

Research article

Heating strategies for the system of PP and Spherical Activated Carbon during microwave cracking for obtaining value-added products

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ABSTRACT

Microwave catalytic cracking of waste plastics is a promising technology. However, how to mix effectively microwave absorber, catalyst and feedstock, and reuse microwave absorbers and catalysts is obviously a challenge. This study has focused on the heat transfer performance and reuse of microwave absorber and the influence of heating strategies on cracked products. Commercial Spherical Activated Carbon (SAC), containing some catalysts, has been used for microwave cracking of polypropylene. The effect of heating strategies on product distribution has been studied. Meanwhile, SAC has been reused many times to test the possibility of industrialization of the system. The results show that the heating strategies such as reducing the input power, choosing appropriate intermittent heating time and co-cracking of PP-Wax are beneficial to the formation of light oil. Compared with the first use, the subsequent heating rate of SAC will decrease, but the average heating rate shows a certain stability in the subsequent multiple use (the change range < 1 °C/min at 32% input power). From the point of view of heat transfer and reuse, SAC has obvious advantages as microwave absorber. However, the catalytic performance is not significant and needs to be improved in the next study.

1. Introduction

As the most popular and promising recovery method, the thermal or catalytic cracking of polyolefins has been widely investigated in recent years [1–5]. But it inevitably suffers the troubles of low thermal conductivity and high viscosity of molten polyolefin. This will lead to increased energy consumption and uneven heating. Our previous studies also involved the cracking of waste plastics [6–9]. The plastics had melted into non-Newtonian fluid after be heated to a certain temperature, and thus it was very difficult for mechanical agitation [6]. Meanwhile, microwave cracking is used in treating and recycling plastic wastes to get better heat transfer effects [10–14]. The use of microwave energy as a heat source for cracking provides several advantages over conventional cracking processes, such as fast heating times, easy control of operating parameters, bulk and targeted heating, and lower operating temperatures and energy requirements [15]. However, hydrocarbons are often not sensitive to microwave, that is, a microwave transparent materials, so it is necessary to use the microwave absorbers,

which are highly lossy materials (e.g. SiC, carbon etc.), to complete the cracking reaction. The microwave absorbers act as a hot spot and transfer heat to the cooler surroundings by conduction and thermal radiation. But at present, most of the studies about the microwave cracking of waste plastics have used excessive microwave absorbers as heat sources. Carlos et al. [10] and Bo Zhang et al. [16] have used microwave absorbent bed, and further the mass ratio of absorber (SiC) to feed is 50:1 in the later study [16]. The carbon powder employed as a microwave absorber was the solid obtained from the MAP of tires. On the other hand, adding catalysts in this process, namely, microwave catalytic cracking can obtain better product distribution. Some researchers have separated the catalyst from the microwave absorber-waste plastic system [18,19], while others have mixed the three together. For the latter, how to effectively mix microwave absorbers, catalysts and waste plastics is a challenge.

Therefore, it is very important to study the heating strategies of microwave catalytic cracking process, which mainly includes polyolefins, catalysis and microwave absorbers, in order to reduce the

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amount of absorber and achieve uniform temperature distribution, and reduce energy consumption at the same time.

As far as I know, there are very few studies concerning the heating strategies of waste plastics in microwave field. Activated carbon (AC) is usually preferred for the microwave heating process, not only because it is very good microwave absorber, but also because it is inexpensive, easily available in different textures, sizes, forms, and do not add any extra inorganic component to the solid residues obtained after pyrolysis [20]. In addition, the density of AC is close to that of waste plastics, so the mixture of AC and waste plastic by microwave heating is also an important advantage.

In this study, commercial Spherical Active Carbon (SAC), which contains some catalysts and is a commonly used product, has been used for microwave cracking of polypropylene (PP). It can be considered that a microwave absorber - catalyst - PP system is formed. The effect of heating strategies such as intermittent heating, choosing the appropriate input power, and the co-pyrolysis of PP and wax on product distribution have been studied. The aim is to try to make microwave absorber and catalyst into spheres and heat them with waste plastics for microwave catalytic cracking. This study will provide a basis for the optimization of microwave absorbents, catalysts and waste plastics systems.

2. Methods and materials

2.1. Materials

The SAC used in this paper is produced by Guangzhou Supei Commodity Co., Ltd. The mineralized SAC contains diatomite mud, attapulgite, sepiolite, zeolite and AC. The main ingredient of diatomite mud is opal ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$). Attapulgite is a natural hydrated magnesium silicate mineral, and the chemical formula is generally considered to be $\text{Mg}_5\text{Si}_8\text{O}_{20}(\text{OH})_2(\text{OH}_2)_4 \cdot 4\text{H}_2\text{O}$. And sepiolite ($\text{Si}_{12}\text{Mg}_8\text{O}_{30}(\text{OH})_4(\text{OH}_2)_4 \cdot 8\text{H}_2\text{O}$) is a kind of fibrous hydrous magnesium silicate. The structural formula of zeolite is $\text{A}_{(x/q)}[(\text{AlO}_2)_x(\text{SiO}_2)_y] \cdot n(\text{H}_2\text{O})$, in which A is Ca, Na, K, Ba, Sr and other cations. The diameter of SAC is about 4 mm.

Compared with polyethylene (PE), the cracking of PP has been less studied. Therefore, PP (k8303) has been selected as raw material in this study, and it is produced by SINOPEC Beijing YanShan Company in the form of 2–4 mm grains. The density (at 20 °C) is 910 kg/m³, and the melting point is 158 °C.

2.2. Microwave heating system

A microwave heating system has four main components [21,22]: (1). The source that generates the microwave fields. (2). The waveguide, guiding the electromagnetic field from the source into the cavity. (3). The cavity, where the resonant pattern occurs. (4). Reactor, containing the materials to be heated.

In this study, the microwave cracking of polyolefins was performed in a closed reactor under nitrogen atmosphere. The microwave cracking apparatus is shown in Fig. 1. The reactor is a 500 ml three-port flask connected with a reflux elbow (5a in Fig. 1) at the outlet. A thermal insulation layer is arranged outside the reactor. The reflux elbow is arranged to increase the residence time of the reaction material to obtain lighter cracking products.

The microwave shielded thermocouple is placed outside the three-port flask (as shown in Fig. 1) and connected with the temperature indicator. Contact thermocouple temperature sensor is used for temperature measurement, with digital online real-time display, and the measurement accuracy is ± 1 °C. It should be pointed out that in this experiment, the temperature measuring device is only used as a temperature measurement, without temperature control. Moreover, this study does not consider the temperature factor, and only takes the input power as one of the comparative factors.

Microwave cracking furnace is designed and manufactured by

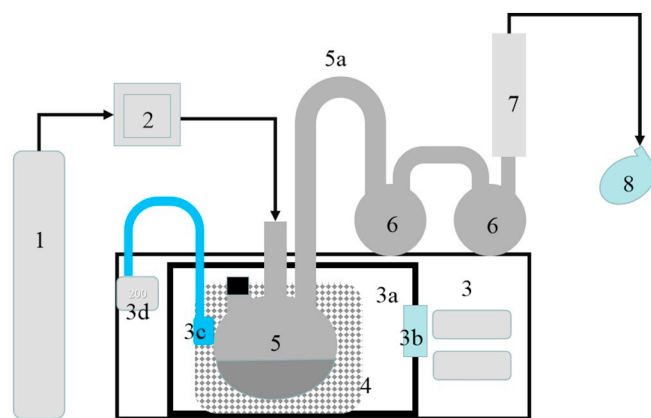


Fig. 1. Schematic diagram of the microwave catalytic cracking reactor system. (1. Nitrogen; 2. Mass flowmeter; 3. Microwave pyrolysis furnace; 3a. Cavity; 3b. Microwave inlet; 3c. Thermocouple; 3d. Temperature display; 4. Thermal insulation layer; 5. Three-port bottle reactor; 5a. Elbow reflux; 6. Liquid collection flask; 7. Cooling device; 8. Gas bag.

Qingdao Mike Wei Microwave Applied Technology Co., Ltd. The maximum input power is 900 W. The actual input power can be adjusted by adjusting the power percentage. For example, the 32% input power mentioned in this paper represents 32% of the maximum input power. The cavity size of the microwave is 260 mm × 260 mm × 260 mm.

2.3. Experimental design

Five series of experiments (A–E) have been designed to study the effects of different heating strategies on product distribution. Influencing factors include input power, mass ratio of PP to AC, heating mode, etc. The experimental conditions of these series have been listed in Table 1. Four input powers are selected in the experiment, which are 16%, 32%, 40% and 48% of the maximum input power.

The heating methods include continuous heating (CH) and intermittent heating (IH). The former can change the input power, but it is always in the heating state. The latter refers to stopping heating for a period of time (the following zero input power means stopping heating) in order to make full heat transfer between the heating materials and SAC.

2.4. Analysis

Gas chromatograph (type GC-9130), supplied by J-H Instruments, coupled with thermal conductivity and flame ionization detectors (GC-TCD/FID) is used to analyze the pyrolysis products. A detailed separation of the mixture of C1 ~ C6 gaseous saturated and unsaturated hydrocarbons, hydrogen and carbon oxides in one sample can be completed.

¹H NMR spectra were recorded on 300 MHz Bruker spectropin instruments. The oil samples were diluted with CDCl_3 . In this study, Eq. (1) is used to calculate the Branching index (BI).

$$\text{BI} = \frac{S_{\text{CH}_3/3}}{S_{(\text{CH}_2+\text{CH})/2}} \quad (1)$$

where, S_{CH_3} is the peak area integral of chemical shift between 0.5–1 ppm in NMR 1H, and $S_{(\text{CH}_2+\text{CH})}$ is the peak area integral of the chemical shift between 1.0–3.5 ppm.

A gas chromatograph coupled to a mass spectrometer (GC-MS) (GCT Premier, Waters), using a DB-5 column (30 m × 0.25 mm I.D.), was employed to analyze the liquid product.

