



Catalytic pyrolysis of waste packaging polyethylene using $\text{AlCl}_3\text{-NaCl}$ eutectic salt as catalyst



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ABSTRACT

Catalytic pyrolysis is an attractive and promising way to recycle waste plastics. In this paper, $\text{AlCl}_3\text{-NaCl}$ eutectic salt was used as the catalyst to pyrolyze waste polyethylene (WPE), and its catalytic activity was studied. Thermogravimetry (TG), gas chromatography-mass spectrometer (GC-MS) and Fourier transform infrared spectroscopy (FTIR) were applied to investigate the pyrolysis behavior of WPE in the presence of $\text{AlCl}_3\text{-NaCl}$ eutectic salt during the catalytic pyrolysis. Subsequently, the char separated from the pyrolysis residue were characterized by scanning electron microscope (SEM), energy dispersive spectrometer (EDS), nitrogen adsorption and desorption testing, respectively. The results show that our strategy allows for the pyrolysis of WPE in the presence of molten $\text{AlCl}_3\text{-NaCl}$ eutectic salt, which can not only reduce the initial pyrolysis temperature (below 200 °C) significantly but also play a key role in increasing the reaction rate. Accordingly, it is a safe and environmentally benign treatment of “white pollutions” by both reducing energy consumption of pyrolysis process and alleviating the environmental pollutions. Besides, another advantage of using the $\text{AlCl}_3\text{-NaCl}$ eutectic salt as catalyst in pyrolysis of WPE is that the components of the heavy oil in the liquid products was much more reduced and no olefin was generated thus narrowing the composition distribution and improving their utilization value for further use. What's more, the char separated from residue contains many pore structures with a BET surface area of 218–277 $\text{m}^2 \text{g}^{-1}$. As results, this strategy provides a new avenue for the applications of eutectic salt for catalytic pyrolysis of waste plastics.

1. Introduction

Plastics have been widely used in packaging, buildings, automobile and appliance field due to the versatile performances of high strength, high durable, elastic and less expensive to produce [1]. It has brought great convenience to human life. However, increasing demand for these plastics and their subsequent disposal is a major environmental concern especially the disposable soft packaging plastics, namely “white pollutions” that caused by plastic products, such as shopping plastic bags, beverage bottles and lunch boxes [2]. As we all know, polyethylene including the low and high-density polyethylene (LDPE and HDPE) is one of the most commonly used packaging materials and WPE contributes major portion of the packaging plastics which is the key fraction of the vastly waste plastics (39.5% in Europe) [3,4].

Due to the difficulty of treatment and occupying large land space, waste plastics cause considerable problems around the world [5].

Although waste plastics is now a significant problem, the high calorific value makes it also a kind of potential available resources [3]. Therefore, many researchers have been looking for preferable approaches to turn these wastes into available resources. Common treatment methods for waste plastics include landfill [6,7], incineration [8,9], molten regeneration [10,11], bacterial decomposition [12,13] and chemical recycling [14,15]. Landfill is a simple but negative treatment method, which needs vast land space and may give rise to soil and water pollution if handled improperly [6]. Incineration of waste plastics can directly generate energy for supplying heating and power generation. Unfortunately, the emission of massive poisonous gases like dioxin and nitric oxide during the incineration process attributes that it is not an efficient solution due to the secondary pollution [8]. Molten regeneration refers to an approach that the waste plastics are granulated and used as raw material to make plastic products for second times. However, the properties of the secondary products tend to get worse

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and it usually requires modification by additional auxiliaries [16]. Bacterial decomposition is a promising approach to degrade waste plastics, which is still in the development stage and is challenging [17]. Usually, chemical recycling refers to the pyrolysis technology, including pure thermal pyrolysis and catalytic thermal pyrolysis. Pyrolysis is a common way to convert waste plastics to small molecule and usable products [18]. Because of the high energy consumption and uncontrollable products, pure thermal pyrolysis was gradually out of sight [19].

In chemical recycling, the pyrolysis of plastics in the presence of catalysts has attracted great attention because the proper selection of catalysts enables the control of the process and the kind of products efficiently. Lopez et al. [4] summarized the advantages and disadvantages of chemical reactors for pyrolysis, such as fixed beds, fluidized bed reactors, spouted beds, screw kilns and molten bath and so on, among which the fluidized bed and fixed bed were most commonly used. Results showed that the use of cracking catalyst has several practical advantages on polyolefin pyrolysis including reducing operating temperature, increasing the conversion ratio of polymer and narrowing down product distribution. Owusu et al. [20] used silica alumina as the catalyst to convert the waste HDPE, PP and PS to useful fuel products via catalytic pyrolysis and demonstrated that the use of a batch reactor was essential because of a highest yield of liquid products compared with continuous pyrolysis. Panda et al. [21] considered that thermolysis is a suitable method for waste plastics management and manufacture of value added products. To improve the oil quality and lower the initial decomposition temperature, plenty of catalysts were used to perform selective pyrolysis, such as natural zeolite, Y-zeolite, MCM-41, SBA15, FCC catalyst, HZSM-5, ZSM-5, most of which are classified into molecular sieve and consist of aluminosilicate [4,19]. These heterogeneous catalysts are mainly composed of granular or powder and prominently rely on their huge specific surface area to increase the contact area with the reactants. However, the char generated during the catalytic pyrolysis process could lead to blocking in the channel of molecular sieve, and then the catalytic activity would have an obvious reduction [22]. In addition, the packaging film is multi-layer composite membrane in general, and the waste plastics mostly are mixture of variety of plastics. In order to simplify the pre-treatment process, co-pyrolysis of plastics is also worthy of attention and could become a research hotspot [23].

