

Plasma-catalytic pyrolysis of polypropylene for hydrogen and carbon nanotubes: Understanding the influence of plasma on volatiles

Haoyu Xiao ^a, Shujiang Li ^a, Zhen Shi ^a, Cunhao Cui ^b, Sunwen Xia ^a, Yingquan Chen ^{a,},
Zhongyue Zhou ^{b,*}, Xin Tu ^c, Xu Chen ^d, Haiping Yang ^a, Hanping Chen ^a*

^aState Key Laboratory of Coal Combustion, School of Energy and Power Engineering, Huazhong University of Science and Technology, Wuhan, 430074, China

^bSchool of Mechanical Engineering, Shanghai Jiao Tong University, Shanghai, 200240, China

^cDepartment of Electrical Engineering and Electronics, University of Liverpool, Liverpool L69 3GJ, UK

^dSchool of Modern Industry for Selenium Science and Engineering, Wuhan Polytechnic University, Wuhan, 430023, China

*Corresponding Author. E-mail address: chenyingquan@hust.edu.cn, zhongyue.zhou@sjtu.edu.cn

Abstract: Plasma-catalytic pyrolysis was developed for upgrading polypropylene (PP) pyrolysis volatiles to co-produce carbon nanotubes (CNTs) and hydrogen. To uncover the role of plasma on the plastic catalytic pyrolysis process, the pyrolysis of polypropylene (PP) over Fe/ γ -Al₂O₃ was carried out in a two-stage pyrolysis system with a coaxial dielectric barrier discharge (DBD) plasma reactor. The results showed that the plastic pyrolysis volatiles were further cleaved and activated with plasma, resulting in more active carbon species for the growth of CNTs. Compared to conventional catalytic pyrolysis, plasma addition shifted the initial formation temperature of CNTs to a lower ambient temperature by ~ 100 °C, and significantly promoted the conversion of liquid and gaseous products to CNTs and hydrogen, with higher carbon and hydrogen yields of ~ 322 mg/g_{plastic} and 30 mmol/g_{plastic}, respectively. In addition, the degree of graphitization of the CNTs in the presence of the plasma was significantly enhanced with less defectivity. The influence of catalytic temperature variation caused by plasma on CNTs growth was also discussed from the perspective of volatile evolution. This work highlights the potential of plasma-catalytic pyrolysis for the production of hydrogen and high-value carbon materials from plastic waste.

Keywords: Plastic; Pyrolysis; Plasma-catalysis; Hydrogen; Carbon nanotubes

1. Introduction

The unstoppable production of plastic waste has brought great dangers to the ocean[1], soil[2], and human health[3]. Catalytic pyrolysis can convert plastic waste into valuable products such as gas, fuels, chemical, and functional carbon materials, it attracted increasing concern[4].

The co-production of CNTs and hydrogen represents an attractive potential solution for further improvement of the economy, applicability and sustainability[5]. Edwards et al.[6] put forward a one-step process that transforms commercial plastic into multiwalled carbon nanotubes and hydrogen with abundant and inexpensive iron-based catalysts. This highlights the potential of plastic waste for the production of high-value carbon materials and hydrogen.

The catalytic temperature is the critical factor in determining the formation of CNTs during plastic catalytic pyrolysis[7]. Acomb et al.[8] performed the catalytic pyrolysis of plastic (LDPE) at various synthesis temperatures, and obtained the highest quality CNTs and hydrogen at 800 °C. Mishra et al.[9] also observed that plastic pyrolysis at 800 °C gives the purest CNTs. Yao et al.[10] observed that the carbon yield was lower and only a very small amount of CNTs were formed at lower temperatures (<700 °C). Zhang et al.[11] reported that low temperatures led to rapid deactivation of catalysts due to surface coke deposition. It can be seen that the co-production of CNTs and hydrogen from plastic requires a high catalytic temperature of around 800 °C. However, high catalytic temperatures tend to cause agglomeration of pyrolysis volatiles, catalyst deactivation, high energy and equipment costs, ultimately limiting its application.

Cold plasma can generate high-energy electrons at nearly room temperature, that break C-H bonds, promoting carbon deposition and hydrogen formation. Meanwhile, the highly reactive environment is conducive to the decomposition of pyrolysis volatiles, allowing thermodynamically unfavourable reactions to occur at low temperatures. Wang et al.[12] used radio frequency-plasma lower the synthesis temperature of CNTs from CH₄ to 180 °C. Blanquet et al.[13] found that the introduction of dielectric barrier discharge (DBD)

plasma increased the hydrogen yield by 3.5 times during the biomass wastes pyrolysis process at a catalytic temperature of 250 °C. Gallon et al.[14] reported that plasma-assisted reduction of NiO catalyst achieved CH₄ conversions of 37% as well as 99% selectivity towards hydrogen and carbon with lots of carbon nanofibers at 330 °C. These showed the great potential of introducing plasma to enhance the formation of CNTs and hydrogen at a lower temperature. However, currently almost all studies about CNT production with plasma technology have focused on using pure gases such as methane, ethylene, propylene, and so on, whereas plastic pyrolysis produces much more complex hydrocarbons (volatiles), resulting in an unclear plasma effect. Furthermore, most studies have concentrated on the effect of plasma on catalysts, with only a few studies focusing on the effect of plasma on volatiles evolution.

Hence, plasma-catalytic pyrolysis of plastic over Fe/Al₂O₃ for the co-production of CNTs and hydrogen was investigated. The evolutions of plastic pyrolysis volatiles caused by plasma were investigated to discover more about the role of plasma for the formation of CNTs and hydrogen. This research was conducted to provide a deeper understanding of the effects of volatiles (carbon sources) on the products of carbon and hydrogen.