Surface area and pore structures of SAC were evaluated by N_2 adsorption/desorption isotherms at 273 K using ASAP 2020HD88 automatic physical adsorbent instrument for Specific Surface Area

Table 1

The experimental series in this study.

Series	A	B	C	D	E
Mass ratio of AC to PP	140:70	140:70	140:100, 140:45	100:40	70:70
Input power	16%, 32%, 40%	32%, 40%, 48%	16%, 32%, 40%	16%	16%
Number of AC recycling use	10	10	12	6	2
Nitrogen purge rate (ml/min)	200	200	200	200	200
Heating process	CH	IH	IH/CH	IH	IH

(Quantachrome instruments, USA). The specific surface area was calculated using the multipoint Brunauer–Emmett–Teller (BET) standard method. The microporous and mesoporous parameters were calculated by the HK and BJH methods, respectively.

The X-ray photoelectron spectroscopy (XPS) analysis was carried out by a ESCALAB 250Xi X-ray photoelectron spectrophotometer (Thermo Fisher Scientific, UK). High-resolution spectra of C 1s, O 1s were recorded using nonmonochromatic Mg Ka X radiation ($hc = 1253.6$ eV).

The surface morphology and the surface element distribution were characterized by an SU8020 field-emission scanning electron microscope equipped with energy dispersive spectrometer (SEM-EDS, HITACHI, Japan). The samples were sputter-coated with a layer of gold before the test. Then the samples were observed at an accelerating voltage of 25 kV.

Powder X-ray powder diffraction (XRD) patterns of the SAC before and after use were collected on a PANalytical X'pert PRO diffractometer using Cu Ka ($k = 0.154$ nm) radiation at 40 kV and 30 mA. The 2 θ angles were scanned from 5 to 90°.

Fourier transform infrared (FTIR) spectra of SAC samples were obtained by a Tensor 27 type spectrometer in the wavenumber range of 4000–400 cm^{-1} .

The yield of liquid products was calculated by the ratio of the mass of liquid products and that of raw material. The yield of solid products was calculated by the ratio of the mass of solid products and that of raw material. The gas product yield is obtained by subtracting the sum of solid yield and liquid yield from 100%.

3. Results and discussion

3.1. The effect of heating strategies on cracking results

3.1.1. Discussions on yield and characters of main products

The experimental conditions and results of the five experimental series are listed in the Table 2 and Fig. 2. The information in Table 2 includes feedstock type and heating procedure. The first column shows the number of rounds of the experiment, that is, the number of times the SAC is used. For example, AR5 represents the fifth experiment in series A and the fifth use of SAC in this series. In the second column, numbers outside brackets denote time, and numbers in brackets represent the percentage of the actual input power to the maximum input power, and zero means stop heating stage. For feedstock type, PP represents new polypropylene as raw material, and the solid products of the previous round are very few, which can be separated and removed by additional sieving procedures each time; S represents the solid product (mainly semi-solid wax) of the previous round of experiments, and is used as the next round of feedstock to co-crack with the newly added PP. Each experiment was repeated twice or three times. When the cracking is sufficient, the solid products are usually very few, mostly black powder. At this time, only weighing is carried out, and then screening is carried out to remove the solid products without further analysis, such as AR1, AR2; if semi-solid wax is included, the next round of cracking is directly carried out without separation: co-cracking of PP/S, Such as AR4, AR6.

Firstly, the Series A has adopted continuous heating method with different input power. The mass ratio of PP to SAC is 1:2 (70 g: 140 g).

Table 2

The experimental conditions in this study.

Round	Feedstock, heating process
AR1	PP, 36 (40)
AR2	PP, 36 (40)
AR3	PP, 42 (32)
AR4	PP/S ^a , 38 (40)
AR5	PP, 50 (16)
AR6	PP/S ^a , 38 (40)
AR7	PP, 40 (16)-15 (40)
AR8	PP, 40 (16)-15(40)
AR9	PP, 38 (40)
AR10	PP, 38 (40)
BR1	PP, 5(48)-5 (0)-5 (48)-5 (0)-20 (48)
BR2	PP, 5(32)-5(0)-5(32)-5(0)-40(32)
BR3	PP/S ^a , 5(32)-5(0)-5(32)-5(0)-5(32)-5(0)-30(32)
BR4	PP/S ^a , 5(32)-5(0)-5(32)-5(0)-5(32)-5(0)-30(32)
BR5	PP/S ^a , 5(32)-5(0)-5(32)-5(0)-5(32)-5(0)-30(32)
BR6	PP/S ^a , 5(40)-5(0)-5(40)-5(0)-5(40)-5(0)-25(40)
BR7	PP, 5(40)-5(0)-5(40)-5(0)-5(40)-5(0)-25(40)
BR8	PP, 5(40)-5(0)-5(40)-5(0)-5(40)-5(0)-25(40)
BR9	PP, 5(40)-5(0)-5(40)-5(0)-5(40)-5(0)-25(40)
BR10	PP, 5(40)-5(0)-5(40)-5(0)-5(40)-5(0)-25(40)
CR1	PP, 40 (40)
CR2	PP, 5(16)-5(0)-5(16)-5(0)-5(16)-5(0)-30(32)-15(40)
CR3	PP, 20(16)-30(32)-15(40)
CR4	PP, 5(16)-5(0)-5(16)-5(0)-5(16)-5(0)-30(32)-15(40)
CR5	PP, 20(16)-30(32)-15(40)
CR6	PP, 5(16)-5(0)-5(16)-5(0)-5(16)-5(0)-30(32)-15(40)
CR7	PP, 20(16)-30(32)-15(40)
CR8	PP, 7(16)-3(0)-7(16)-3(0)-7(16)-3(0)-25(32)-3(0)-16(40)
CR9	PP, 20(16)-5(0)-25(32)-5(0)-16(40)
CR10	PP, 15(16)-5(0)-10(32)-5(0)-15(32)-5(0)-10(40)-5(0)-10(40)
CR11	PP, 20(16)-5(0)-25(32)-5(0)-10(40)
CR12	PP, 20(16)-25(32)-10(40)
DR1	PP, 5(16)-5(0)-5(16)-5(0)-5 (16)-5(0)-20(16)-5(0)-5(16)-5(0)-30(16)
DR2	PP, 5(16)-5(0)-5(16)-5(0)-5 (16)-5 (0)-20(16)-5(0)-5(16)-5(0)-40(16)
DR3	PP, 5(16)-5(0)-5(16)-5(0)-5 (16)-5 (0)-20(16)-5(0)-5(16)-5(0)-43(16)
DR4	PP, 5(16)-5(0)-5(16)-5(0)-5 (16)-5 (0)-20(16)-5(0)-5(16)-5(0)-58(16)
DR5	PP, 5(16)-5(0)-5(16)-5(0)-5 (16)-5 (0)-20(16)-5(0)-5(16)-5(0)-48(16)
DR6	PP, 5(16)-5(0)-5(16)-5(0)-5(16)-5(0)-20(16)-5(0)-5(16)-5(0)-20(16)-5(0)-5(16)-5(0)-5(16)-5(0)-20(16)-5(0)-20(16)
ER1	PP, 5(16)-5(0)-5(16)-5(0)-5 (16)-5 (0)-40(16)-5(0)-5(16)-5(0)-55(16)
ER2	PP, 5(16)-5(0)-5(16)-5(0)-5 (16)-5 (0)-40(16)-5(0)-60(16)

^a This means the co-pyrolysis of PP and wax.

There are four experiments (AR1, AR2 and AR9, AR10) adopting the same input power and heating mode. High gas yield has been obtained and the liquid products contain some waxes in AR1 and AR2. However, the gas yield has decreased, and the liquid products have become yellow transparent liquid in AR9 and AR10. These differences may be related to the heating characteristics of SAC: the heating performance of SAC may decrease after repeated use. Reducing the input power and prolonging the heating time, such as AR3 and AR5, can reduce the gas yield. But the solid product increases significantly, which is mainly yellow wax. This indicates that it is difficult for wax generated to continue cracking to produce oil or gas under this power condition. Then, newly added PP and wax were mixed and co-cracked, such as AR4 and AR6. In these two experiments, the input power is increased, and the solid product has been significantly decreased, while the liquid yield has been increased to > 70%. Therefore, blend cracking of PP and

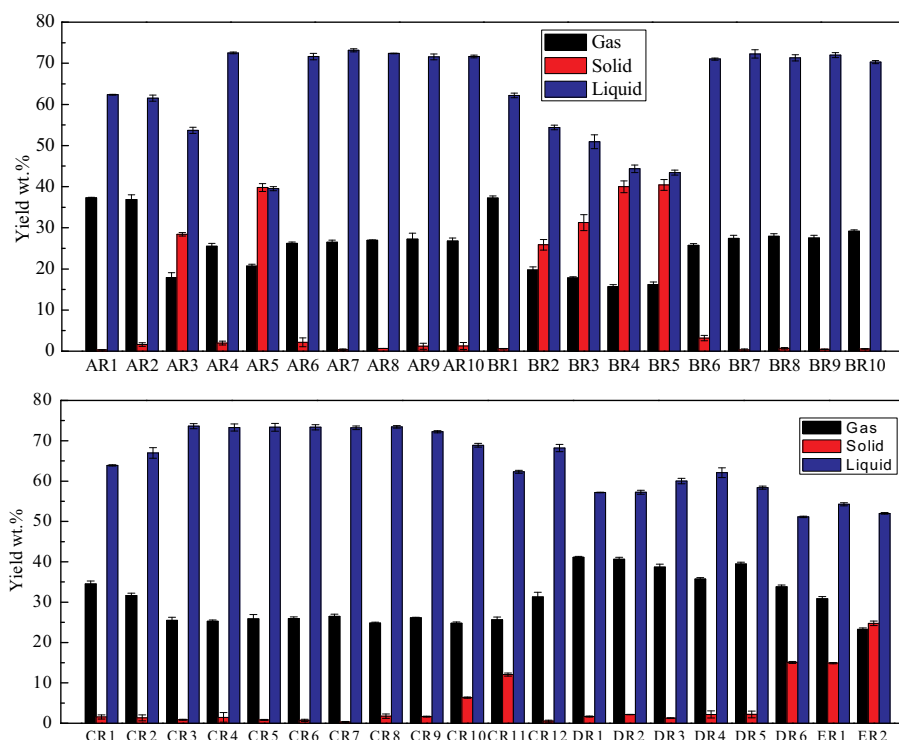


Fig. 2. The cracking results of series A, B, C, D and E.

wax is also a good heating strategy. The combination of different input powers has been also attempted, such as AR7, AR8. The lower power stage mainly corresponds to the melting and long chain breaking stage of PP, and the higher power stage mainly corresponds to the secondary cracking stage, such as from wax to light oil. Under these conditions, the yield of liquid products increased to $> 70\%$, while the yield of solid products decreased to $< 1\%$.