It is generally accepted that the catalytic activity of the catalysts, including Y-zeolite, FCC catalyst and MCM-41 etc., comes from their acid sites (Based on Lewis acid theory) [24]. Most homogeneous catalysts for polyolefin degradation were classical Lewis acids such as AlCl_3 [25]. Ivanova et al. [26] summarized the pyrolysis mechanism of PE catalyzed by AlCl_3 , NaAlCl_4 and $\text{MgCl}_2 \cdot \text{AlCl}_3$ at 370 °C, respectively, and the gas yields were 47.6 wt%, 47.9 wt% and 88.2 wt%. At first, the initial interest was focused on recovery of valuable gaseous hydrocarbons, thus no detailed characterization of liquid products and residue were reported [26]. Nanbu et al. [27] reported catalytic degradation of polystyrene at 50 °C for 1–4 h in the presence of AlCl_3 . Results showed that the only volatile degradation product was benzene and the molecular weight of the residual polymers decreased, linearly with reaction time (1–4 h), down to 5.3×10^3 (number-average molar mass). Afterwards, Adams et al. [28] executed the cracking reactions of polyethylene at 120 °C, 200 °C and 250 °C in several ionic liquids containing AlCl_3 and the major products were C_3 – C_5 gaseous alkanes and branched cyclic alkanes with yields of 60–85 %. Pantano et al. [29] studied the mathematical modeling of the catalytic degradation of polystyrene in the presence of AlCl_3 . Karmore et al. [30] reported thermal degradation of polystyrene by Lewis Acids (AlCl_3 , FeCl_3 , SnCl_4 and boron trifluoride etherate) in solution. In addition, ZnCl_2 [31,32] CdCl_2 [33] were also ever used to catalytic degradation of waste plastics.

Although the previous researches have reported the pyrolysis of waste plastics using AlCl_3 as catalyst alone or using its solution, the idea

Table 1
Characteristics of the WPE.

Moisture content (wt%)	Melting point (°C)	Ash content (wt%)
0.23	134	0.02

of eutectic salt was not proposed. As is known, AlCl_3 is a kind of covalent compound, and its nature of easy sublimation (at about 120 °C) [34,35] brings obstacles for its application in pyrolysis of waste plastics. Fortunately, many researches have revealed that the addition of NaCl into AlCl_3 may form a low-temperature eutectic salt (containing Al_2Cl_6 , AlCl_4^- , Al_2Cl_7^- , Na^+ and Cl^-), which can lower the melt temperature and reduce the sublimation of AlCl_3 [36]. Moreover, the liquid eutectic salt may allow more contact between reactants and catalyst thus forming more uniform mixture between them. Herein, we report the catalytic pyrolysis of WPE using AlCl_3 - NaCl eutectic salt as catalyst, which provides a new concept and method for the pyrolysis of waste polymers with low energy consumption and high value products.

2. Materials and methods

2.1. Materials

The WPE used was recycled high density polyethylene granules with diameter of 3–5 mm which was granulated by a two-screw extruder and its characteristics were provided in Table 1. The AlCl_3 and NaCl , supplied from Tianjin TIANLI Chemical Reagents Ltd., were analytically pure and ground into powders together with a molar ratio of 3:2 to form the AlCl_3 - NaCl eutectic salt. Since the AlCl_3 would absorb water in air, the grind step was carried out in a glove box with argon (DELLIX P175 series).

2.2. Experimental apparatus and procedures

The apparatus used in this work was shown in Fig. 1. The pyrolysis reaction was carried out in a three-necked flask with stirring, and the other two necks were used for feeding and the escape of volatile products, respectively. After assembling the experimental apparatus, the nitrogen was inlet through the feed port to exhaust the inside air and check the air tightness of the apparatus. The apparatus was set to reach the designed temperatures (300 °C, 350 °C, 400 °C, 450 °C and 500 °C, as shown in Table 1), and then the stirring and condensing water circulation system were turned on. Afterwards, 6 g of the mixture of AlCl_3 - NaCl eutectic salt and 14 g of polyethylene was put into the flask as soon as possible through feedstock inlet and the inlet was quickly closed by frosted glass plug. The time consumed was recorded when there was no bubble escaped and no liquid product outflowed. After the reaction finished, the liquid products were filtered to remove the possible AlCl_3 and other insoluble impurities and the filtrated liquid products were stored in glass bottles. The residue in flask was washed out by diluted hydrochloric acid for further wash and dry. The weight of the liquid products and residue were weighed.

2.3. Analysis

2.3.1. Mass balance analysis

The weighing method of the products mass are shown in Fig. 1, and the products yields were calculated as follow:

$$W_g = W_{1a} - W_{1b} \quad (1)$$

$$W_v = W_{2a} - W_{2b} \quad (2)$$

$$\text{Gas yield} = (W_g / W_{pe}) \times 100\% \quad (3)$$

$$\text{Liquid yield} = (W_v / W_{pe}) \times 100\% \quad (4)$$

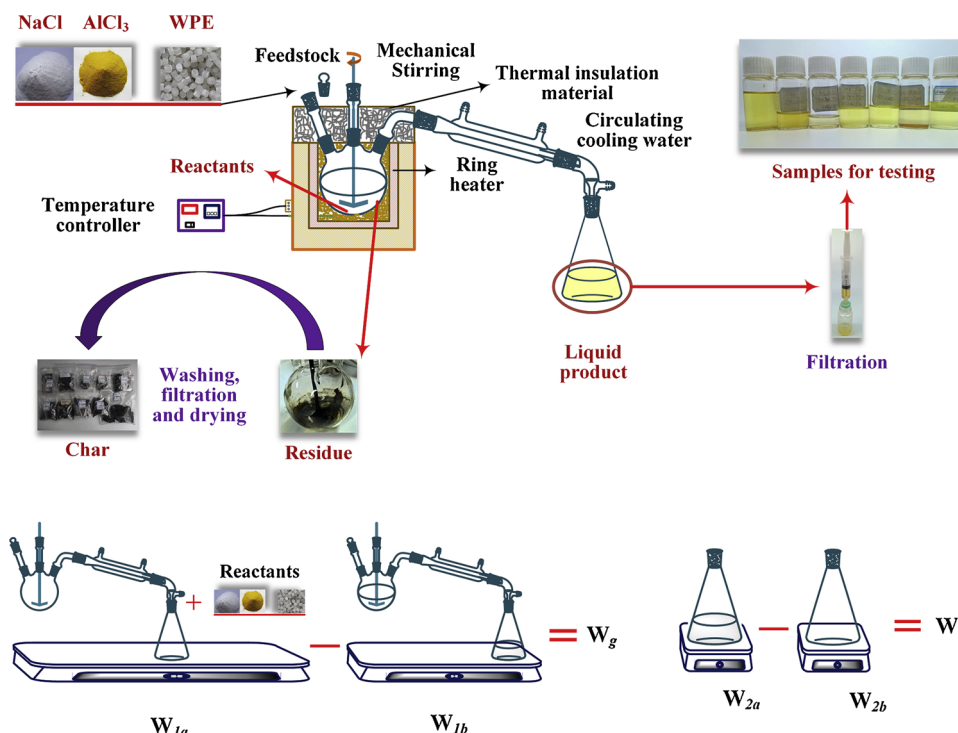


Fig. 1. Pyrolysis apparatus and experimental flow path.

$$\text{Char yield} = [(W_{pe} - W_v - W_g) / W_{pe}] \times 100\% \quad (5)$$

Where, W_{pe} was the weight of WPE fed into flask, W_s was the weight of char washed out from flask, W_v was the weight of liquid products, and W_g was the weight of gas products. Besides, W_{1a} was sum of the weight of all the reactant and whole weight of assembled glassware including flask, condenser, conical flask, stopper and stirring paddle. W_{1b} was the whole weight of assembled glassware containing eutectic salt, residue and liquid products after pyrolysis reaction. W_{2a} was the weight of the conical flask containing liquid products, and W_{2b} was the weight of empty conical flask. The pyrolysis experiments at different temperatures were carried out for three times, and the yields of gas, liquid products and residue as well as the composition of liquid products in this work were average value of three sets of data from repeated experiments.

2.3.2. TG analysis of pyrolysis behavior

The thermogravimetric curves were measured by TG (NETZSCH TG209F3) with the heating rate of $20^\circ\text{C}\cdot\text{min}^{-1}$ under a nitrogen flow of $60\text{ ml}\cdot\text{min}^{-1}$ and the contents of catalyst were 0 wt%, 10 wt%, 20 wt%, 30 wt%, 40 wt%, 50 wt%, 60 wt%, 100 wt%, respectively. In this testing, in order to make sure AlCl_3 , NaCl and WPE were well mixed, the WPE granule was pulverized at low temperature with the help of liquid nitrogen, then the WPE powder was dried and put in glove box. The AlCl_3 and NaCl were ground and mixed with WPE powder in a glove box in argon atmosphere, then 15 mg of mixture was transferred to the special Al_2O_3 crucible and stored in a sealed box. Finally, the crucible containing reactants in sealed box was took out for TG testing.

2.3.3. Composition of products

The composition of liquid products was tested by GC–MS (PerkinElmer Turbo Matrix 16-Clarus 600-Clarus 600 T). A Thermo TR-5MS column ($30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$ thickness 5% phenyl(equiv) polysilphenylene-siloxane film) was used. The carrier gas was helium with a flow rate of $1\text{ ml}\cdot\text{min}^{-1}$. $1\text{ }\mu\text{l}$ of liquid products were injected with a split ratio of 20:1. The temperature program of column oven began with a hold at 80°C for 1 min followed by an increase with a rate

of $20^\circ\text{C}\cdot\text{min}^{-1}$ to 100°C , then an increase with a rate of $20^\circ\text{C}\cdot\text{min}^{-1}$ to 260°C and finally an increase to 400°C with a rate of $15^\circ\text{C}\cdot\text{min}^{-1}$, which was held for 2 min. The ionizing voltage and range of m/z of mass spectrometer were set at 70 eV and 30–650, respectively. The content of each component was calculated based on the relative GC/MS peak area %. The functional groups of liquid products were characterized by Shimadzu FTIR-8400S Fourier transform infrared (FTIR) spectrometer using KBr pellets as the sample matrix by transmittance mode. The frequency range was $1000\text{--}4000\text{ cm}^{-1}$ and the number of scans was $32\text{ times}\cdot\text{s}^{-1}$. The micro-morphology of the char from pyrolysis residue were observed on a Hitachi SU8000 field emission scanning electron microscope (SEM) at 20 kV. Nitrogen adsorption and desorption isotherms were recorded using the JW-BK100 A analyzer (JWGB). The pore size distribution was obtained using nitrogen adsorption and desorption data via the Barrett-Joyner-Halenda (BJH) model and specific surface area was calculated by Brunauer-Emmett-Teller (BET) model.

3. Results and discussion

3.1. Catalytic activity of AlCl_3 -NaCl eutectic salt

The melting point of WPE and thermal behavior of AlCl_3 -NaCl eutectic salt were confirmed by differential scanning calorimeter (DSC). As shown in Fig. 2, the melting point of WPE was about 134°C , so the WPE was molten state during the pyrolysis experiments. Furthermore, there was a relatively wide endothermic peak (about 120°C) and an exothermic peak (about 152°C) in the DSC curve of AlCl_3 -NaCl eutectic salt. According to previous studies, the endothermic peak was probably caused by the sublimation and decomposition of AlCl_3 . The exothermic peak may attribute to the generation of AlCl_4^- and Al_2Cl_7^- : NaCl ionized to Na^+ and Cl^- , and the Cl^- combined with AlCl_3 [35].