2. Materials and methods

2.1. Materials

The PP sample used in this study was obtained from Mingjin Plastic Ltd., China. The proximate analyses were conducted according to ASTM standards E790, E897, and E830, respectively, and the ultimate analyses were determined with a CHNS/O elementary analyzer (Vario Micro Cube, Elementar, Germany)[15]. Samples contained abundant

volatile matter (99.87 wt%) as well as limited fixed carbon and ash. The elemental content was 85.18 wt% C, 13.74 wt% H, and 0.87 wt% O on a dry basis.

$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ($\geq 98.50\%$) and $\gamma\text{-Al}_2\text{O}_3$ ($\geq 99.99\%$) with a particle size of 10 nm were purchased from Sigma Aldrich (China). Absolute ethyl alcohol ($\geq 99.7\%$) was purchased from Sinopharm Chemical Reagent Co. Ltd. (China). The $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$ catalyst was prepared using an impregnation method. Firstly, 7.214 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in 20 ml absolute ethyl alcohol, then 9 g of $\gamma\text{-Al}_2\text{O}_3$ was added to ensure the initial Fe loading 10 wt.%. The precursors were stirred for 4 h at 50 °C with a magnetic stirrer, then dried in an oven at 105 °C overnight, followed by calcination at 800 °C for 2 h under an air atmosphere with a heating rate of 10 °C min^{-1} . The catalyst was crushed and sieved to a size smaller than 0.1 mm. It needs to be pointed out that no reduction before the catalytic pyrolysis as the gases produced during the pyrolysis-catalytic process such as H_2 and CH_4 might reduce the metal oxides in situ.

2.2. Plasma-catalytic pyrolysis experiment

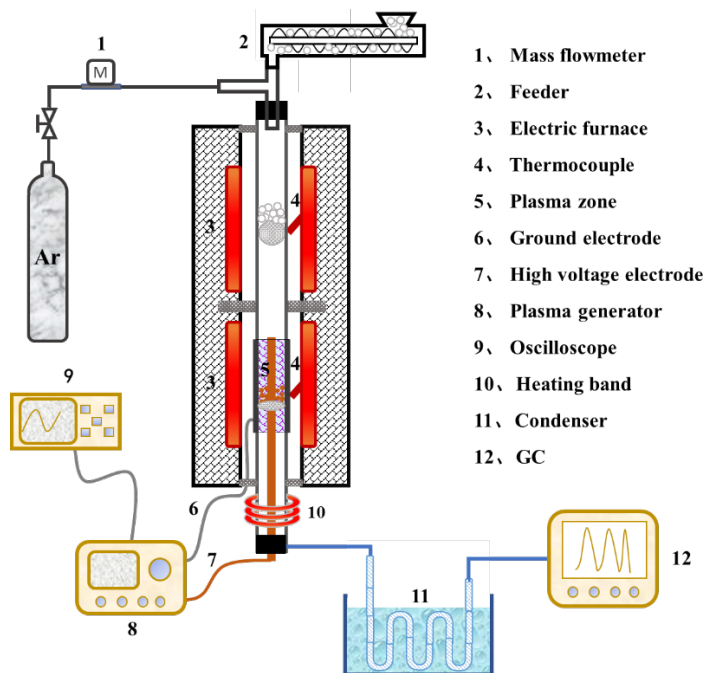


Fig.1. Schematic diagram of a reactor system for the plasma-catalytic pyrolysis of plastic.

Plasma-catalytic pyrolysis of plastic was performed in a two-stage reactor system (**Fig. 1**). The upstage is the plastic pyrolysis zone, while the downstage is the plasma-catalysis stage with a coaxial cylindrical dielectric barrier discharge (DBD) plasma generator. The details have been described in our work[16]. For each experiment, 2 g of PP and 1 g of catalyst were put in the feeder and plasma zone, respectively. Usually, the catalytic temperature would rise by 10-20 °C after the plasma was turned on. The PP sample was dropped into the pyrolysis zone (500 °C) after waiting for the furnace to adjust the plasma zone to the set temperature (600, 650, 700, 750, 800, 850 °C) and stabilize. Then the plastic pyrolysis volatiles were carried by argon (10 ml/min) to the plasma zone for 15 min reaction. The input power (120 W) remained constant by adjusting the input frequency and voltage parameters. The condensable liquids were obtained by an ice-water condenser, and the liquid yield was determined by the mass difference of the condenser. The uncondensed products were collected in a gas bag for gas chromatography (GC) analysis. The yield of carbon was determined as the weight difference between fresh and spent catalysts divided by the mass of feedstock. Each experiment was repeated two or three times and marked with error bars. All data obtained for the calculation of the product yields were average values within an error of $\pm 2\%$.

2.3.Products characterization

The gaseous products were analyzed offline using a dual channel GC system (Micro-GC 3000A, Agilent Technologies, USA), equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). Porapak Q (He as carrier gas) and 5A zeolite molecular sieve (MS-5A, He as carrier gas) are connected with TCD for the analysis of H₂,

N₂, O₂, CO₂, CO. Another column (Alumina) is connected with FID for the measurement of C₁-C₅. The N₂ concentration and flow rate were used as the tracer to calculate the mass of each gas (in volume, at 1 atm and 25 °C).

The species of liquid product were analyzed by GC-MS (HP7890 series GC and HP5975 MS detector), equipped with a capillary column (DB-5MS, 30 m×0.25 mm×0.25 μm, Agilent). The temperature was heated from 40 °C to 180 °C at 4 °C/min, then it was heated up to 280 °C at the rate of 10 °C/min. Finally, the temperature remained at 280 °C for 10 min. The split ratio of the sample was 80:1. Each specie was identified using the Agilent software with the NIST library, and determined according to the match score of software and experimental conditions.