Secondly, the Series B has selected intermittent heating mode with different input power. The mass ratio of PP to SAC is 1:2 (70 g: 140 g). When 48% of maximum input power with two stop heating stages has been adopted, BR1 has obtained a higher gas yield, and the liquid product has contained some waxes. This result may be related to two factors, one is that SAC has good heating performance in the initial use, which is consistent with the experimental results of series A, and the other is that the selected power is too high. Reducing the input power and prolonging the heating time can reduce the gas yield, but the solid product increases, such as BR2-BR5, and the solid product is mainly waxy. As a result, the co-cracking of PP and wax has been carried out in BR3-BR5. The liquid yields of these experiments are not very high, but they are light yellow transparent liquid. These results indicate that the co-cracking of PP and wax is easier to produce light products at lower input power, and further, the co-cracking can be carried out repeatedly. The BR6-BR10, adopting the 40% of maximum input power, have reduced the solid yield to $< 1\%$ and increased the liquid yield to $> 70\%$. Moreover, many rounds of experiments have been carried out and similar yields have been obtained. This shows that the SAC is very stable and suitable for repeated use under the same cracking conditions.

Thirdly, the Series C is intermittent heating or continuous heating method. PP has increased to 100 g or reduced to 45 g in these experiments (100 g: 140 g or 45 g: 140 g). In CR1, 40% of maximum input power with continuous heating method has been selected, and the gas yield is high. Compared with AR1, the input of PP has been increased by about 43% in this experiment, but the heating time was only increased by 11.11%. The results show that the unit energy consumption can be reduced by increasing the input of PP in a certain range, and this is the key content of the follow-up study. Then, two heating methods were

designed for comparative experiments in CR2-CR7. CR3, CR5 and CR7 have adopted three input power (16%, 32% and 40%) and continuous heating method. While CR2, CR4 and CR6 have adopted three input power (16%, 32% and 40%) and intermittent heating method. The liquid yields of these experiments are $> 70\%$ and this result shows that the combination of different input power can enhance the cracking reactions of PP. Moreover, the intermittent heating of the latter is mainly used for heating and melting stage, and the total heating time is decreased compared with the former (CR3, CR5 and CR7). Because the microwave heating speed is faster than the heat transfer speed between SAC and PP, the intermittent heating method can make the heat transfer between materials more uniform, thus reducing the microwave heating time and improving the heating efficiency. Then, different methods have been adopted for CR8, CR9 and CR10, and the liquid products with high yield are yellow without wax. Therefore, the time setting of intermittent heating also needs to be optimized according to the materials. About 45 g PP was used as input material to study the effect of higher SAC-PP ratio on cracking products in CR11 and CR12. Among them, CR11 used intermittent heating and it obtains the light-yellow liquid, but the solid wax yield is about 10%. CR12 adopted the continuous heating method and the same total heating time, then the yields of gas products and liquid products increased, while the yields of solid products decreased to $< 1\%$, but the liquid product was dark yellow.

Fourthly, the Series D has adopted intermittent heating mode, and the lowest input power (16%) was used in the whole process. The mass ratio of SAC to PP was kept at 100:40. Compared with the previous series, the total heating time of this series is relatively long and the gas product yields are higher. DR1-DR5 have used five stopping heating stages, and the stopping heating is 5 min. The first three heating stages are all 5 min, corresponding to the heating and melting stage. And the fourth heating stages are 20 min, which corresponds to the cracking process, and this process is the main cracking process. And then, there are two heating stages, the former corresponds to the heating transfer process, and the latter takes a long time, corresponding to the cracking of waxes produced. But the cracking efficiency of this heating stage is

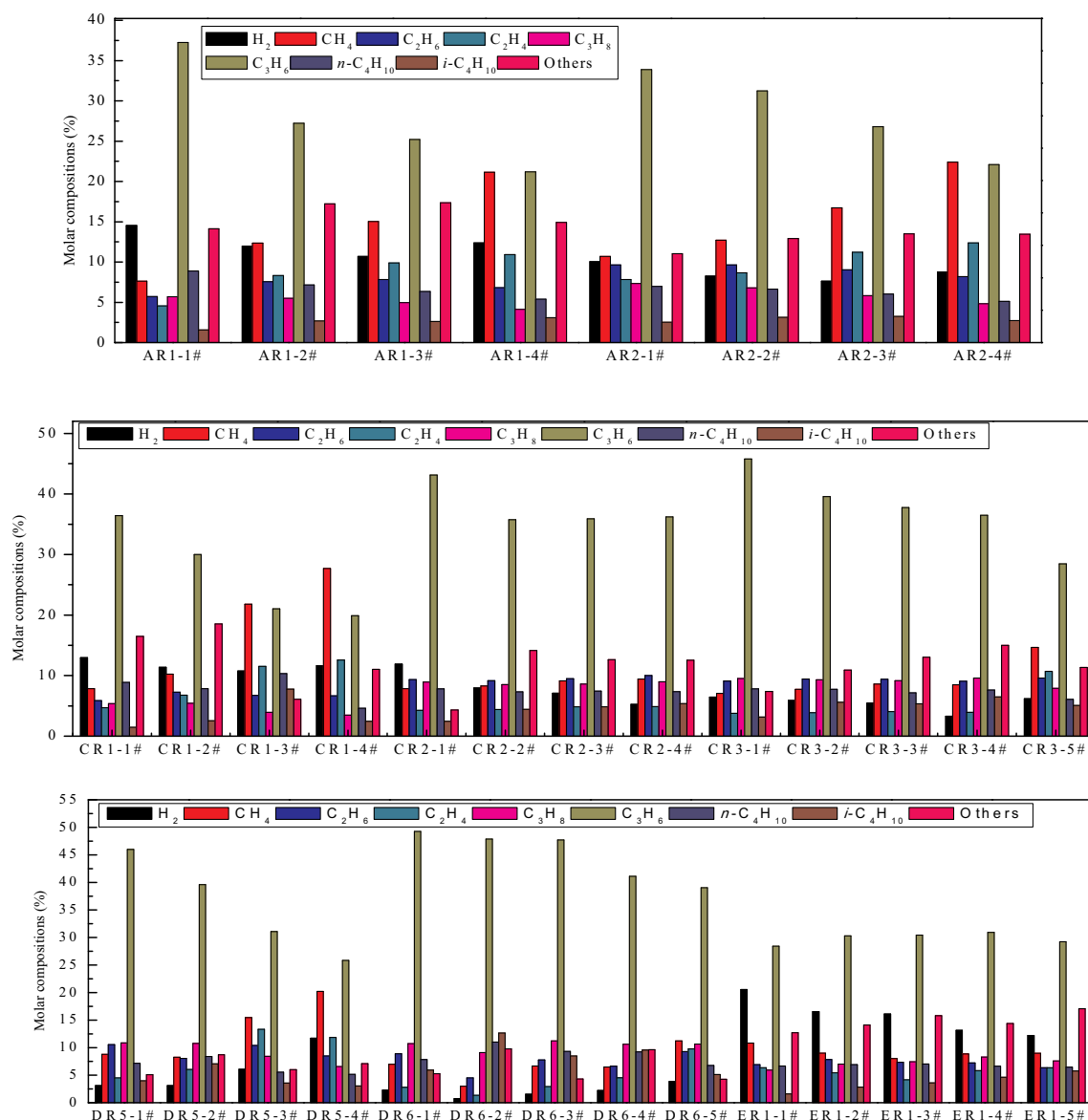


Fig. 3. The molar compositions of the main gas products from typical experimental processes.

low. In these cases, the liquids are yellow without waxes. This may be related to the high mass ratio of SAC to PP. Meanwhile, DR6 has adopted 8 stopping stages, and the waxes is higher due to the lower temperature, but the liquid is light yellow.

Finally, the Series E has selected the same proportion of SAC and PP for experiments. The lowest input power (16%) was used in the whole process. Intermittent heating is also adopted, and the total heating time is longer. The yield of solid products is higher, mainly wax. The results show that there is a possibility of low heating efficiency in the case of higher mass ratio of PP to SAC and lower input power.

In these experiments, SAC can be reused many times. This is a good attempt to show that the spherical microwave absorber is easy to recycle and reuse. Of course, the size optimization, composition design and energy consumption calculation of spherical microwave absorbers are the key issues for future research.

3.1.2. Discussion on compositions and changes of gas products

Because of the fast heating rate of microwave heating, it was observed that the gas products were produced shortly after the heating started. This indicates that the end carbon chain breaks at the early stage of heating, resulting in the production of small molecular

hydrocarbons. In the reaction process, the composition of gas products will change with the increase of temperature and the decrease of the ratio of PP to SAC. Therefore, multiple sampling and analysis have been carried out during the cracking process to observe the changes of gas products. The molar compositions of the main gas products from typical experimental processes are listed in the Fig. 3. H_2 was detected in the cracking process, indicating the breakage of carbon hydrogen bond.