Fig. 3 shows the TG curves and DTG curves of WPE, AlCl_3 -NaCl eutectic salt and samples of WPE added with different content of AlCl_3 -NaCl eutectic salt, respectively. According to Fig. 3, the initial cracking temperature of WPE without adding AlCl_3 -NaCl eutectic salt was about 400°C and reaction rate was very slow at this temperature. However,

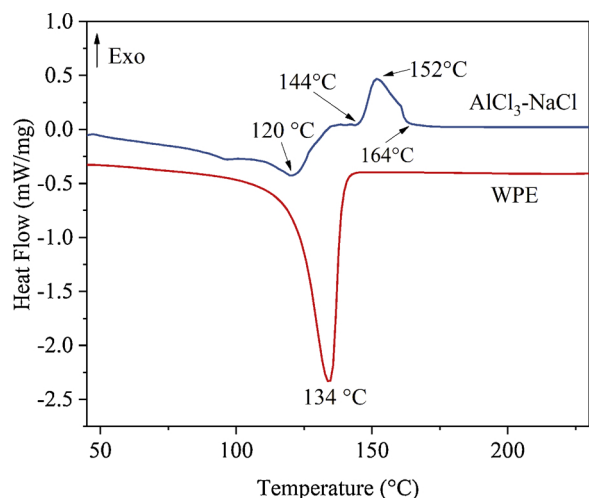


Fig. 2. DSC curves of $\text{AlCl}_3\text{-NaCl}$ eutectic salt and WPE.

the weight loss of the samples added $\text{AlCl}_3\text{-NaCl}$ eutectic salt were more obviously than either the WPE alone or the $\text{AlCl}_3\text{-NaCl}$ eutectic salt at the same temperature below 450°C , which illustrated that $\text{AlCl}_3\text{-NaCl}$ eutectic salt reduced the initial cracking temperature. Besides, with the increase of the amount of $\text{AlCl}_3\text{-NaCl}$ eutectic salt added, the weight loss speed increased at first and then decreased when the amount of $\text{AlCl}_3\text{-NaCl}$ eutectic salt was greater than 30 wt%. Because that the high amount of $\text{AlCl}_3\text{-NaCl}$ eutectic salt might hinder the escape of pyrolysis products. Based on this, the addition amount of the eutectic salt was kept at 30 wt% in subsequent cracking experiments.

In the DTG curves, there are two main weight loss peaks. The first peak, at about $132\text{--}155^\circ\text{C}$ which was consistent with the DSC result approximately, was possibly caused by the sublimation and decomposition of AlCl_3 and corrosion of WPE particles that just starting to melt. It is worth noting that the temperature of this peak shifted towards low temperature as the content of $\text{AlCl}_3\text{-NaCl}$ eutectic salt increased from 10 wt% to 60 wt%, which is due to that more WPE powder may hinder the escape of the sublimed AlCl_3 molecules. The second peak, at about 475°C , is the temperature of maximum weight loss rate of undecomposed WPE.

3.2. Yields of pyrolysis products and reaction elapsed time

Table 2 shows the yields of liquid products, gas products and residues as well as the reaction time in different conditions. It can be found that the higher the temperature was, the less time the reaction

takes with or without $\text{AlCl}_3\text{-NaCl}$ eutectic salt. The reaction at 500°C was very intense and uncontrolled, in which lots of gas and more residues were generated. Besides, the yields of gas and residue increased with the increase of temperature, and the yields of liquid products decreased accordingly. Therefore, too high temperature was not good for getting more liquid products, especially when the temperatures were above 460°C , which was also observed in the TG and DTG curves. In addition, the data in Table 2 also illustrated that the addition of the eutectic salt can increase the reaction rate thus reduce the time and energy consumption of the whole reaction process. Meanwhile, the $\text{AlCl}_3\text{-NaCl}$ eutectic salt can also reduce the yields of liquid products and increase the yields of gas and residue.

3.3. Composition of liquid products

Table 3 shows the components of liquid products in different pyrolysis conditions. Normally, the liquid products are mixture of hydrocarbons including olefin, alkane, cyclic hydrocarbon and aromatic hydrocarbon [26]. In this work, the components were divided by the number of carbon atoms of the liquid compound. In Table 3, the C_n refers to the hydrocarbon products that have n ($n = 1, 2, 3, \dots$) carbon atoms. It can be observed that the use of $\text{AlCl}_3\text{-NaCl}$ eutectic salt can make the molecules of liquid products smaller. For example, the largest molecule of the liquid products obtained at 450°C was C_{15} when used $\text{AlCl}_3\text{-NaCl}$ eutectic salt. However, without catalyst, there were 37.5% molecules larger than C_{15} and the largest molecule was C_{27} at same temperatures. Furthermore, according to the TG analysis, polyethylene molecular chain would not crack below 400°C without catalyst. However, when the $\text{AlCl}_3\text{-NaCl}$ eutectic salt was used, the initial cracking temperature was below 200°C and the largest molecular of liquid products in 300°C and 350°C was C_{25} and C_{23} respectively. We assume that not only the melting salt can catalyze the pyrolysis of polyethylene, the sublimed AlCl_3 in the flasks can further catalyze the volatile products crack into smaller molecular. Moreover, the number of relatively larger molecules of liquid products was reduced with the increase of pyrolysis temperature. Another phenomenon worth noting was that the components of the obtained sample at 350°C were greatly different with that of 400°C . However, the difference of the components with maximum carbon number of each sample was very small when the temperatures were above 400°C . Besides, the TG curves between $350\text{--}400^\circ\text{C}$ were smooth. Therefore, in order to obtain more liquid products, the optimum temperatures should be between $350\text{--}400^\circ\text{C}$. Furthermore, the olefin was only detected in the products from pyrolysis of WPE without catalyst. The content of cyclic hydrocarbon increased with the increase of pyrolysis temperature and aromatic hydrocarbon was detected only in the samples at 500°C .

