and 2

At the same time, the content of C_1 and C_2 compounds in the gas products significantly increases as the temperature rises. In the proportion of total gas products, the product content of C_1, namely, methane (CH_4), increases from 1.76 wt.% to 31.60 wt.%, and the total content of C_2 products rises from 37.35 wt.% to 40.44 wt.%. Among them, the content of ethane (C_2H_6) decreases from 7.25 wt.% to 3.87 wt.%, the content of ethylene (C_2H_4) increases from 10.95 wt.% to 34.56 wt.%, and the content of acetylene (C_2H_2) changes the most from 19.19 wt.% to 2.01 wt.%. Meanwhile, the content of C_3 products decreases from 34.21 wt.% to 20.03 wt.%, with the majority of C_3 products being propylene (C_3H_6), and the content of propylene drops from 30.73 wt.% to 18.37 wt.%.Compared with the research conducted by Das et al. [30], the yield of CH_4 generated in this study is higher, which is speculated to be due to the higher pyrolysis temperature compared to Das [30] (350ºC-400ºC). Therefore, the dehydrogenation reaction in the product is enhanced, producing more CH_4, which is similar to the research results of Shi [31].

The comparison of the content of different liquid products in the total product between Samples 1 and 2 is shown in Figure 9. The distribution of products in the total product indicates that products of low carbon atomic number in Sample 1 account for a larger proportion of the total product, while C_{25} products account for a larger proportion in the pyrolysis results of both samples. After the temperature increases, the proportion of alkane content in the product significantly rises from 26.21 wt.% to 34.37 wt.%. Therefore, an increase in temperature can improve the fracture of carbon–carbon multiple bonds. The pyrolysis results of both samples contain a high proportion of alcohol substances, which is speculated to be caused by the fracture of silicon oxygen bonds in talc powder and the reformation of carbon oxygen bonds between carbon and oxygen atoms. At the same time, the increase in temperature reduces the generation of alcohol, and the proportion of alcohol substances decreases from 43.58 wt.% to 40.23 wt.%.