As can be seen from the Fig. 3, C_3H_6 is always the main component of pyrolysis gas. This is consistent with our previous research [9]. Unlike previous studies, this study has focused more on the changes of gas composition in the reaction process. It can be observed that C_3H_6 content decreases with the increase of reaction time, and while the CH_4 content increases with the increase of reaction time in many cases. This indicates that β -scission dominates in the initial stage of pyrolysis, but with the reaction proceeding and the temperature rising, on the one hand, C_3H_6 generated may continue to react to produce more stable small molecular hydrocarbons, on the other hand, CH_4 is more likely to be generated directly from waxes when the temperature is too high. H_2 is relatively large in the first two rounds of experiments (AR1, AR2, CR1, CR2 and ER1), showing that more carbon hydrogen bond breaking reactions occur due to the fast heating speed of SAC with fewer times of

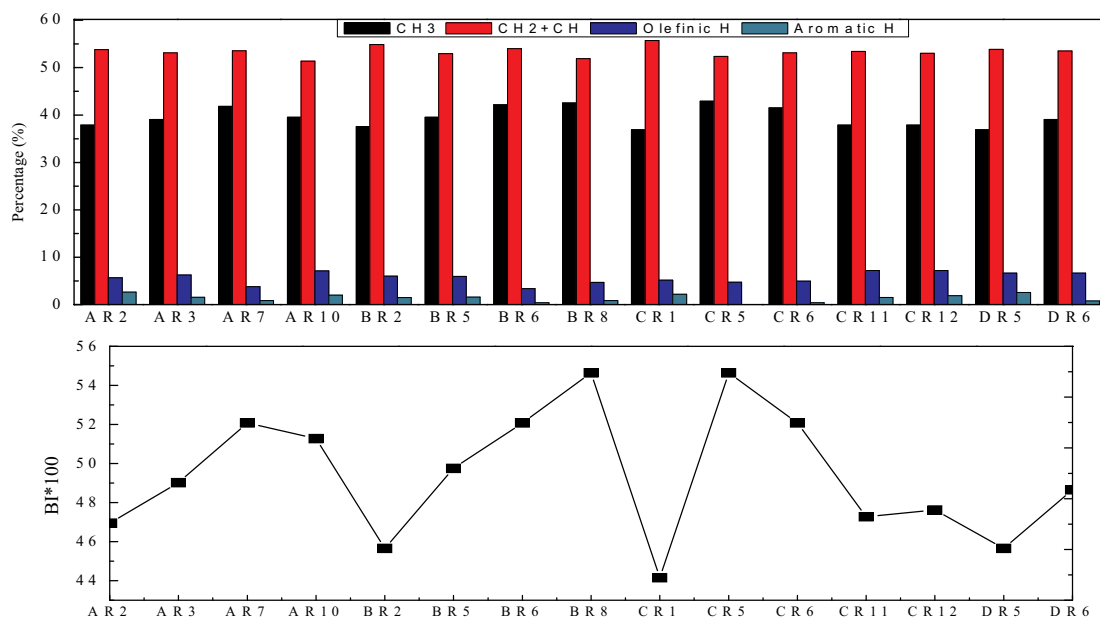


Fig. 4. ¹H NMR analyses of the liquid products (Up: H content; down: BI*100).

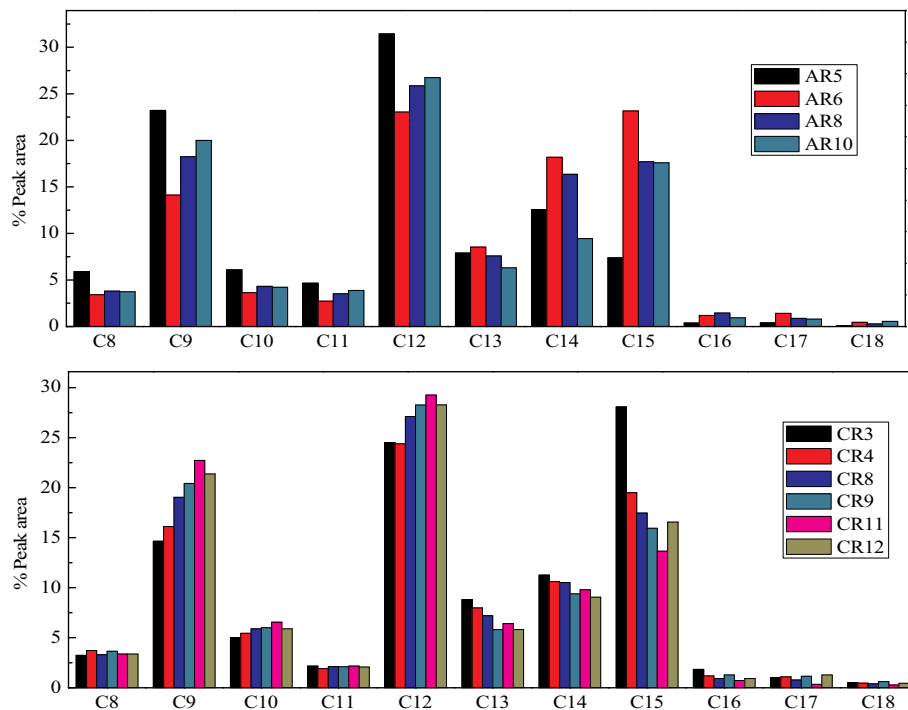


Fig. 5. Carbon number distribution of liquid products from Series A and C.

use. This is consistent with the analysis in the previous part. Comparing DR5, DR6 with ER1, the H₂ content of the former is lower than that of the latter. This may be related to the ratio of SAC to PP. The mass ratio of SAC to PP of the latter is 70:70, and the heating time is relatively long. This shows that there is less SAC around the material particles as a heat source, and the temperature difference of the material particles will inevitably increase, which will lead to uneven heating. Compared with DR5, DR6 and other series, it can be found that the content of other gases (mainly C₄–C₆) in the former is less than that in the latter, because the former has a higher mass ratio of SAC to PP, and PP and the cracked products have a longer exposure to SAC, which leads to a fuller cracking reaction.

3.1.3. Discussion on compositions and application of liquid products

3.1.3.1. NMR analysis. The detailed ¹H NMR analyses of the liquid products are given in Fig. 4. Each of the ¹H NMR spectra contains the dominant aliphatic peaks. The integrated area of ¹H NMR spectra illustrates the presence of the –CH₃ group in the aliphatic region between 0.5 and 1 ppm while the presence of >CH₂ and C–H functional groups in the aliphatic region between 1 and 3.5 ppm. The olefinic hydrogen corresponds to region between 4.00 and 6.00 ppm, while the aromatic structures are clearly indicated by the peaks in the between 6.00 and 8.00 ppm region. As observed from Fig. 4, paraffinic hydrogens give almost 90% in liquid products obtained from the series A–D, while olefinic and aromatic hydrogens are very low (below 10%).

Although the olefinic hydrogens are very low, it can be found that

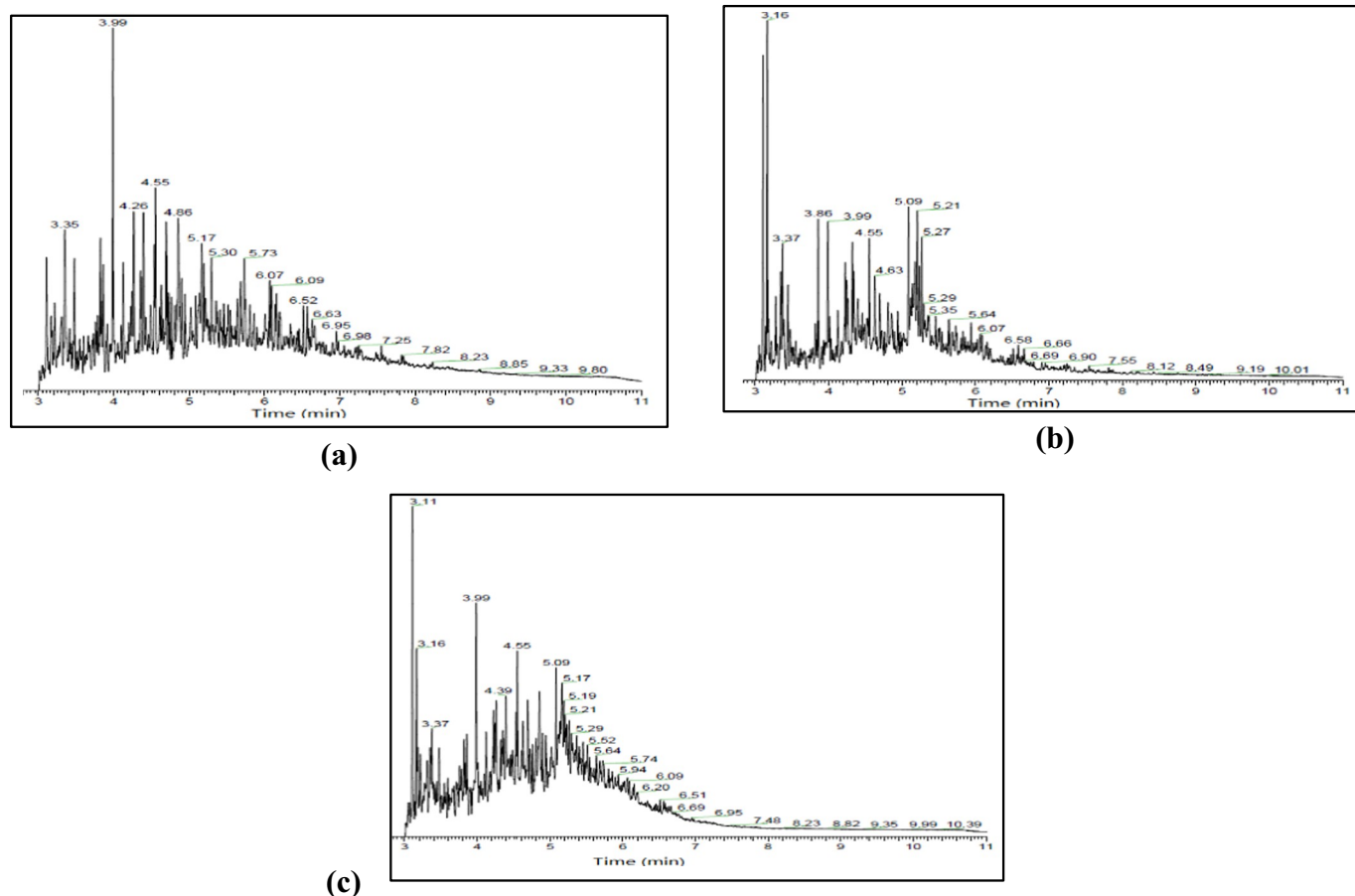


Fig. 6. Gas chromatogram of DR1 (a), DR5 (b) and ER1 (c) (RT 3.11: 4,4,5-trimethyl-1-hexene; 3.37: 2,3,3-trimethyl-1-hexene; 4.26: 2,2-dimethyl-3-octene; 4.39: 2,3,3-trimethyl-1,7-octadiene; 5.09: 2,2-dimethyl-3-decene; 10.01: C_{18}).

the liquid products from CR11, CR12, DR5 and DR6 give the higher contents of olefinic hydrogens. In these cases, the mass ratio of SAC to PP is relatively high, and therefore the contact time between the pyrolysis products and SAC is relatively long, leading to relatively more secondary cracking.