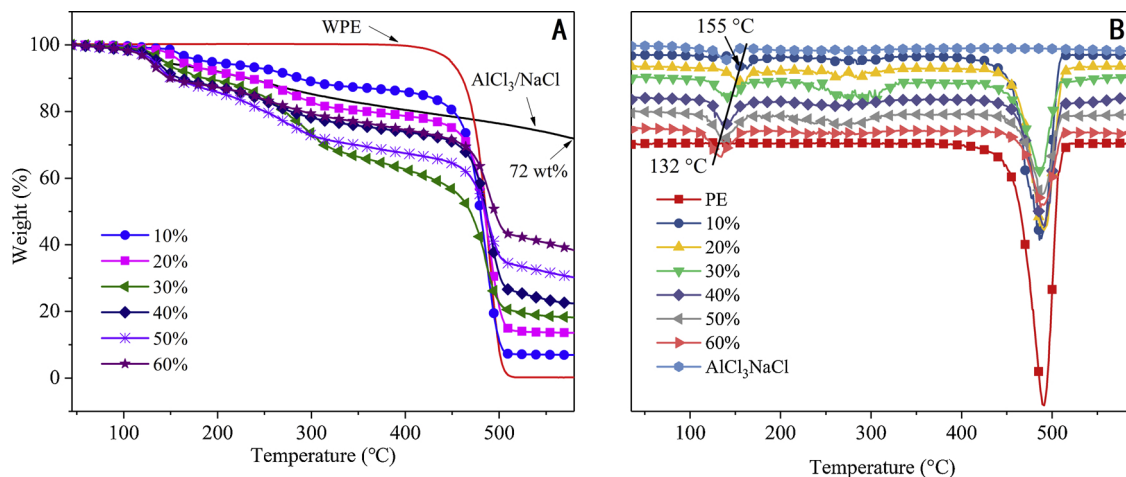


Fig. 3. TG (A) and DTG (B) curves of WPE, $\text{AlCl}_3\text{-NaCl}$ eutectic salt and samples with different content of $\text{AlCl}_3\text{-NaCl}$ eutectic salt.

Table 2

Yield of pyrolysis products and reaction time in different pyrolysis conditions (wt%).

Serial number	Pyrolysis temperatures (°C)	Salt content (wt%)	Consuming time (min)	Liquid wt%	Gas	Residue
A1	450	0	482 ± 11	94.6 ± 0.56	4.3 ± 0.53	1.1 ± 0.23
A2	500	0	19 ± 2.6	71.7 ± 2.1	27.2 ± 2.4	1.1 ± 0.26
B1	300	30	198 ± 10	91.7 ± 0.89	5.1 ± 0.53	3.2 ± 0.31
B2	350	30	147 ± 12	90.5 ± 0.66	5.6 ± 0.79	3.9 ± 0.36
B3	400	30	94 ± 6.2	89.4 ± 0.75	6.3 ± 0.36	4.3 ± 0.52
B4	450	30	52 ± 5.0	87.2 ± 0.80	7.1 ± 0.79	5.7 ± 0.55
B5	500	30	13 ± 1.7	62.1 ± 1.2	30.1 ± 0.95	7.8 ± 0.43

Table 3

Components of liquid products in different pyrolysis conditions (peak area %).