For each experiment, almost no residue remained in the upper stage after pyrolysis, indicating that plastics were completely converted into volatiles. The amount of carbon deposited on the catalyst was determined with a Thermogravimetric analysis (STA-449F3 NETZSCH, Germany) by temperature-programmed oxidation method. The samples were heated from room temperature to 800 °C in the mixed gas of N₂ (79 ml/min) and O₂ (21 ml/min,) at a rate of 15 °C/min and a hold time of 30 min at 105 °C and 800 °C. The morphology of carbon products was measured by scanning electron microscopy (Gemini Sigma 300, Carl Zeiss AG Corporation, Germany). Furthermore, the degree of graphitization of the solid products was examined using Raman spectroscopy (LabRAM HR 800 Evolution Raman instrument, Horiba JobinYvon, France) with Raman spectra from 800 cm⁻¹ to 3200 cm⁻¹ with an excitation wavelength of 532 nm. Each sample was measured three or four times for the homogeneity of sampling, see Fig. S2.

3. Result and discussion

3.1. Plasma-catalytic pyrolysis behaviour of plastic waste

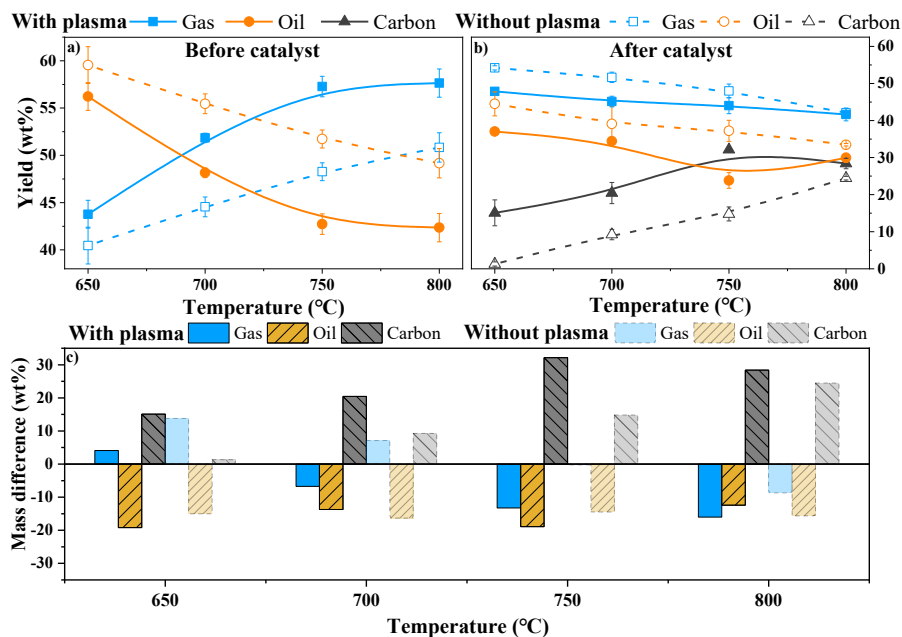


Fig.2. Comparison of product distribution between conventional catalytic and plasma-catalytic pyrolysis of PP at different catalytic temperatures a) before catalysis, b) after catalysis, and c) the mass increase after catalysis over that before catalysis.

The comparison of plasma-catalytic pyrolysis behaviour with conventional catalytic pyrolysis was first investigated. The yield distribution before catalysis at various catalytic temperature are shown in **Fig. 2a**. Without plasma, direct pyrolysis of PP produced large amounts of liquid (62 wt%) with some gas (38 wt%) at 650 °C, while no solid product was produced. Upon increasing the catalytic temperature, the oil and gas yields decreased and increased to nearly 50 wt%, respectively. With plasma add-in, the gas yield increased relative to the absence of plasma, while the liquid yield decreased. And the increase in gas yield as well as the decrease in liquid yield gradually became larger as the catalytic temperature increased. At 800 °C, the gas products reached the highest 56 wt%, and the

liquid products dropped to the lowest 44 wt%. These results suggest that plasma can promote liquid-to-gas conversions as much as increasing temperature.

After catalysis, as shown in **Fig. 2b**, large amounts of carbon products were formed, and the increasing temperature promoted the formation of carbon but decreased the yield of gas and liquid products. Introducing plasma further increased the carbon yield and greatly decreased the generation of gas and oil products at 650-750 °C, but no obvious variation of yield distribution was found when the temperature was raised to 800 °C. This indicates that plasma promoted the conversion of gas and liquid into carbon products, especially at lower temperatures. It might be attributed to that hydrocarbons from the plastic pyrolysis are decomposed to C and H ions by plasma, thus promoting carbon species adsorption on the catalyst, finally enhanced carbon deposition[17].

Fig. 2c shows the mass increase of various products after catalysis through the product difference before and after catalysis. The distribution of products before catalysis can be approximated as the components of pyrolysis volatiles, then used to determine which component of the volatiles is causing the product increase after catalysis. When the mass difference is positive, it means that it is the increased product that converted from other components in the volatiles. On the contrary, this kind of component in the volatiles is converted to other products when it is negative.

Without plasma, the mass difference of liquid was negative while the mass differences of gas and carbon were positive at 650 °C. It means that nearly 17 wt% of liquid components in the volatiles were converted into gaseous products (16 wt%) and little carbon deposits (1 wt%). Upon increasing catalytic temperature, the carbon increment kept increasing, while the liquid as the most weightless components showed no obvious

variation. In contrast, the gas increment began to decrease dramatically, and became negative when the temperature was higher than 750 °C. These results imply that the conversion of liquid components seems to be independent of temperature, whereas gas-phase components require higher temperatures for conversion to carbon products. Moreover, it is noteworthy that the reduction of liquid components has been greater than that of gas components. This result reveals that liquid components contribute more to carbon product formation than gaseous components during the conventional catalytic pyrolysis process[18].