Because of the high aliphatic H fraction, the BI (branchiness index) of the liquid product can be calculated approximately by the Eq. (1). The BI can relatively represent the degree of carbon chain breakage in a system. The series A has selected four experiments for the analysis of NMR. The AR2 has given a relatively small BI and relatively high aromatic H content. This is related to high input power, good microwave absorption performance and short reaction time. The produced gases, oils and waxes have moved out quickly and avoided secondary cracking, and meanwhile higher temperatures caused by high input power and good microwave absorption performance also make some aromatics appear. Then the BI value of AR3 is increased, showing that there are more cracking reactions due to the longer residence time and lower input power. And further, the BI values of AR7 and AR10 continue to increase. The combination of multi-power heating has been chosen to reduce the heating rate properly in the initial stage of heating for AR7, which can enhance the cracking reactions. Compared with AR2, AR10 has obtained a higher BI at the same input power. This indicates that the heating performance of SAC has changed after many times of use, which is consistent with the analysis in the previous part.

From BR2 to BR8, the BI value increases gradually, and the $-CH_3$ group also increases gradually. BR2 has adopted the 32% input power, and there are many waxes as solid product. Compared with AR10, the BI value of BR8 is higher, and the content of aromatic and olefinic H is lower. This result shows that intermittent heating can make the heat

transfer between SAC and PP more fully and then enhance the cracking reactions.

The BI value of CR1 is the smallest, which is also related to the experimental conditions. The mass ratio of PP to SAC is the largest in this experiment, and the continuous heating mode is adopted. As a result, the reaction time of PP is relatively short, and the liquid products have some waxes. Then, by choosing the combination of various input power or intermittent heating, the pyrolysis reaction can be significantly enhanced, such as CR5 and CR6, and the BI values of the two experiments increased significantly.

As observed from Fig. 4, the content of olefinic H is higher in the last four experiments, because the mass ratio of PP to SAC is relatively small, PP has enough heat supply, resulting in over-cracking and more olefins. This can be proved in the later analysis.

3.1.3.2. GC-MS analysis. In order to understand the composition of liquid products in detail, several typical liquid products have been selected for GC-MS analysis. The liquid products of PP are very complex, and it mainly contains *i*-alkanes or *i*-olefins. More than 400 compounds have been detected by chromatography in these typical liquid products.

Fig. 5 shows the carbon number distribution of liquid products from Series A and C. At the same time, Fig. 6 shows the chromatograms of DR1, DR5 and ER1. As observed from Figs. 5–6, the liquid products in this study are distributed between C_8 and C_{18} , mainly between C_8 and C_{15} . AR5 has obviously obtained a lighter liquid product, compared with AR6, AR8 and AR10. This is related to the experimental conditions of AR5. In this experiment, PP and pyrolysis products can be fully cracked to produce lighter liquid products with lower input power and

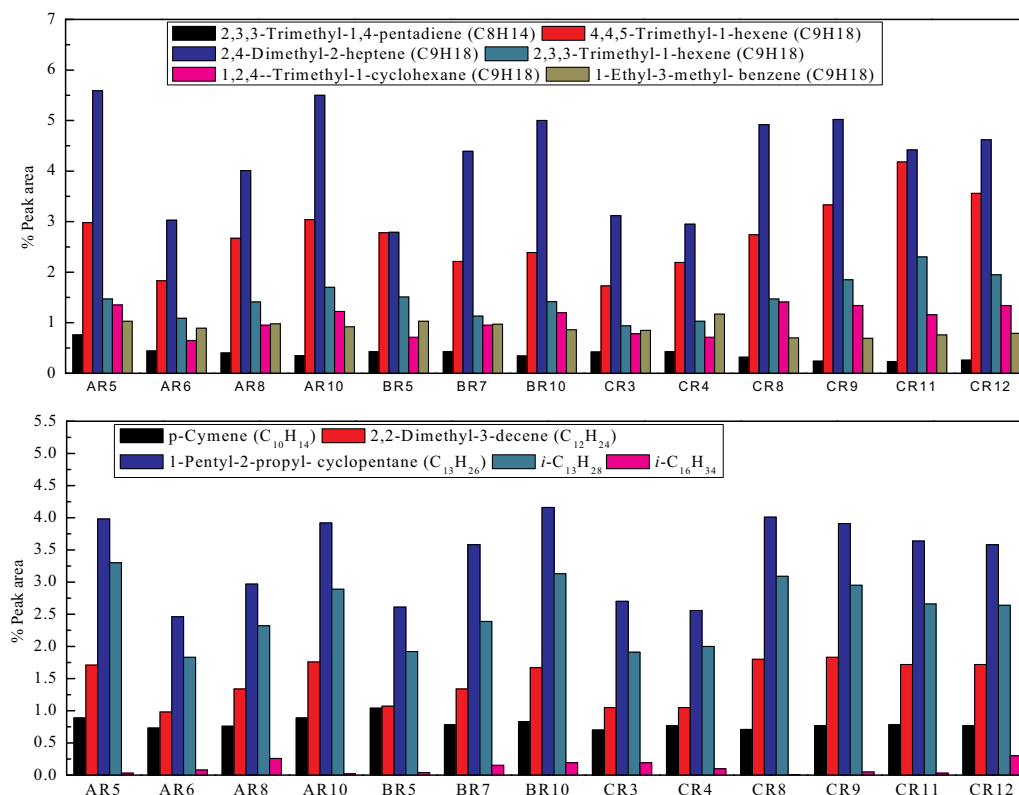


Fig. 7. Main components of liquid product from Series A, B and C.

longer heating time. Then, the solid products of AR5 and PP have been co-cracked in AR6, and the liquid product yield was increased by using higher input power. Therefore, the above experimental combination is also a good heating strategy. Likewise, CR4, CR8 and CR9 have obtained lighter liquid products compared with CR3, and CR11 has also obtained lighter liquid products compared with CR12. This is because these experiments (CR4, CR8, CR9 and CR11) have adopted intermittent heating method, and there has sufficient time to heat transfer between PP and SAC, and then, more cracking can be obtained.

As observed from Fig. 6, the chromatograms of these liquid products are quite similar. Compared with DR1, the chromatographic peaks of DR5 and ER1 are significantly enhanced at 3.11 min and 3.16 min, indicating that more light hydrocarbons have been obtained in these two experiments. DR5 used the same experimental conditions as DR1, but the heating time increased significantly, which led to more cracking reactions. In addition, ER1 has increased the mass ratio of PP to SAC to 70:70, which weakened the heat transfer between SAC and PP, and increased the heating time significantly. Therefore, PP and cracked products can have more sufficient residence time for further cracking.

Fig. 7 has lists the main components of liquid products from Series A, B and C, and it shows that the liquids in this study are mainly *i*-olefins, *i*-dienes, *i*-alkanes, aromatics and naphthenes. In particular, as shown in Figs. 6–7, there are more *i*-olefins in liquid products, which may be related to the shorter reaction time in the reactor during microwave cracking. Olefins are generally unstable. If the residence time is long, secondary reactions are likely to occur to produce short-chain hydrocarbons or aromatics. Compared with previous cracking experiments, the overall time of this experiment is shorter, so it can be considered that *i*-olefins are directly produced by long chain bond breaking without further secondary reaction.

Therefore, the microwave cracking of PP and SAC can produce light liquid products, mainly containing *i*-alkanes or *i*-olefins, which are in the range of gasoline and diesel fractions. It can be used as gasoline or diesel oil after subsequent treatment.

3.2. Analysis of material reuse and process energy consumption

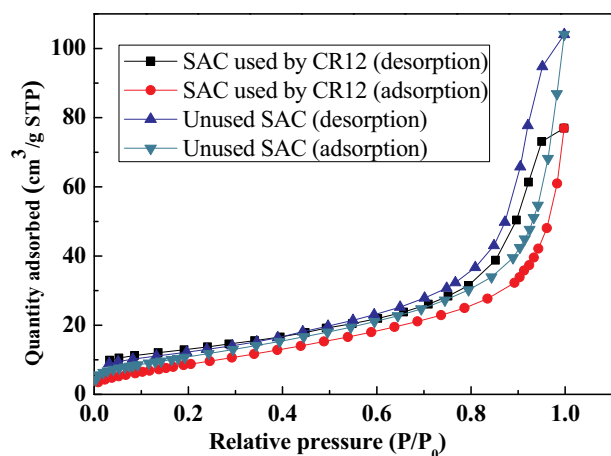
3.2.1. Discussion on SAC characterization

SAC used in this experiment is a kind of commercial activated carbon. In order to analyze its composition, structure, surface properties and the changes before and after reaction, a series of tests were carried out.