Component	Samples						
	A1	A2	B1	B2	B3	B4	B5
C ₄	1.6 ± 0.15	3.8 ± 0.21	3.9 ± 0.34	5.8 ± 0.36	15.8 ± 1.3	16.5 ± 1.2	17.1 ± 0.95
C ₅	2.8 ± 0.11	4.7 ± 0.35	8.3 ± 0.43	7.1 ± 0.64	12.6 ± 1.4	15.9 ± 0.92	17.9 ± 0.46
C ₆	4.0 ± 0.10	4.1 ± 0.29	9.2 ± 0.21	12.1 ± 0.96	12.3 ± 0.87	16.6 ± 1.0	17.0 ± 0.95
C ₇	6.7 ± 0.44	8.5 ± 0.38	10.2 ± 0.50	13.5 ± 1.1	13.2 ± 0.80	12.5 ± 0.79	13.8 ± 1.3
C ₈	6.0 ± 0.28	7.3 ± 0.34	9.7 ± 0.56	12.9 ± 0.78	10.2 ± 0.66	10.5 ± 0.96	9.6 ± 0.56
C ₉	5.4 ± 0.42	5.2 ± 0.28	8.6 ± 0.37	7.2 ± 0.43	8.4 ± 0.62	8.3 ± 0.44	7.6 ± 0.41
C ₁₀	5.3 ± 0.11	5.2 ± 0.61	6.8 ± 0.50	8.0 ± 0.97	7.1 ± 0.61	6.5 ± 0.40	5.5 ± 0.36
C ₁₁	6.3 ± 0.29	5.4 ± 0.22	5.5 ± 0.25	7.5 ± 0.50	6.0 ± 0.44	4.9 ± 0.17	3.7 ± 0.17
C ₁₂	6.1 ± 0.16	5.3 ± 0.32	7.9 ± 0.13	5.4 ± 0.38	4.5 ± 0.36	3.5 ± 0.26	3.6 ± 0.26
C ₁₃	5.9 ± 0.14	5.5 ± 0.27	4.7 ± 0.14	5.0 ± 0.39	3.1 ± 0.26	2.5 ± 0.17	1.7 ± 0.11
C ₁₄	6.3 ± 0.21	5.7 ± 0.18	3.9 ± 0.26	3.7 ± 0.24	2.0 ± 0.17	1.4 ± 0.13	1.6 ± 0.12
C ₁₅	6.0 ± 0.37	5.6 ± 0.32	4.1 ± 0.20	4.0 ± 0.20	4.0 ± 0.26	0.5 ± 0.00	/
C ₁₆	6.2 ± 0.37	5.3 ± 0.37	4.2 ± 0.35	1.6 ± 0.15	0.3 ± 0.020	/	/
C ₁₇	6.0 ± 0.070	5.1 ± 0.45	3.5 ± 0.16	1.8 ± 0.056	/	/	/
C ₁₈	5.4 ± 0.11	5.0 ± 0.29	1.9 ± 0.15	0.9 ± 0.056	/	/	/
C ₁₉	5.1 ± 0.21	4.7 ± 0.36	0.6 ± 0.052	0.8 ± 0.036	/	/	/
C ₂₀	4.5 ± 0.17	3.6 ± 0.28	1.7 ± 0.62	0.8 ± 0.043	/	/	/
C ₂₁	3.6 ± 0.18	3.2 ± 0.27	1.5 ± 0.14	0.7 ± 0.053	/	/	/
C ₂₂	2.4 ± 0.14	2.1 ± 0.13	1.5 ± 0.11	0.4 ± 0.043	/	/	/
C ₂₃	2.0 ± 0.15	2.0 ± 0.16	0.7 ± 0.020	0.3 ± 0.026	/	/	/
C ₂₄	1.2 ± 0.11	1.0 ± 0.026	0.7 ± 0.053	/	/	/	/
C ₂₅	0.5 ± 0.26	0.8 ± 0.053	0.3 ± 0.020	/	/	/	/
C ₂₆	0.3 ± 0.020	0.2 ± 0.017	/	/	/	/	/
C ₂₇	0.3 ± 0.017	/	/	/	/	/	/
Total	99.9 ± 0.10	99.3 ± 0.43	99.4 ± 0.41	99.5 ± 0.53	99.5 ± 0.27	99.6 ± 0.55	99.1 ± 0.53
Olefin	14.8 ± 0.79	15.4 ± 0.22	/	/	/	/	/
Alkane	85.1 ± 0.80	63.5 ± 0.84	82.5 ± 0.64	79.4 ± 1.3	76.3 ± 1.5	67.8 ± 1.8	75.2 ± 1.3
Cyclic hydrocarbon	/	5.4 ± 0.36	16.9 ± 0.89	20.2 ± 1.3	23.2 ± 1.4	31.8 ± 1.7	11.6 ± 0.72
Aromatic hydrocarbon	/	15.0 ± 0.85	/	/	/	/	12.4 ± 1.1

In addition, it is difficult to use the pyrolysis oil directly due to the diverse components. But the valued gasoline and diesel components could be separated by distillation. Usually, petrol and diesel consist mostly of C₄–C₁₂ hydrocarbon and C₁₀–C₂₂ hydrocarbon respectively. Table 4 lists the approximate proportion of gasoline and diesel fuel components in the oil products obtained under different pyrolysis conditions. Obviously, the catalytic pyrolysis could produce more light components compared with thermal pyrolysis of WPE. When the AlCl₃–NaCl eutectic salt was used, the gasoline components proportion in oil

products was not less than 90% when the pyrolysis temperature was above 400 °C. It can be seen that this method is a reasonable way to turn the WPE into fuel.

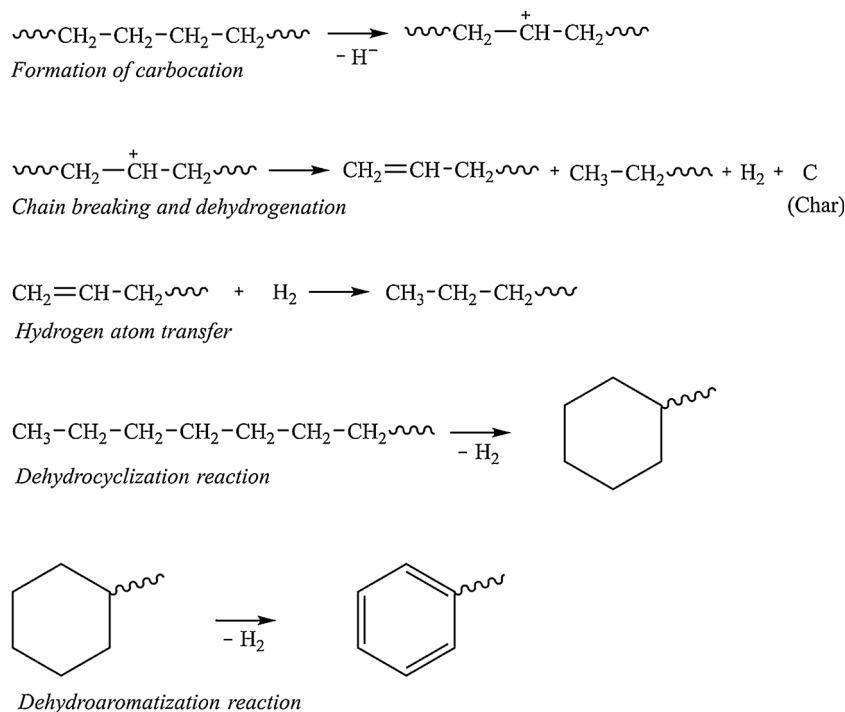
3.4. Functional groups of liquid products

Fig. 5 shows the FTIR spectrum of liquid products obtained in different conditions. The peaks at 2958 cm^{−1}, 2873 cm^{−1}, 1458 cm^{−1} and 1377 cm^{−1} were attributed to the presence of –CH₃ and –CH₂ groups

Table 4

Proportion of gasoline and diesel components respectively of liquid products in different pyrolysis conditions (peak area %).