With plasma, much more carbon (15 wt%) and less gas (6 wt%) were converted from liquid components at 650 °C compared to those in the absence of plasma. When varying the temperature from 650 °C to 800 °C, the carbon products increased first and reached a maximum of 32 wt%, then dropped to 28 wt%. It might be attributed to that higher temperature leads to the volatiles polycondensation which prevents carbon species from adsorbing to the catalyst surface. The mass difference of gaseous components became negative from 700 °C and kept decreasing as the temperature increased. The liquid components were still the main components for carbon products at a low temperature, but the proportion gradually became similar to that of the gaseous components as the temperature increased. These results suggest that plasma promoted the gaseous components of volatiles, which would have been relatively hard to convert by catalysis, to form carbon products, and the liquid components also have been further converted into carbon products by plasma. These results could be ascribed to the fact that a large number of active particles in the plasma decompose gaseous and liquid components into C and H ions and other reactive carbon sources at relatively low temperatures, thus facilitating the

chemical vapour deposition process at relatively lower temperatures. Meanwhile, the produced H ions could improve the wetting ability and activity of catalysts through reduction reaction[12].

3.2. Gaseous and liquid products releasing behaviour

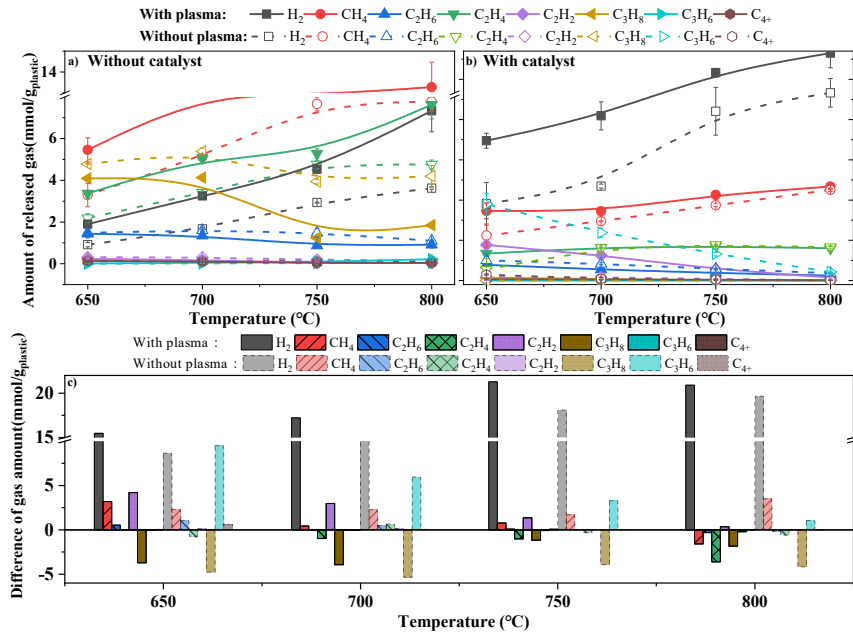


Fig.3. Comparison of gas composition between conventional catalytic and plasma-catalytic pyrolysis of PP at different catalytic temperatures a) without catalyst, b) with catalyst, and c) the mass increase with catalysis over that without catalysis.

Fig. 3a shows the variation of pyrolysis products without catalyst and plasma. At a lower temperature (650 °C), the gaseous components in plastic pyrolysis volatiles are mainly C₃H₈, CH₄, C₂H₆, and C₂H₄. Increasing the catalytic temperature increased the release of CH₄, C₂H₄, and H₂, and decreased the release of C₃H₈ and C₂H₆. When the temperature increased from 750 °C to 800 °C, almost no variation was observed in the amount of each released gas. Introducing plasma increased the release of CH₄, C₂H₄, and H₂ in the range of 650-800 °C, while a reduction of C₃H₈, and C₂H₆ was observed from 650 °C to 750 °C.

Further increasing temperature did not change the release of C_3H_8 , and C_2H_6 , indicating the decomposition of liquid components by plasma.

After catalysis, H_2 , CH_4 , and C_3H_6 are the main gas products (over $5 \text{ mmol/g}_{\text{plastic}}$) with trace C_2H_6 , C_2H_4 , C_2H_2 , C_3H_8 , and C_{4+} without plasma. As the temperature went up, the amount of H_2 increased significantly, while C_3H_6 suffered from a sharp decrease. Other gases change relatively weakly with increasing temperature. With the introduction of plasma, C_3H_6 was rarely produced, C_2H_2 was formed in large quantities at low temperatures, and the amount of H_2 released further increased significantly, reaching a maximum of $28 \text{ mmol/g}_{\text{plastic}}$ at $800 \text{ }^\circ\text{C}$. Increasing the catalytic temperature also slightly promoted the formation of CH_4 , but reduced the amount of C_2H_2 released. These results reflected that plasma enhanced the cleavage of C-H.

The mass increases of the gas amount after catalysis is shown in **Fig. 3c**. In the absence of plasma, the pre-and post-reaction changes of H_2 , CH_4 , C_3H_6 , and C_3H_8 are most significant. It was obvious that C_3H_8 is the only gaseous component that had been negatively increasing after the reaction, which reflected that C_3H_8 is an important reaction intermediate. When the catalytic temperature is between 650 and $750 \text{ }^\circ\text{C}$, the increasing amount of H_2 showed an upward trend, with a stagnation in growth as the temperature increases further, suggesting that the thermal catalytic effect is reaching its limit on the breaking of hydrocarbon bonds. The increment of C_3H_6 decreased sharply with increasing temperature, while CH_4 did not change significantly at the lower temperature stages and only showed a significant increase when the temperature rose to $800 \text{ }^\circ\text{C}$, this implied that CH_4 required a higher reaction activation temperature. With plasma, the variations of H_2 , CH_4 , C_2H_2 , and C_3H_8 became dominant, with only C_3H_8 showing negative growth. As the

catalytic temperature increased, the growth of all gases except H_2 and C_3H_8 began to decrease, and CH_4 as well as C_2H_2 gradually shifted from positive to negative growth. This indicates that plasma promoted the formation of C ions from CH_4 and C_2H_2 to enhance the deposition process.