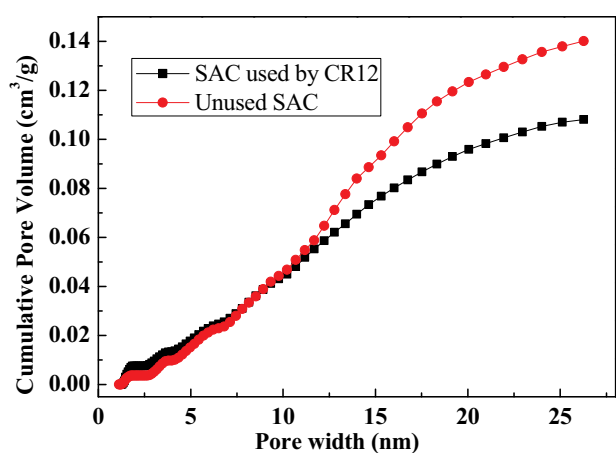
3.2.1.1. BET surface area and pore size distribution. The adsorbate employed in the physisorption process is N_2 . The adsorption and desorption isotherms are used to estimate the surface area and pore distribution of each of the samples. Fig. 8 shows the isotherm plot of the SAC before and after use, and Table 3 presents the adsorption and desorption parameters of the SAC before and after use.

As shown in Table 3, the BET surface area of unused SAC is $42.85 \text{ m}^2/\text{g}$. This value is significantly smaller than the surface area of general activated carbon, because SAC used in this study is a spherical particle with a diameter of 2–4 mm and a smooth surface, which reduces the total surface area. Mesoporous area (S_{meso}) and volume (V_{meso}) account for most of the total area (S_{BET}) and volume (V_{total}), indicating that SAC mainly contains mesopore. The average pore size is 15.03 nm. The N_2 adsorption/desorption isotherms of SAC before and after use performed at 273 K is type IV with a hysteresis loop, also suggesting the existence of mesopore as depicted in Fig. 8(a). After use, the S_{BET} and V_{total} were reduced, indicating that the cracking products have partially covered the surface of SAC. In addition, the average pore diameter of SAC after use decreases, especially when the pore diameter is small ($< 5 \text{ nm}$), the pore volume and $dV(d)$ of SAC after use shows an increase (as shown in Fig. 8(b) and (c)), which may be the overall decrease of pore diameter after heating.

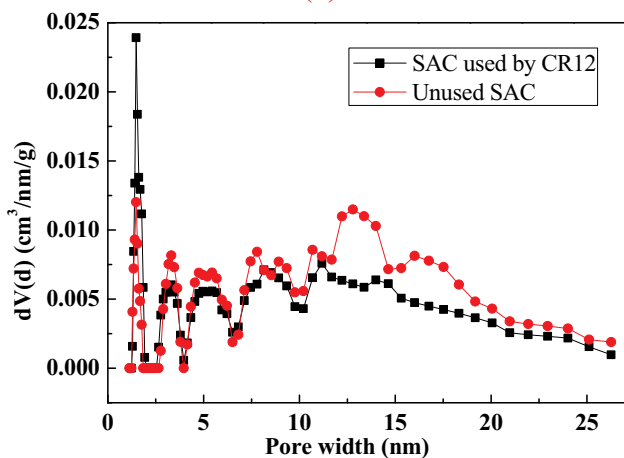
3.2.1.2. XPS analysis. Fig. 9 exhibited all-spectrum analysis of SAC to preliminarily determine the chemical composition of the surface. The binding energy of C1s is 298.98 eV, corresponding to graphite



(a)



(b)



(c)

Fig. 8. N₂ adsorption and desorption isotherm of SAC (a) and pore size distribution (b, c).

Table 3

The adsorption and desorption parameters of the SAC before and after use.

Sample	S_{BET} (m ² /g)	S_{meso} (m ² /g)	V_{total} (m ³ /g)	V_{meso} (m ³ /g)	Average pore size (nm)
Unused SAC	42.85	31.29	0.16	0.14	15.03
SAC used by CR12	37.40	30.61	0.12	0.11	12.73

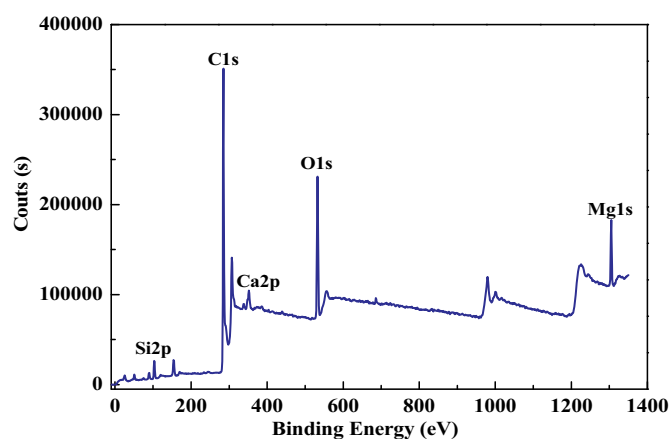


Fig. 9. All-spectrum analysis of XPS for SAC before use.

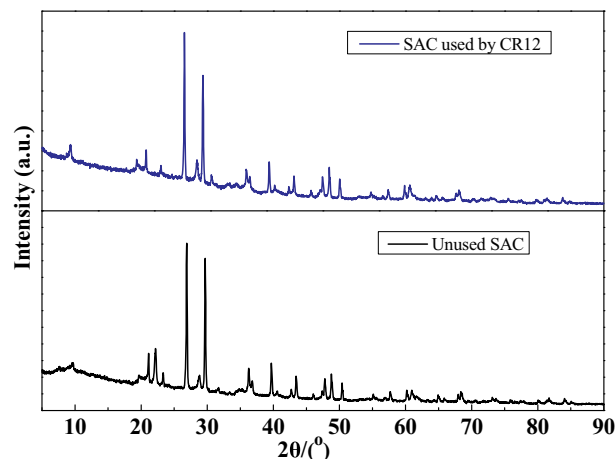


Fig. 10. XRD patterns of SAC before and after use.

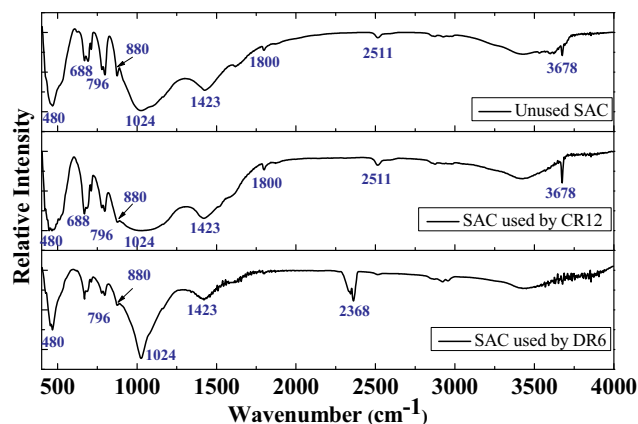


Fig. 11. FTIR spectra of SAC before and after use.

carbon-carbon bonds, and the O1s (binding energy = 531.88 eV) is corresponding to metal oxides or oxygen doubly bonded to carbon. The surface of SAC mainly contains C and O, as well as a small amount of Si, Ca and Mg. These elements come from minerals in SAC.

3.2.1.3. XRD analysis. X-ray diffraction is an effective method to determine the crystal structure and chemical phase composition of the materials. The XRD pattern of SAC before and after use is presented in Fig. 10. Multiple diffraction peaks are shown. This is related to the fact that SAC contains many minerals. Especially there are two