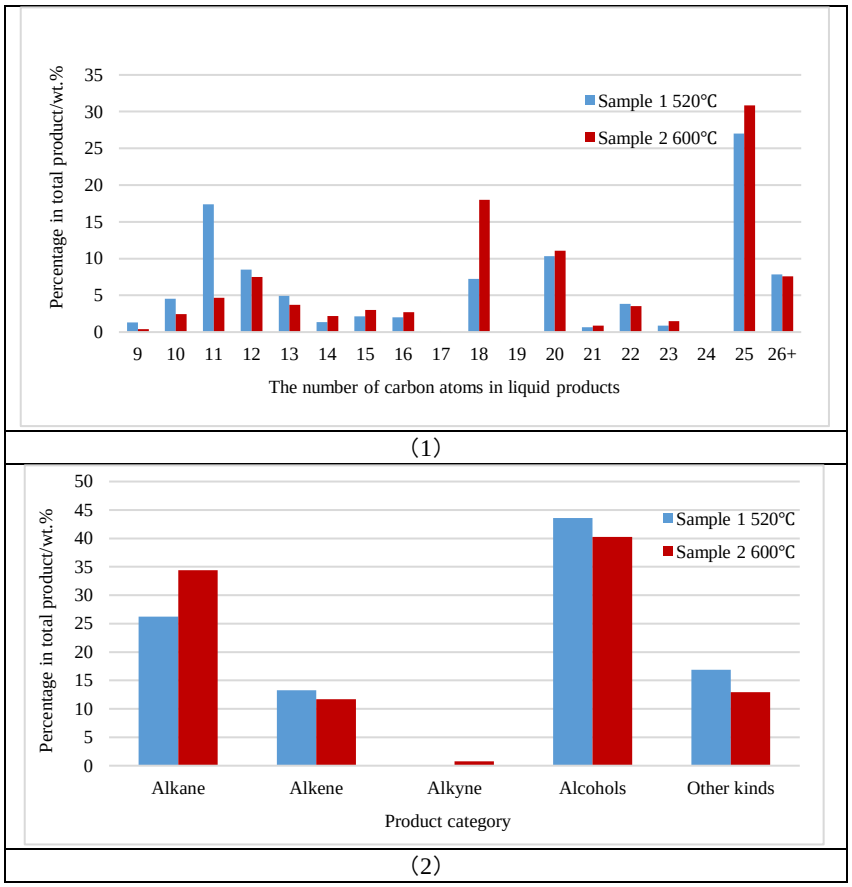


Figure 9. Comparison of liquid product composition between Samples 1 and 2:
(1) Carbon atom number distribution of two sample products
(2) Distribution of two sample product types

3.4.2. Effect of microwave power on products

The gas products of Samples 2 and 3 are compared in Figure 10. As shown in the diagram, after the increase in microwave power, the content of gas escape significantly improves, and the total content in the collected gas rises to 20.77 wt.%. As the microwave heating power increases, the heating rate also enhances, which makes the carbon bonds in the polymer more easily broken, and the content of products with low carbon atomic number in the gas products also rises.

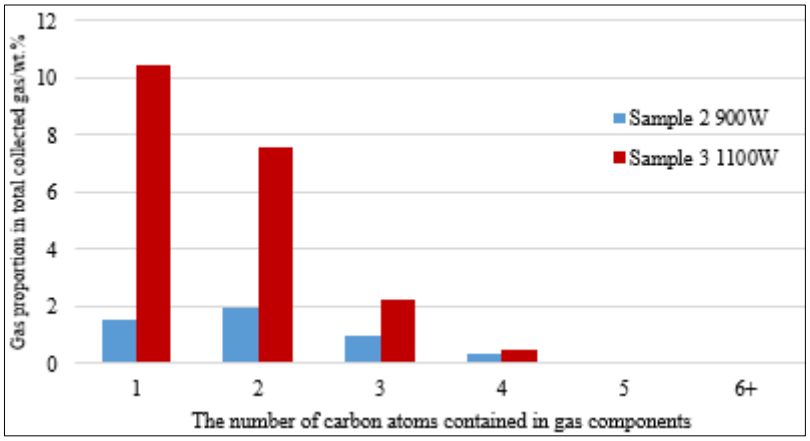


Figure 10. Comparison of gas product composition between Samples 2 and 3

After the increase in microwave power, the content of C_1 compounds in the gas products significantly rises. In the proportion of total gas products, the product content of CH_4 increases from 31.59 wt.% to 50.24 wt.%. Compared with the rise in temperature, the total content of C_2 compound products decreases from 40.44 wt.% to 36.51 wt.%. Among them, the content of C_2H_6 improves from 3.87 wt.% to 4.29 wt.%, the content of C_2H_4 decreases from 34.56 wt.% to 31.54 wt.%, and the content of C_2H_2 drops from 2.01 wt.% to 0.66 wt.%. Meanwhile, the content of C_3 products declines from 20.03 wt.% to 10.75 wt.%, with the majority of C_3 products still being C_3H_6, and the content of propylene decreases from 18.37 wt.% to 10.09 wt.%. With the increase of microwave power, the yield of gas products has significantly improved, which is similar to literature [30]. After the increase of microwave power, the heating rate will significantly increase, and a large amount of PP will further decompose, resulting in the production of more gas.