Liquid products from the direct pyrolysis of plastics at 500 °C are mainly wax, which will stick to the inner wall of the reactor and is difficult to collect. A similar phenomenon has been reported in other studies[19, 20]. After the catalyst adding, the waxes are partly converted into light oils that can be easily collected and are mainly aromatics, as shown in **Fig. S1**.

3.3. Influence of plasma on carbon deposition

The morphology observations of carbon deposits at different temperatures are shown in **Fig. 4**. Without plasma, a large amount of granular carbon was obtained at low temperatures, and few fibrous carbons began to form at 700 °C. More homogeneous and longer nanotubes were seen at 750 °C, but small amounts of amorphous deposits still could be found. When the temperature reached 800 °C, the proportion of fibrous carbon further increased. As the temperature increased further, the carbon deposits became coral-like and fibrous carbon was greatly reduced, Moreover, the length of fibrous carbon became shorter, and a helical shape appeared. It might be that the excessive catalytic temperature leads to the polymerization of volatiles from plastic pyrolysis.

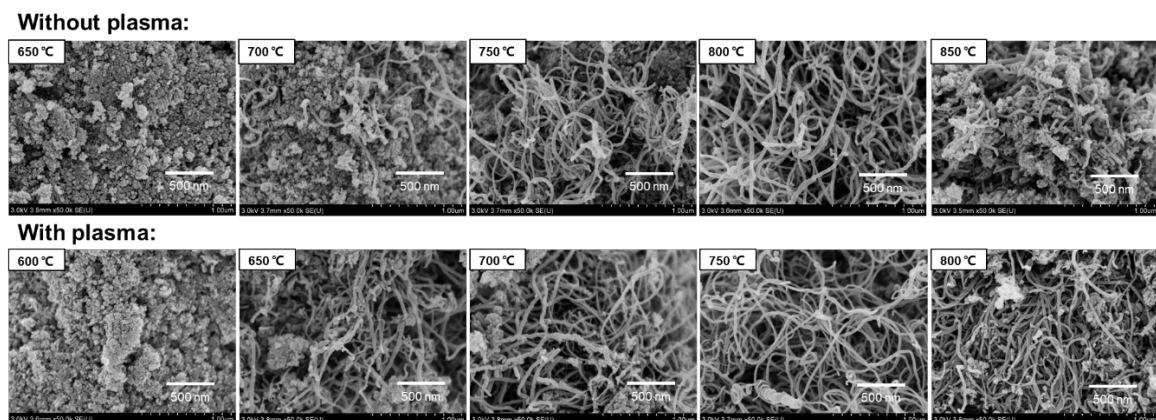


Fig. 4. SEM images of different carbon products from conventional catalytic pyrolysis and plasma-catalytic pyrolysis.

With plasma, the carbon deposits from the catalytic temperature of 600 °C appeared to be granular and irregular. When it increases to 650 °C, some filamentous carbons begin to be observed, showing lower catalytic activity. Upon the catalytic temperature increasing further, filamentous carbon was widely distributed and its length increased obviously. With the temperature rising to 750 °C, large amounts of carbon fibre were entwined with each other, clumping together. In addition, the length of filamentous carbon also increased significantly, to at least a few tens of microns. This means that the activity of the Fe catalyst has been greatly improved. However, when the temperature increased to 800 °C, the amount of filamentous carbon decreased. Meanwhile, only a small proportion of disordered carbon was found.

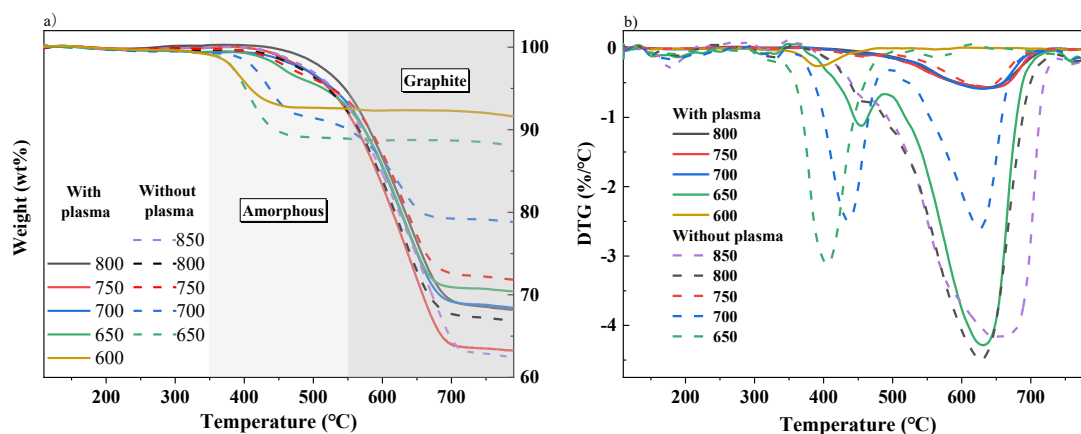


Fig. 5. Thermogravimetric analysis (TGA) of the carbon deposits from plasma-catalytic pyrolysis with the conventional case as control

The oxidation properties of carbon nanomaterials from the surface of used catalyst samples were investigated by temperature-programmed oxidation (**Fig. 5**). According to the loss weight ratio of catalysts after oxidation, the residues increased from 61 wt.% to 90 wt.%, when the catalytic temperature increased from 600 °C to 850 °C, indicating a larger amount of metal-based carbon growth with higher catalytic temperature. It is almost consistent with the previous carbon yield results (**Fig. 2**) that plasma-catalytic pyrolysis produced higher carbon deposits than conventional catalytic pyrolysis at high temperatures. Two types of carbon with oxidation temperature were defined by other work[8], where a lower temperature of TPO peak from 350 °C to 550 °C was related to amorphous carbons, and a higher temperature between 550 °C and 700 °C was associated with the filamentous graphite. Graphite can hardly be produced at 650 °C in the absence of plasma, As the catalytic temperature increased, progressively a higher proportion of graphite was observed in the carbon products. The introduction of the plasma results in a higher carbon content of graphite at 650 °C than even at 750 °C without the plasma. However, with the further increase in temperature, the increase in graphite carbon content

was not significant. This suggests that the plasma somewhat blunts the effect of temperature.