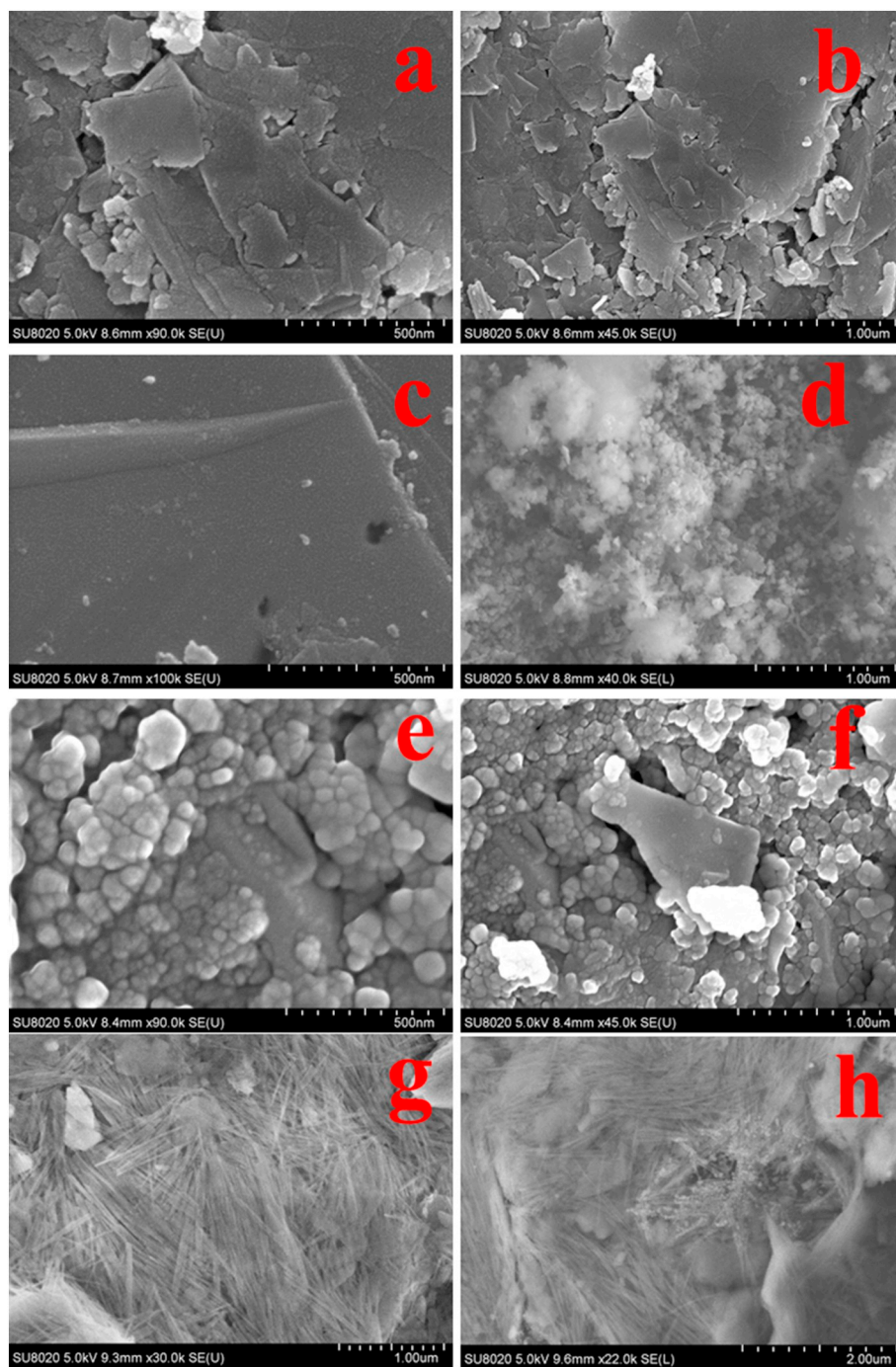


Fig. 12. SEM images of SAC (a, b-Unused SAC, c, d-SAC used by CR12, e, f-SAC used by DR6, g - internal of unused SAC, f-internal of SAC used by CR12).

significant peaks at 26.6° and 29.4° . The characteristic peaks at 2θ values of 26.6° , 20.6° and 50.2° peaks were attributed to the crystal planes of the quartz (PDF No. 00-046-1045) [23]. While the diffraction peaks at $2\theta = 23.1^\circ$, 29.4° , 36.1° , 39.4° , 43.3° , 47.6° , 48.7° , 57.4° and 83.7° corresponded to the crystal planes of calcium carbonate (PDF No. 00-005-0586).

3.2.1.4. FTIR analysis. The Fourier transform infrared spectroscopy (FTIR) was used to determine the functional groups of the unused and used SAC and the results are depicted in Fig. 11.

Some function groups like C=O and OH are usually formed during the production of activated carbons. It can be seen that the SACs before and after use, have similar adsorption peaks, which contain OH ,

C=O , and C=C at 3678 , 1800 and 1423 cm^{-1} , respectively. The bending vibration of C-H corresponds to the absorption peak of 880 cm^{-1} . On the other hand, SAC contains some minerals, and the peak observed at 3678 cm^{-1} is also attributed to the hydroxyl groups of diatomite mud, attapulgite, sepiolite and zeolite. The absorption band around 688 cm^{-1} is ascribed to the Si-O vibrations. Meanwhile, the peak at 796 cm^{-1} may correspond to the stretching vibration of Al-O-Si . The characteristic peaks appearing at 480 and 1024 cm^{-1} were observed, which can be associated with the bending vibration of Si-O-Si bond [24].

3.2.1.5. SEM-EDS analysis. The morphology of SAC was imaged by the SEM, which is presented in Fig. 12. It can be seen that the surface of

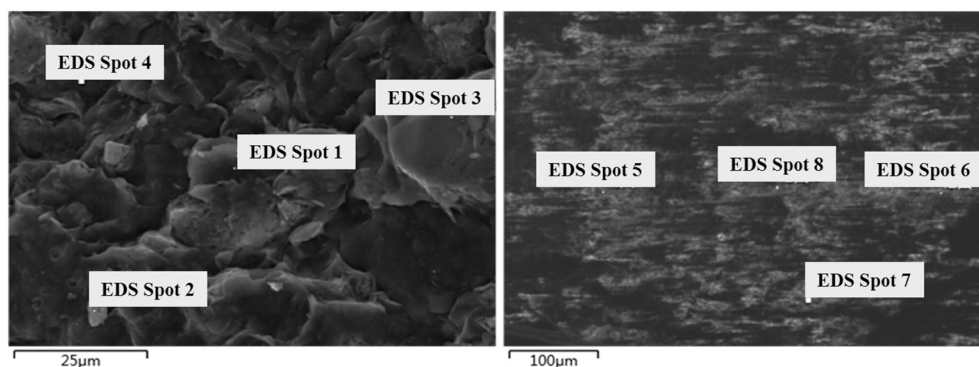


Fig. 13. EDS element analysis of SAC: (left) SAC used by CR12 and (right) unused SAC.

Table 4

EDS element analysis results of SAC surface and interior (wt%).

Items	C	O	Mg	Al	Si	K	Ca	Fe
EDS Spot 1 ^a	22.04	32.01	9.61	1.96	31.64	0.25	1.30	1.19
EDS Spot 2 ^a	17.63	47.44	3.45	0.78	5.19	0.13	25.16	0.21
EDS Spot 3 ^a	15.25	47.00	0.35	0.05	0.26	0.06	36.97	0.05
EDS Spot 4 ^a	21.91	29.17	11.57	3.44	30.07	0.56	1.73	1.53
EDS Spot 5 ^a	18.15	50.36	6.99	3.12	16.58	0.62	2.96	1.22
EDS Spot 6 ^a	14.14	56.70	6.03	1.92	11.84	0.03	8.64	0.72
EDS Spot 7 ^a	19.84	40.94	7.28	2.37	20.88	0.59	6.72	1.39
EDS Spot 8 ^a	13.44	41.68	10.70	3.07	23.90	0.71	4.69	1.55
SAC used by CR12 ^b	61.55	19.90	2.21	3.77	8.00	0.41	2.73	1.43
Unused SAC ^b	56.57	29.13	2.99	1.20	8.93	0.16	0.51	0.50

^a Spot scan of the internal of SAC, corresponding to the position in Fig. 13.

^b Surface scanning of the external surface of SAC.

unused SAC is an irregularity with random pore spread all over the relatively smooth surface. These pores are belonging to macropores with an average pore size of about 15 nm (Table 3). The surface of SAC is heavily covered after use, and these covers come from solid products of PP cracking, as shown in Fig. 12(c)–(f). In addition, the SEM images of SAC internal are shown in Fig. 12(g)–(h), and there are many fibers on the inner surface, which should be related to sepiolite and attapulgite contained in SAC.

In order to investigate elements distribution in the surface and interior of SAC, the EDS surface element analysis has been also employed and the results are described in Fig. 13 and Table 4. The surface of SAC was analyzed by surface scan. And the sphere is then cut into hemispheres for internal element analysis by spot scan (Fig. 13).

It can be seen from Table 4 that SAC surface contains more C and less other elements. Moreover, the C content of SAC surface increases after use, which proves that the surface is covered by cracking products. However, there are more O, Si, Ca and other elements in the interior, and the contents of K, Ca, Al and Si in different points are quite different. Therefore, the surface of SAC used in this study is mainly activated carbon, forming mesopores, meanwhile, the internal part of SAC mainly contains diatomite mud, attapulgite, sepiolite, zeolite and a small amount of AC, and moreover, the mixture of such minerals and activated carbon is very uneven.

3.2.1.6. Heating characteristics. In order to test the heating performance of SAC, 140 g SAC has been taken without adding material, and the thermocouple has been inserted into the same position. It has been heated to 450 °C each time, and the temperature readings are recorded every minute. Fig. 14 shows the temperature-time curves of the SAC before and after different experiments, as well as the heating curves of different input power. Because SAC contains a certain amount of water, the heating curve before dehydration appears a temperature drop zone, which is caused by water evaporation, as shown in Fig. 14(a). The temperature curves are quite different under three different input

power conditions (16%, 32% and 40%). As shown Fig. 14(b), it takes only about 20 min to reach 450 °C at 40% input power, and it takes 35–40 min at 16% input power.

It can be seen that the heating rate before use is significantly higher, and after use, the heating performance decreases. However, the decline is obvious after the first two use, which is consistent with the previous study. This can also explain the experimental results of the previous part. The heating rate of AR1 and AR2 is faster and the gas yield is higher, while the heating rate decreases and the liquid yield increases significantly in AR9 and AR10. Meanwhile, the temperature-time curves of SAC are very close after different experiments (CR3, CR6, CR12 and AR6). As shown in Fig. 14(c), the heating rate of the first use (new SAC, before or after drying) is generally higher than that of the subsequent use, and this difference is related to the heating power. Compared with the first use, the average heating rate of the SAC used by CR12 decreased by 3.8%, 12% and 22% respectively at 32%, 16% and 40% input power. Moreover, the difference of heating rate in the following uses is small (< 3.8%), and the heating rate fluctuates randomly, which has no linear relationship with the number of use. This shows that the SAC can be reused many times, and this has practical significance for the follow-up industrial application research.

3.2.2. Discussion on the process energy consumption

The advantage of microwave heating is bulk heating. Concern about heating efficiency is also a hot spot. According to heating time and input power, energy consumption of PP pyrolysis has been estimated in this study and compared with our previous pyrolysis [6,9]. Table 5 shows the energy consumption of this study and the comparison with the previous experimental values.

It can be seen from the table that the energy consumption varies greatly under different experimental conditions. The energy consumption per unit mass can be reduced by combining multiple power or increasing the input of PP. Compared with our previous experiments, the unit energy consumption in this study is significantly reduced. Most of the energy consumption of traditional electric heating occurs in the melting process of polyolefins, which takes a long time. On the contrary, the microwave heating process greatly shortens the heat transfer process between SAC and PP, thus improving the energy efficiency.