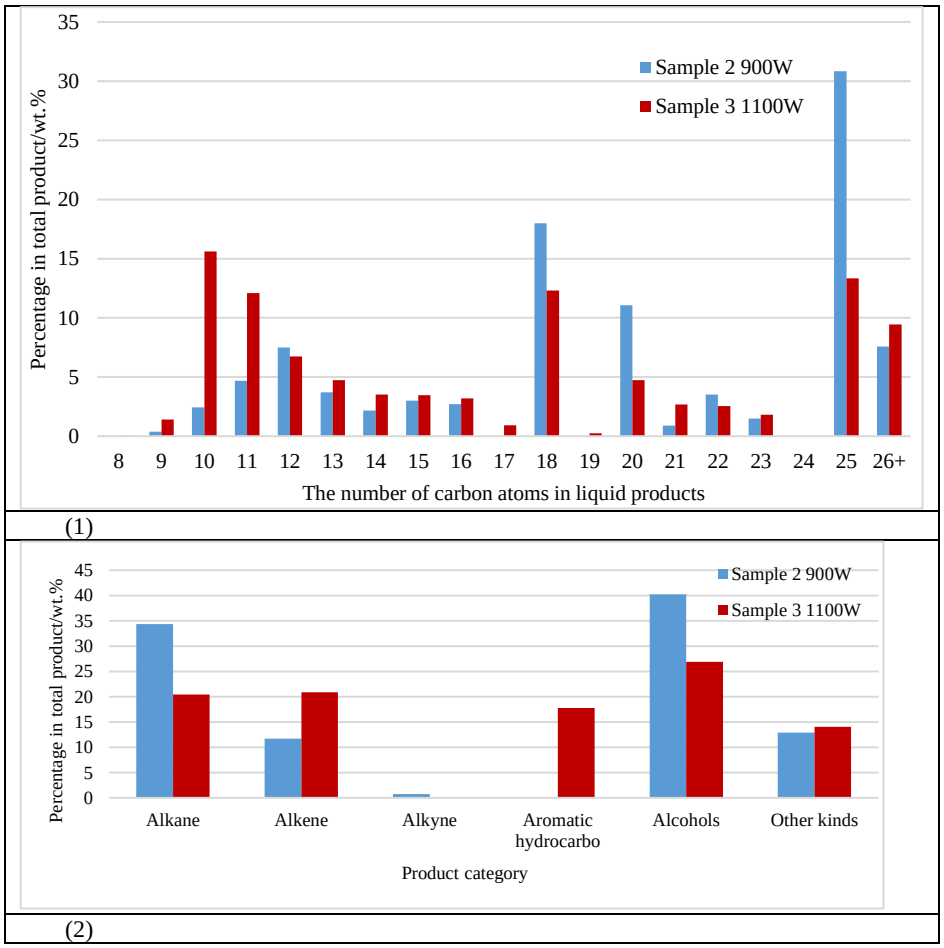


Figure 11. Comparison of liquid product composition between Samples 2 and 3: (1) Carbon atom number distribution of two sample products (2) Distribution of two sample product types

The comparison of the content of different liquid products in the total product between Samples 2 and 3 is shown in Figure 11. The percentage of substances with different carbon atom numbers in the total product indicates that, as the microwave power increases, the percentage of products with higher carbon atom numbers in the total product significantly decreases, while the content of products with lower carbon atom numbers rises. The most significant decrease is in the C_{25} compound, which drops in percentage from 30.84 wt.% to 13.35 wt.% after increasing the microwave power. The most significant increases are in the C_{10} and C_{11} compounds, with the C_{10} compounds improving from 2.45 wt.% to 15.62 wt.% and the C_{11} compounds enhancing from 4.67 wt.% to 12.10 wt.%. Meanwhile, the distribution map of product types indicates that the increase in microwave power promotes the

aromatization of PP, and the content of aromatic hydrocarbons significantly rises and accounts for 17.78 wt.% of the total product. After the increase in microwave power, the content of alcohol in the product also significantly decreases from 40.23 wt.% to 26.86 wt.%.

3.4.3. Effect of polymer surface painting on products

The gas products of Samples 3 and 4 are compared in Figure 12. As shown in the diagram, the addition of paint inhibits the formation of gas products, and the total gas production decreases from 20.77 wt.% to 14.39 wt.%. At the same time, the percentage changes of each component in the gas products exhibit no significant difference.