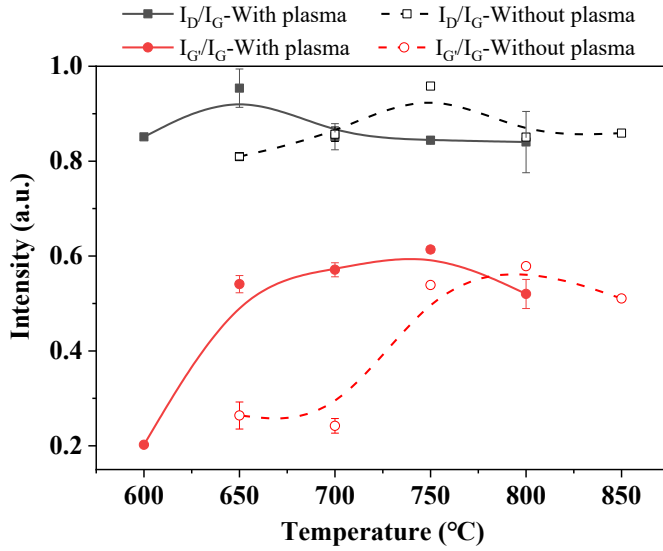


Fig. 6. Raman spectroscopy of the carbon deposits from plasma-catalytic pyrolysis with conventional one as the control

The carbon structure measured with Raman analysis as the crystallinity and graphitization degree of carbon deposits (**Fig. 6**). The defect and graphitization degree of carbon deposits are estimated through the peak intensity ratio of I_D/I_G and I_G/I_G . Without plasma, a higher ratio of I_G/I_G was observed, when the catalytic temperature was more than 750 °C, reflecting the higher purity of CNTs. In the meantime, the I_D/I_G ratio fluctuated within a small range (from 0.81 to 0.96), which indicates that the carbon defects are not strongly correlated with catalytic temperature. With plasma, a higher ratio of I_G/I_G was obtained at 650 °C, reflecting that plasma significantly reduced the growth temperature of CNTs. It can be seen that the carbon deposits obtained from plasma-catalytic pyrolysis at 650 °C to 800 °C and conventional catalytic pyrolysis at 750 °C to 850 °C have the I_D/I_G ratio between 0.84 and 0.96, and the I_G/I_G ratio from 0.51 to 0.61, comparably with the

CNTs in a commercial application or with other literature [21]. It is worth noting that the I_G/I_G ratio tends to decrease at high temperatures with or without plasma. This may be caused by the partial deactivation of the catalyst due to the polymerization of volatiles at high temperatures.

3.4. Possible mechanism for plasma-catalytic pyrolysis

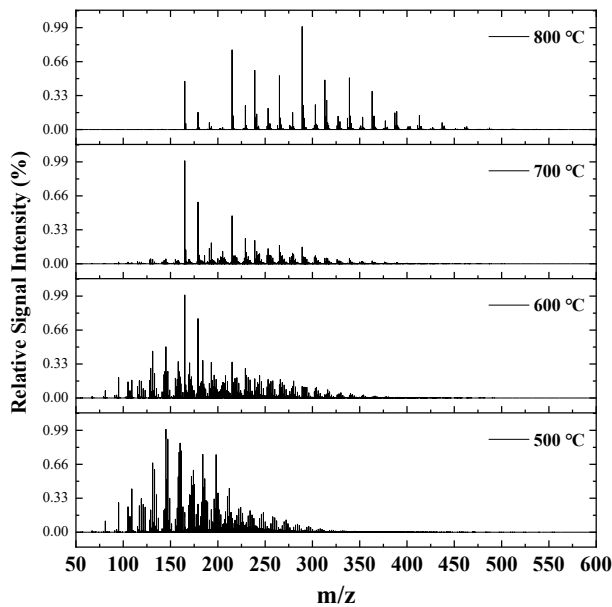


Fig. 7. High-resolution mass spectra of plastic pyrolysis volatiles.

In addition to cracking and activating the volatiles directly by plasma, the decrease in catalytic temperature indirectly caused by plasma may also affect the volatiles. To clarify the effect of lower catalytic temperature on the volatiles, an in-situ Atmospheric-pressure Photoionization High Resolution Mass Spectrometer (APPI HRMS) was used for direct detection of volatiles without secondary reaction (Fig.S3), and details are shown in our previous research[22]. **Fig. 7** compares the effect of different catalytic temperatures on the volatile fraction of plastic pyrolysis at 500°C. Remarkably, the component of volatiles was significantly altered by catalytic temperature. The plastic pyrolysis volatiles with a mass

distribution ranging from 50 to 330 Da were detected when the catalytic temperature was 500°C. As the catalytic temperature increased, the mass distribution became progressively larger, and the strongest signals also shifted towards higher mass distribution, indicating an increasing content of heavy components. When the catalytic temperature reached 800°C, a large number of components with a mass distribution above 300 were formed, probably due to polymerization reactions of volatile fractions caused by high temperatures. Obviously, the catalytic temperature has a great influence on the volatiles. This means that in addition to the direct effect of plasma on volatiles, the reduction of catalytic temperature caused by plasma cannot be ignored.