3.3. Discussion on cracking mechanism and heating strategies

The degradation mechanism of PP is radical chain mechanisms for thermal cracking or carbonium ion reaction mechanism for catalytic cracking. According to our previous studies [6,7], the polymer is firstly molten at about 100–200 °C, and then cracked to intermediates at about 300–330 °C. The intermediates are white solids in room temperature. With the temperature increasing, the intermediates further decomposes into wax, oil and gas at about 370–420 °C. Because of the special heating method and high heating speed, this study needs to explore the cracking pathway and the mechanism of PP in the microwave field.

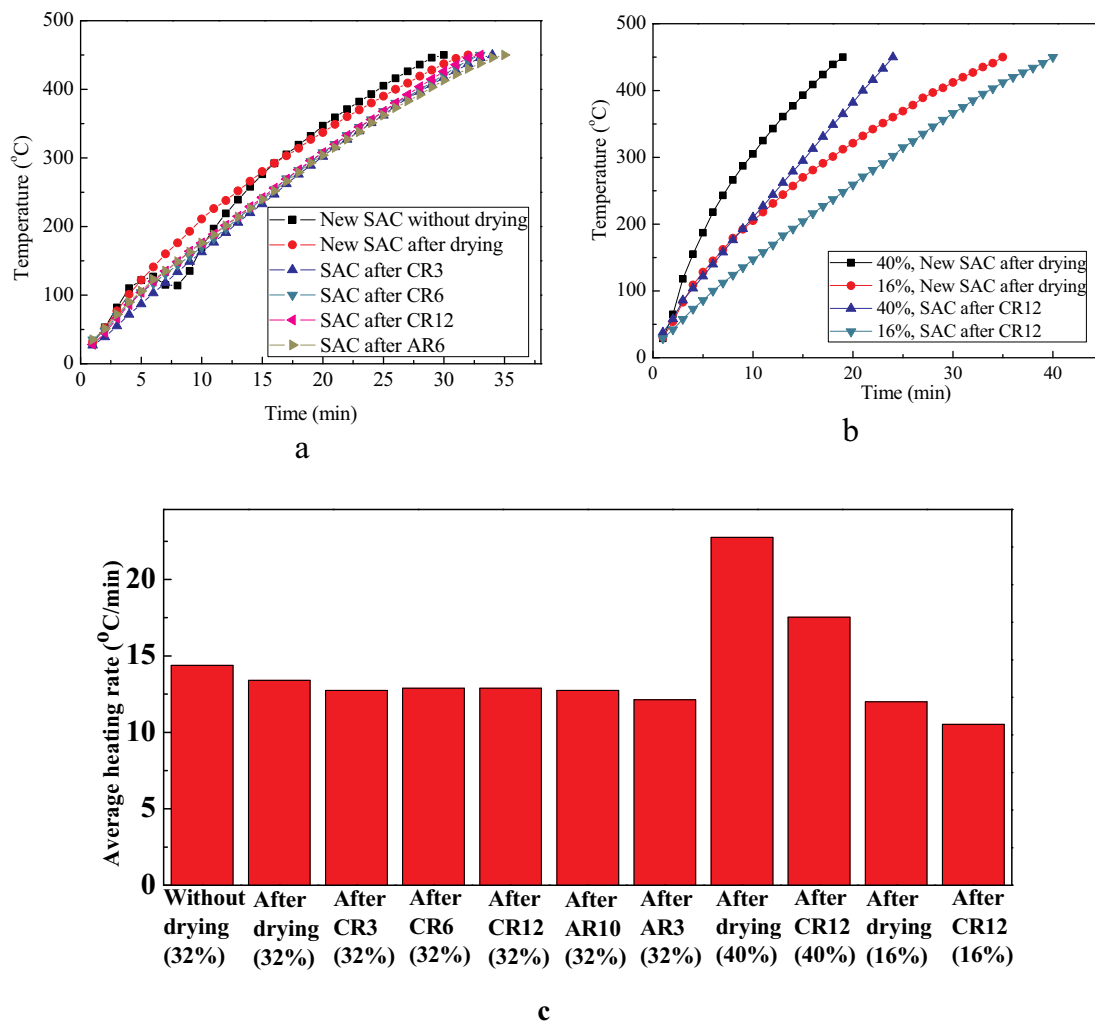


Fig. 14. Temperature-time curve of SAC at a fixed temperature measuring point (a: 32% input power, b: 16% and 40% input power, c: Average heating rate).

Table 5

List of energy consumption in major experimental series.

	Input power (W)	PP:SAC (g)	Heating time (min)	Energy consumption per unit mass of PP ($\text{W} \cdot \text{min} \cdot \text{g}^{-1}$)
AR1	360	70:140	36	185.12
AR3	288	70:140	42	172.80
AR5	144	70:140	50	102.86
AR10	360	70:140	38	195.43
BR1	432	70:140	30	185.14
BR10	360	70:140	40	205.71
CR1	360	100:140	40	144.00
CR6	144/288/360	100:140	60	162.00
DR1	144	40:100	70	252.00
ER1	144	70:70	115	236.57
Our study [6]	1000	200	120	600
Our study [9]	150	30	80	400

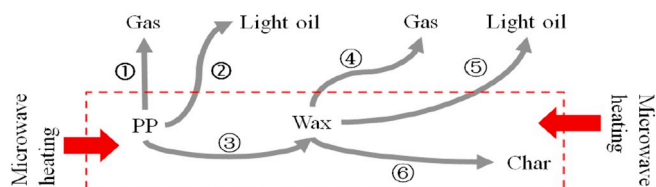


Fig. 15. The reaction path proposed in this study.

Fig. 15 shows the cracking reaction path proposed in this study, which considers only the main reactions in order to evaluate the competitive reaction paths.

Because the temperature of SAC increases rapidly after absorbing microwave, the heat of SAC is transferred to the surrounding PP. The heat transfer coefficient of PP is very small, which results in the heating speed of microwave is much faster than that of heat conduction. Therefore, compared with traditional heating, the time for cracking products to appear under microwave heating is significantly earlier. Especially in high power experiments, gas and liquid products were observed after several minutes of heating, which indicated that PP cracked first to produce gas, light oil and wax ((1) ~ (3) in Fig. 15). If the heating rate is too fast, wax may be carried into the receiving bottle, so wax precipitation occurs in one experiment such as AR1.

The generated wax can be converted into gas, light oil and char by secondary reaction due to longer reaction time and heating ((4) ~ (6) in Fig. 15). So the liquid products obtained in this study contain little olefins. Because the length of carbon chain of wax is much shorter than that of PP, and the energy required for chain breaking is also higher, more wax is often produced at lower input power. That is to say, path (4) and (5) needs more energy. Therefore, the combination of multi-power is a good choice for microwave pyrolysis. Among them, low power corresponds to the initial cracking reaction, while high power corresponds to the later secondary cracking reaction, especially the reaction from wax to oil ((4) ~ (5) in Fig. 15).

In the research of waste plastics pyrolysis recovery, how to promote

heat transfer and reuse heating medium or catalyst is the key to restrict the development of this technology. As a microwave absorbent, SAC can be reused many times to reduce cracking cost. Because SAC contains some catalysts, this paper aims to study the catalytic effect and mechanism of catalyst in sphere, so as to provide technical support for the following optimization and design of microwave cracking of absorber-catalyst-feedstock system. When the heating rate is too fast, such as AR1 and CR1, PP produces gases and liquid products which flow out with the carrier gas, and meanwhile there are some waxes in the liquid. When low input power or intermittent heating is used, such as AR5 and BR2, PP can be melted into a melting state and then cracked into wax, light oil and gas. In this case, the formation of liquid bands between SAC can be observed, which is conducive to enhancing the heat transfer of feedstocks. When the ratio of SAC to PP is high such as DR2, DR3 and CR12, PP and cracked products can contact SAC for a longer time. More importantly, the molecules in the cracking products may enter into the SAC, and catalytic cracking occurs in contact with the catalyst to produce smaller molecules. However, the surface of the SAC is mainly AC, while the interior is mainly minerals and catalysts. Moreover, the average pore size is small (15.03 nm), and BET area is not large. All these factors have a certain barrier to the effect of catalysts in the sphere. As a result, the catalytic effect is not significant. On the basis of ensuring the heating performance of SAC, the following research will expand the pore size and surface area, improve the catalyst activity and thus enhance the catalytic effect.

From the point of view of heat transfer and reuse, SAC has obvious advantages as microwave absorbent. Of course, the spherical size of AC is still possible to be optimized. In a word, as far as microwave cracking of PP is concerned, the combination of multiple input power, intermittent heating and co-cracking of PP and wax are better heating strategies.

4. Conclusions

In this study, commercial SAC, which contains some catalysts, has been used for microwave cracking experiments. The effect of heating strategies on product distribution has been studied. The aim is to try to make microwave absorbent and catalyst into spheres and heat them with waste plastics for microwave catalytic cracking. Meanwhile, the SAC has been reused many times to test the possibility of industrialization of the system. The following conclusions can be drawn.

- (i) The mixing of SAC with PP is conducive to heat transfer and uniform temperature distribution by adopting some heating strategies, and it is feasible to crack PP with SAC as microwave absorbers.
- (ii) The heating process of polyolefin-absorber mixture is in fact a simultaneous process of microwave heating and heat conduction. The heating rate of the former is much larger than that of the latter. Therefore, heating strategy is needed to adjust the product.
- (iii) The heating strategies including combination of different input power, co-cracking of PP-Wax and intermittent heating are beneficial to the formation of light oil.
- (iv) The SAC can be used many times. The heating characteristic of SAC decreases after one or two times of use, but it does not change much after many times of use, which is of great significance for subsequent industrial applications.
- (v) Due to the special composition and structure of SAC in this experiment, the catalytic effect is not significant, which is an important part of the follow-up study.

Acknowledgments

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Declaration of competing interest

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled, “Heating strategies for the system of PP and Spherical Activated Carbon during microwave cracking for obtaining value-added products” (FUPROC.2019_1480).”

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