Composition	Samples						
	A1	A2	B1	B2	B3	B4	B5
C ₄ –C ₁₂	44.2 ± 0.36	49.1 ± 0.69	70.1 ± 0.55	79.5 ± 0.76	90.1 ± 0.25	95.2 ± 0.17	95.8 ± 0.56
C ₁₀ –C ₂₂	69.1 ± 0.47	60.7 ± 0.42	47.8 ± 0.42	40.6 ± 0.35	27.0 ± 0.27	19.3 ± 0.28	16.1 ± 0.20
> C ₂₂	4.3 ± 0.25	4.0 ± 0.17	1.7 ± 0.031	0.3 ± 0.030	/	/	/
< C ₄	0.1 ± 0.013	0.7 ± 0.052	0.6 ± 0.021	0.5 ± 0.028	0.5 ± 0.014	0.4 ± 0.033	0.9 ± 0.066

Fig. 4. Catalytic pyrolysis mechanism of WPE with AlCl₃-NaCl eutectic salt.

of aliphatic hydrocarbons in liquid products [3]. What's more, the peaks at 2925 cm⁻¹, 2852–2855 cm⁻¹, 1465 cm⁻¹ and 1301 cm⁻¹ were due to asymmetrical stretching, symmetric stretching, bending vibration and twisting vibration of the –CH₂ groups of alkanes compounds, respectively. On the other hand, the relatively weak peak at 3078 cm⁻¹ of sample A1 and A2 was assigned to the –CH₂ antisymmetric stretching of olefins. Mono substituted double bond (R–CH=CH₂) showed two peaks in the spectrum of sample A1 and A2: one at about 990 cm⁻¹ and the other at about 910 cm⁻¹. The peak near 720 cm⁻¹, pointed to the cis di-substituted double bond [3], and the peak at 965 cm⁻¹ also indicate the presence of olefins. Finally, the peaks around 3077 cm⁻¹, 1643 cm⁻¹, 991 cm⁻¹ and 910 cm⁻¹, which attribute to the presence of olefins, were only observed in the spectrum of sample A1 and A2. Thus, it seems that the AlCl₃-NaCl eutectic salt have a certain effect to restrain the generation of olefins, which was consistent with the results in Table 3. If so, it could reduce the composition diversity of liquid products and make them easier to use.

3.5. Catalytic pyrolysis mechanism

Many researchers suggested that the pyrolysis catalyst by Lewis acid follows the carbocation mechanism and most important catalyst pyrolysis processes are random chain breaking with hydrogen atom transfer, dehydrocyclization reaction and dehydroaromatization reaction, thus leading to a broad variety of products [20,37,38]. Fig. 4 shows the probably catalytic pyrolysis mechanism of WPE with AlCl₃-NaCl eutectic salt. The electrophilic AlCl₃-NaCl eutectic salt decreased the activation energy of the formation of carbocation reducing the initial pyrolysis temperature. The electrophilic action of AlCl₃-NaCl eutectic salt enhanced the dehydrogenation with more carbocation and breaking sites. Meanwhile, the enhanced dehydrogenation resulted in the formation of both shorter chains of hydrocarbons and char. As shown in Table 3, the principal pyrolysis products were gas and liquids and almost no char was generated without catalyst. Because no hydrogen was added into reaction system, the breaking of chains led to formation of carbon-carbon double bond. When the catalyst was used, a certain amount of char was generated with redundant hydrogen. A part of hydrogen was combined with carbocation to generate saturated

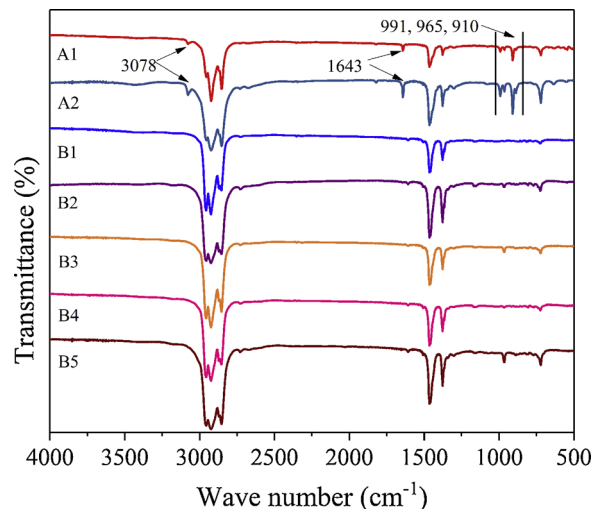


Fig. 5. FTIR spectrum of the liquid products obtained in different conductions.

hydrocarbon by hydrogen atom transfer and the residual might form H₂. Therefore, almost no olefin was detected in the liquid products from catalyst pyrolysis. According to previous researches, a relatively high temperature (about 500 °C) [39] was required for the dehydroaromatization reaction, thus the aromatic hydrocarbon was only detected in the samples from the pyrolysis of WPE at 500 °C.

3.6. Morphology and structure of char

It is mentioned in previous researches that even though the char formation in pyrolysis process was commonly less, the properties and usage of the char are worth noting to fully maximize the potential of plastic pyrolysis [18]. In this work, the residue of experiments was put into diluted hydrochloric acid solution with stirring for 12 h to sufficiently dissolve the AlCl₃ and NaCl, then the char was separated by washing and suction filtration. Fig. 6 shows the microstructure of the char separated from pyrolysis residue. The obtained char had a fluffy