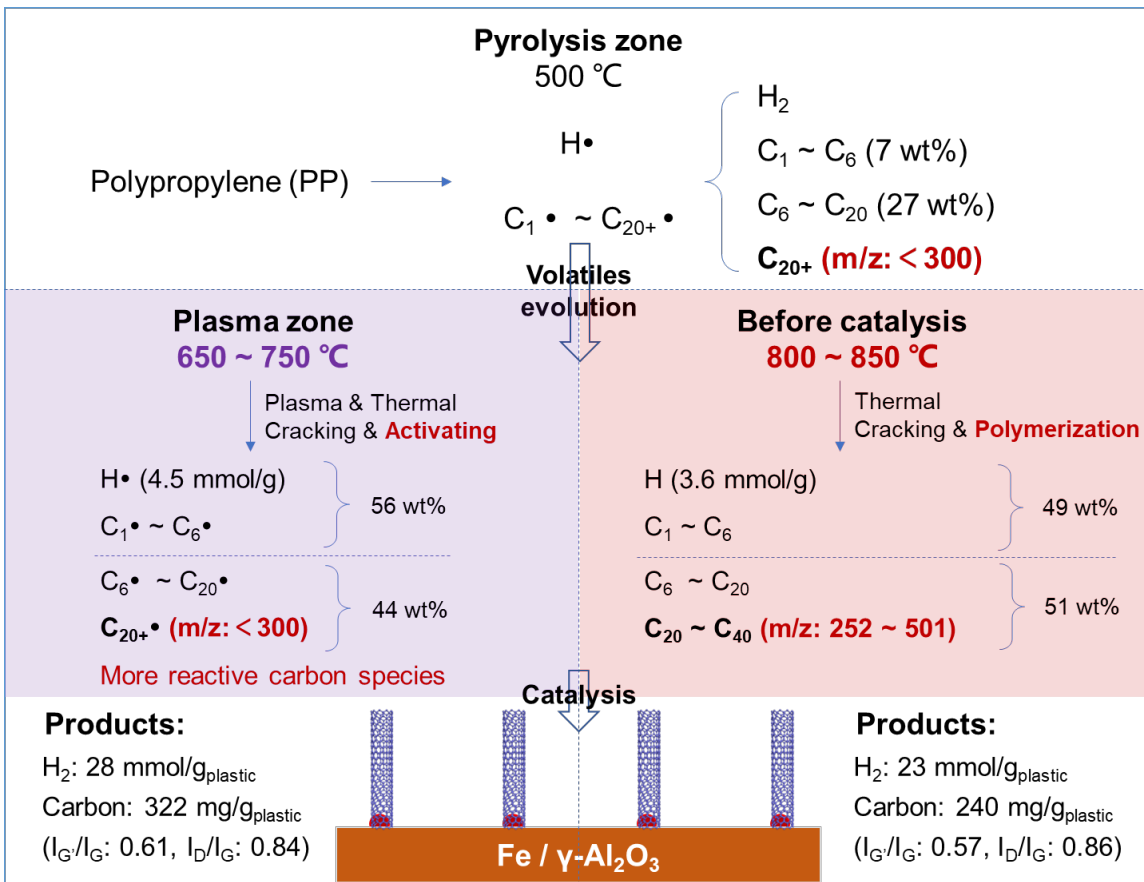


Fig. 8. Possible reaction mechanism for the plasma-catalytic pyrolysis process of plastic at a variety of temperatures.

According to the yield distribution, chemical compositions of disparate products, and discussion above, a possible reaction mechanism was proposed in **Fig. 8**. The plastic undergoes pyrolysis at 500°C, completely converting into the volatiles. Then a secondary reaction occurs when the volatiles enter into the catalytic zone. Volatiles can be divided into gas components (C_1-C_6) and liquid components (C_{6+}). In the absence of plasma, products are predominantly converted from the liquid components of the volatiles until the gas begins to partly participate in the conversion at 800 °C. The catalyst has to be around 800 °C to be active. As a result, the volatiles enter the catalytic zone and are further cleaved to generate light C and H species while also polymerizing to form a large number of heavy hydrocarbons (m/z : 252~501). Heavy hydrocarbons have been proven to be the primary precursor of amorphous carbon[23], which easily leads to catalyst deactivation and a reduction of CNT yield and quality. In contrast, the addition of plasma enables the catalyst to keep highly active at relatively lower temperatures, reducing the temperature in the catalytic zone, therefore limiting the polymerization of volatiles caused by higher temperatures. Moreover, plasma directly decomposes hydrocarbons especially gas components into C and H ions and other reactive radicals at lower temperatures. The concentration of C ions can thus keep high even when the cracking temperature is insufficient, meanwhile, the increasing H ions enhance the activity and wetting ability of the catalyst through its reduction reaction[24].

4. Conclusion

A simple plasma-catalytic pyrolysis process was described for rapidly deconstructing common plastics into high-value carbon materials and hydrogen. Plasma addition shifted the initial formation temperature of CNTs to a lower ambient temperature by ~100 °C, and

considerably promoted the production of CNTs and hydrogen. The increased production of CNTs and hydrogen is primarily due to the gaseous components of volatiles, which are difficult to convert but are assisted by plasma activation. And, regardless of the presence or absence of plasma, the liquid components of volatiles have been the major intermediates of the carbon product. On the other hand, the addition of plasma reduces the optimal catalytic temperature, therefore inhibiting the polymerization of volatiles caused by higher temperatures. Plasma technology can be extended to other ex-situ catalytic pyrolysis process for optimizing volatiles by reducing the discrepancy between the ideal temperature of pyrolysis and catalysis. These findings are important in representing an attractive potential solution for plastic waste through producing value-added carbon products and clean H₂.

Conflicts of interest

There are no conflicts to declare.

Acknowledgments

The authors wish to express sincere thanks for the financial support from the National Science Fund for Distinguished Young Scholars program (52125601), and National Natural Science Foundation of China (52006086). The authors are also grateful for the assistance on the catalyst analysis provided by the Analytical and Testing Center at Huazhong University of Science & Technology (<http://atc.hust.edu.cn>), Wuhan 430074, China.