After paint is added, the proportion of CH_4 in the product decreases slightly, but the drop is insignificant, which is from 50.24 wt.% to 44.93 wt.%. The total amount of C_2 compounds increases from 36.51 wt.% to 37.99 wt.%, the C_2H_6 content rises from 4.29 wt.% to 4.49 wt.%, the C_2H_4 content improves from 31.54 wt.% to 33.03 wt.%, and the C_2H_2 content decreases from 0.66 wt.% to 0.48 wt.%. Meanwhile, the content of C_3 products rises from 10.75 wt.% to 12.74 wt.%, with the majority of C_3 products still being C_3H_6, and the content of propylene enhances from 10.09 wt.% to 11.92 wt.%.

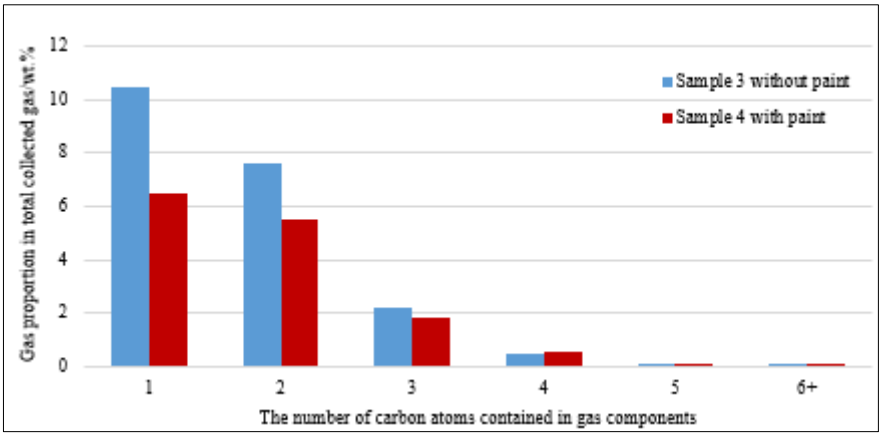
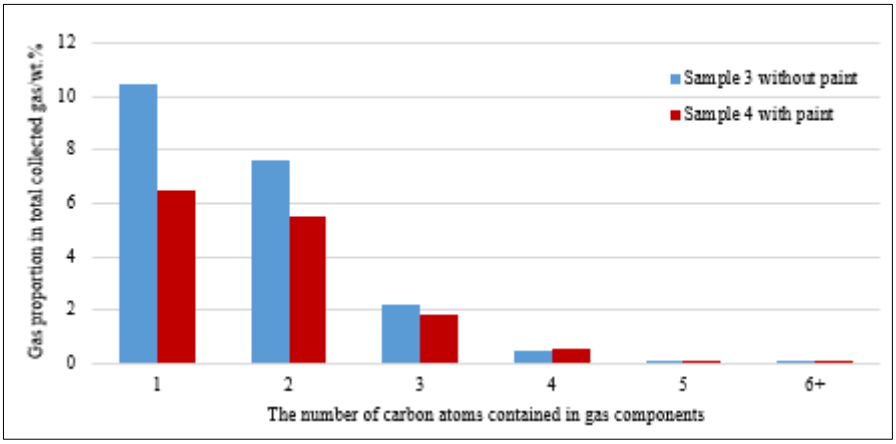


Figure 12. Comparison of gas product composition between Samples 3 and 4



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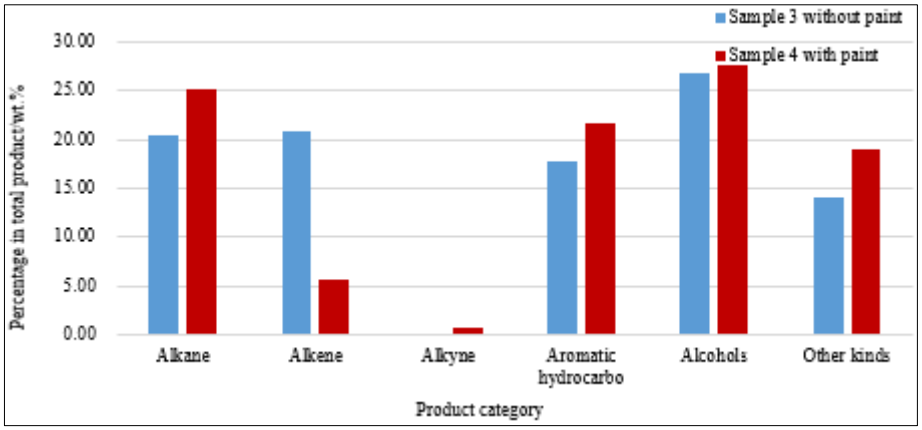