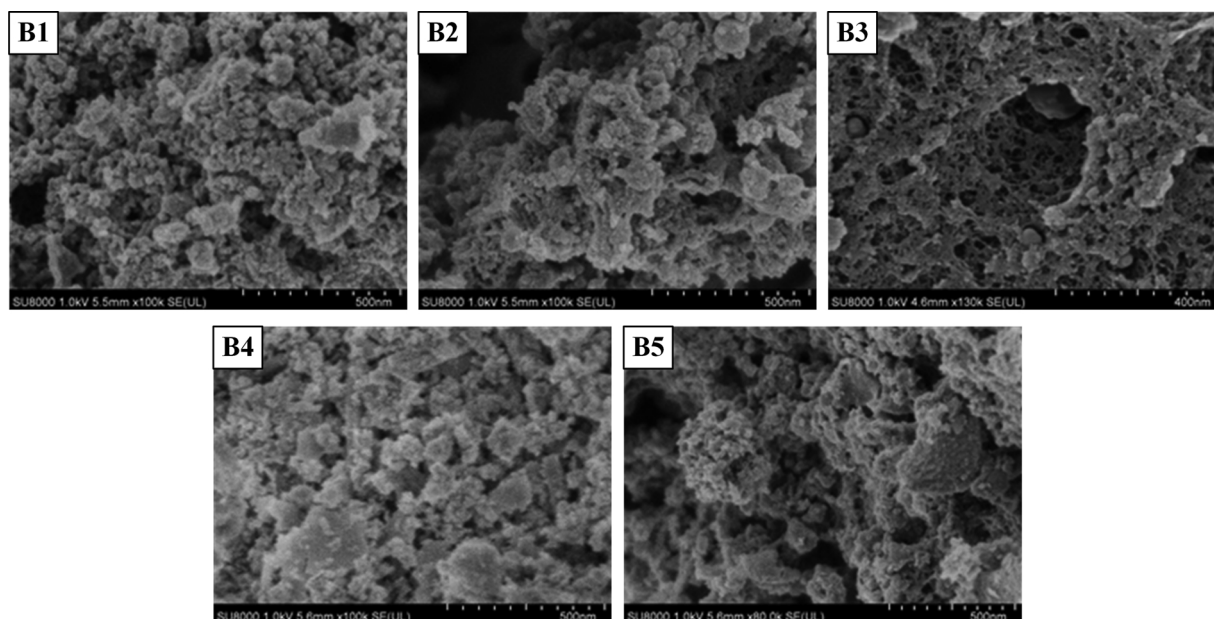


Fig. 6. SEM images of the char of samples B1-B5.

Table 5

The BET surface area, pore volume and elements content of the char.

Samples	BET surface area (m ² ·g ⁻¹)	Pore volume (cc·g ⁻¹)	Elements (%)			
			C	Al	O	other
B1	251 ± 13	0.331 ± 0.030	89.62 ± 0.60	3.58 ± 0.33	5.21 ± 0.48	1.59 ± 0.19
B2	218 ± 9.2	0.276 ± 0.027	93.18 ± 0.31	2.31 ± 0.26	2.79 ± 0.20	1.72 ± 0.096
B3	223 ± 11	0.298 ± 0.027	94.63 ± 0.76	1.37 ± 0.23	2.32 ± 0.46	1.68 ± 0.16
B4	255 ± 13	0.337 ± 0.037	90.12 ± 0.60	3.16 ± 0.36	5.31 ± 0.39	1.41 ± 0.16
B5	277 ± 8.7	0.346 ± 0.034	91.37 ± 0.15	2.53 ± 0.23	4.33 ± 0.47	1.77 ± 0.21

pores structure with a BET surface area of 218–277 m² g⁻¹ and pore volume of 0.276–0.346 cc·g⁻¹. The formation mechanism of pores was probably as follow: the char generated in pyrolysis was dispersed in AlCl₃-NaCl eutectic salt. When the reaction was finished, the char and salt condensed into clumps during the cooling process and after that the salt was washed out while the char with gap was remained. Table 5 shows the BET surface area, pore volume and elemental analysis. The main element of the char is carbon, and contains a small amount of aluminum and oxygen elements and the molar ratio of aluminum to oxygen is about 3:2. Because AlCl₃ is very easy to absorb moisture, it was very difficult to isolate the moisture in air from AlCl₃ completely in the process of the experiments. AlCl₃ generated Al(OH)₃ and HCl with H₂O. Then the Al(OH)₃ became to Al₂O₃ and H₂O when heated during pyrolysis. So, these aluminum and oxygen elements probably from Al₂O₃ which formed in the pyrolysis process. The char obtained had a potential utilization value in the fields of adsorption and energy storage. As is well known, the molecular sieve catalysts are easy to lose catalytic activity due to blockage of porous channel [40]. However, the AlCl₃-NaCl eutectic salt can still maintain catalytic activity after pyrolysis, and WPE could be added into flask again for secondary or more pyrolysis reactions until too much char was deposited in the flask.

4. Conclusion

Pyrolysis of WPE was catalyzed by AlCl₃-NaCl eutectic salt in this work. The eutectic salt can not only reduce the initiation pyrolysis temperature of WPE but also increase the reaction speed thus reducing

reaction time and energy consumption of pyrolysis. Due to the presence of AlCl₃-NaCl eutectic salt, the initial cracking temperature of WPE (below 200 °C) was much lower than that without catalyst (about 400 °C). What's more, AlCl₃-NaCl eutectic salt can further reduce the heavy oil components in liquid products and thus improve its practical use value. In addition, AlCl₃-NaCl eutectic salt could inhibit the formation of olefins which can reduce the complexity of the liquid products. More significantly, the char separated from residue contains many pore structures with a BET surface area of 218–277 m² g⁻¹, which might have potential utilization in the field of adsorption and energy storage. Furthermore, considering the reaction rate, yield and composition of liquid products in this work, the optimal parameters should be 30 wt% eutectic salt addition and 350–400 °C for pyrolysis from a comprehensive perspective. Overall, the experimental results on catalytic pyrolysis of WPE and analyses of products show that the AlCl₃-NaCl eutectic salt could be a very good option which could ultimately transforms waste to energy materials.

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