Reference

- [1] Jambeck JR, Geyer R, Wilcox C, Siegler TR, Perryman M, Andrady A, et al. Plastic waste inputs from land into the ocean. *Science*. 2015;347:768-71.
- [2] Chae Y, An YJ. Current research trends on plastic pollution and ecological impacts on the soil ecosystem: A review. *Environmental Pollution*. 2018;240:387-95.

- [3] Lehner R, Weder C, Petri-Fink A, Rothen-Rutishauser B. Emergence of nanoplastic in the environment and possible impact on human health. *Environmental Science & Technology*. 2019;53:1748-65.
- [4] Geyer R, Jambeck JR, Law KL. Production, use, and fate of all plastics ever made. *Science Advances*. 2017;3:5.
- [5] You S, Sonne C, Ok YS. COVID-19: Resource recovery from plastic waste against plastic pollution. *Cogent Environmental Science*. 2020;6:1801220.
- [6] Jie XY, Li WS, Slocombe D, Gao YG, Banerjee I, Gonzalez-Cortes S, et al. Microwave-initiated catalytic deconstruction of plastic waste into hydrogen and high-value carbons. *Nature Catalysis*. 2020;3:902-12.
- [7] Huang C-W, Wu H-C, Lin W-H, Li Y-Y. Temperature effect on the formation of catalysts for growth of carbon nanofibers. *Carbon*. 2009;47:795-803.
- [8] Acomb JC, Wu C, Williams PT. Effect of growth temperature and feedstock:catalyst ratio on the production of carbon nanotubes and hydrogen from the pyrolysis of waste plastics. *Journal of Analytical Applied Pyrolysis*. 2015;113:231-8.
- [9] Mishra N, Das G, Ansaldo A, Genovese A, Malerba M, Povia M, et al. Pyrolysis of waste polypropylene for the synthesis of carbon nanotubes. *Journal of Analytical and Applied Pyrolysis*. 2012;94:91-8.
- [10] Yao D, Li H, Dai Y, Wang C-H. Impact of temperature on the activity of Fe-Ni catalysts for pyrolysis and decomposition processing of plastic waste. *Chemical Engineering Journal*. 2021;408:127268.
- [11] Zhang YS, Zhu HL, Yao DD, Williams PT, Wu CF, Xu D, et al. Thermo-chemical conversion of carbonaceous wastes for CNT and hydrogen production: a review. *Sustainable Energy & Fuels*. 2021;5:4173-208.
- [12] Wang H, Moore JJ. Low temperature growth mechanisms of vertically aligned carbon nanofibers and nanotubes by radio frequency-plasma enhanced chemical vapor deposition. *Carbon*. 2012;50:1235-42.
- [13] Blanquet E, Nahil MA, Williams PT. Enhanced hydrogen-rich gas production from waste biomass using pyrolysis with non-thermal plasma-catalysis. *Catalysis Today*. 2019;337:216-24.
- [14] Gallon HJ, Tu X, Twigg MV, Whitehead JC. Plasma-assisted methane reduction of a NiO catalyst—Low temperature activation of methane and formation of carbon nanofibres. *Applied Catalysis B: Environmental*. 2011;106:616-20.
- [15] Yao D, Yang H, Chen H, Williams PT. Co-precipitation, impregnation and so-gel preparation of Ni catalysts for pyrolysis-catalytic steam reforming of waste plastics. *Applied Catalysis B: Environmental*. 2018;239:565-77.
- [16] Xiao H, Harding J, Lei S, Chen W, Xia S, Cai N, et al. Hydrogen and aromatics recovery through plasma-catalytic pyrolysis of waste polypropylene. *Journal of Cleaner Production*. 2022;350:131467.
- [17] Kumar M, Ando Y. Chemical vapor deposition of carbon nanotubes: A review on growth mechanism and mass production. *Journal of Nanoscience and Nanotechnology*. 2010;10:3739-58.
- [18] Cai N, Xia S, Xiao H, Chen Y, Chen W, Yang H, et al. Distinguishing the impact of temperature on iron catalyst during the catalytic-pyrolysis of waste polypropylene. *Proceedings of the Combustion Institute*. 2022.
- [19] Lu Y, Huang Z, Hoffmann R, Amundsen L, Fogler HS. Counterintuitive effects of the oil flow rate on wax deposition. *Energy & Fuels*. 2012;26:4091-7.
- [20] Arabiourrutia M, Elordi G, Lopez G, Borsella E, Bilbao J, Olazar M. Characterization of the waxes obtained by the pyrolysis of polyolefin plastics in a conical spouted bed reactor. *Journal of Analytical and Applied Pyrolysis*. 2012;94:230-7.

- [21] Awadallah AE, Aboul-Enein AA, Aboul-Gheit AK. Effect of progressive Co loading on commercial Co–Mo/Al₂O₃ catalyst for natural gas decomposition to CO_x-free hydrogen production and carbon nanotubes. *Energy Conversion and Management*. 2014;77:143-51.
- [22] Liu C, Chen X, Liu X, Cui C, Zhou Z, Jia L, et al. Evidence of a phenolic pool as a key intermediate for zeolite-catalyzed lignin pyrolysis. *Angewandte Chemie-International Edition*. 2021;60:2643-7.
- [23] Chen Y, Zhang X, Chen W, Yang H, Chen H. The structure evolution of biochar from biomass pyrolysis and its correlation with gas pollutant adsorption performance. *Bioresource Technology*. 2017;246:101-9.
- [24] Shao S, Ye Z, Sun J, Liu C, Yan J, Liu T, et al. A review on the application of non-thermal plasma (NTP) in the conversion of biomass: Catalyst preparation, thermal utilization and catalyst regeneration. *Fuel*. 2022;330:125420.