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Figure 13. Comparison of liquid product composition between Samples 3 and 4:
(1) Carbon atom number distribution of two sample products
(2) Distribution of two sample product types

The comparison of the content of different liquid products in the total product between Samples 3 and 4 is shown in Figure 13. According to the distribution map of carbon atom number, the addition of paint increases the proportion of compounds with high carbon atom number, especially the proportion of C_{19} and C_{20} compounds in the product. The content of C_{19} compounds increases from 0.24 wt.% to 3.86 wt.%, while the content of C_{20} compounds rises sharply from 4.75 wt.% to 14.43 wt.%; at the same time, the proportion of low-carbon compounds decreases, with the proportion of C_{10} compounds dropping from 15.62 wt.% to 9.11 wt.%, and the content of C_{13} compounds declining from 4.73 wt.% to 1.08 wt.%. The proportion of other carbon compounds slightly changes. The distribution map of product types shows that the addition of paint significantly reduces the content of olefins, while alkanes and aromatic compounds increase: the content of olefins decreases from 20.90 wt.% to 5.77 wt.%; the content of alkanes increases from 20.42 wt.% to 25.26 wt.%, and the content of aromatic compounds rises from 17.78 wt.% to 21.63 wt.%. At the same time, the content of alcohols and other substances improves, which is speculated to be due to the complex composition of the paint, high oxygen atom numbers, and impurities. This phenomenon leads to the combination of C atoms and other substances, which produces alcohols and other impurities. This finding is consistent with the higher content of oxygen atoms in PP-containing paint in the elemental analysis.

4. Conclusions

With the development of automobile lightweight, the proportion of plastics used in automotive is increasing rapidly. Microwave pyrolysis is a convenient and efficient method for treating waste plastics that can effectively reduce environmental pollution. Currently, research on the microwave pyrolysis of automotive plastics is limited.

In the study, a microwave atmosphere tube furnace was used to conduct comparative pyrolysis experiments on waste automotive PP under different conditions. First, technical analysis, elemental analysis, and TGA were performed on automotive PP. Then, microwave pyrolysis experiments were conducted on automotive PP using temperature, microwave power, and the presence or absence of paint as variables. The composition of the products was analyzed using GC and GC-MS to explore the influence of the three factors on the pyrolysis products of automotive PP.

The complete reaction temperature of both types of automotive PP is approximately 500 ℃. The calculation results show that the activation energy of PP containing paint ranges from 189.145 kJ/mol-199.513 kJ/mol, with an average value of 193.903 kJ/mol. The activation energy of PP without paint is between 215.506 kJ/mol-265.794 kJ/mol, with an average value of 242.425kJ/mol. The increase in temperature can promote the generation of gases and the fracture of carbon–carbon multiple bonds into carbon–carbon single bonds, which raises the content of alkanes in liquid products. The rise in

microwave power can further promote gas generation, with methane and other low-carbon compound gases being more significantly enhanced. The product content of CH_4 increases from 31.59 wt.% to 50.24 wt.%. At the same time, the increment in microwave power can improve the occurrence of aromatization reactions, which results in an increase in the content of aromatic hydrocarbon compounds. The addition of paint has a relatively small effect on the products of automotive PP. Automotive PP containing paint can be heated by microwave heating while reducing gas production and increasing the content of aromatic hydrocarbons in liquid oil.

The study indicates that using microwave pyrolysis to treat automotive PP with and without paint is feasible. The proportion of different substances in the product can also be changed by adjusting the maximum heating temperature and microwave power. In the future, further exploration will be conducted on the activation energy of pyrolysis reactants under the action of catalysts and the composition of pyrolysis products.

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