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Influence of process conditions on the formation of 2 − 4 ring polycyclic aromatic hydrocarbons from the pyrolysis of polyvinyl chloride

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ABSTRACT

Municipal solid waste (MSW) contains significant amounts of polyvinyl chloride (PVC). The reactivity of PVC may form polycyclic aromatic hydrocarbons (PAHs) during the pyrolysis of MSW, which can become a key challenge during the development of pyrolysis technologies. However, there is very limited work in relation to the influence of pyrolysis process conditions in terms of temperature and heating rate on PAHs formation during pyrolysis of PVC. In this work, the formation of 2-4-ring PAHs from the pyrolysis of PVC at temperatures of 500, 600, 700, 800, or 900 °C and at fast and slow heating rates was investigated under a N_2 atmosphere in a fixed bed reactor. With the increase of temperature from 500 to 900 °C, HCl yield decreased from 54.7 to 30.2 wt.%, while the yields of gases and PAHs in the tar increased. Slow pyrolysis generated higher HCl yield, and lower gas and tar yield than fast pyrolysis; the PAH yield obtained from the slow pyrolysis was much lower compared to fast pyrolysis. The results suggest that for fast pyrolysis, the dehydrochlorination of the PVC might be incomplete, resulting in the formation of chlorinated aromatic compounds.

Keywords: Waste; Plastics; Pyrolysis; PAH; PVC

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1. Introduction

Waste plastics can be recycled by mechanical and chemical means. These two recycling process are complementary in solving the problems of environmental pollution from waste plastics. Mechanical recycling of plastic materials is used in some countries to reduce the amount of plastics in the waste stream destined for chemical recycling via thermochemical processes.

Advanced thermal conversion processes, including pyrolysis, are considered to be important methods for the utilization of waste plastics to produce, energy, fuels and chemicals [1-3]. Therefore, the pyrolysis of waste plastics are generating increasing interest [4,5].

Polyvinyl chloride (PVC) is produced in two forms, rigid PVC which is used in applications such as for example, piping, roofing tiles and window frames, and flexible PVC used for example in flooring material and cable coverings. Approximately 10.7% of plastics produced in Europe are represented by PVC, associated with this demand is the generation of waste and it is estimated that 25.2 Mt of waste plastics are produced each year in Europe [6]. Consequently, a significant tonnage of plastic waste containing PVC will be generated, particularly in the municipal solid waste stream [6,7]. Under pyrolysis conditions, the thermal degradation of the PVC results in a two-stage process [8,9]. As the pyrolysis temperature is increased, it has been reported that the C-Cl bond in PVC is one of the first to break; which is due to the formation of long conjugated double bonds leading to the formation of polyene [10]. Literature shows that the C-Cl bond breaking is followed by intermolecular chain transfer, resulting in the evolution of HCl gas via dehydrochlorination [11]. A residual polyene structure undergoes further thermal degradation in the second stage decomposition at higher temperature [12,13].

The pyrolysis of waste plastics are known to produce polycyclic aromatic hydrocarbons (PAHs) [14]. There are concerns in relation to the emissions of PAHs in the environment

because of their perceived human health hazard [15-17]. Therefore, understanding the emissions of PAHs from plastic pyrolysis is an important research topic in order to control, prevent or minimise their formation. Conesa et al. [18] compared the PAHs emissions from pyrolysis of nine different kinds of wastes at 850 °C. The pyrolysis of PVC generated the largest yield of phenanthrene and the second largest amount of naphthalene among these nine kinds of wastes [18]. Müller et al. [19] reported on the influence of aluminium on the formation of PAHs during the pyrolysis of PVC. They showed that increased aluminium addition to the PVC resulted in an increase in char yield, an increase in alkane gas concentration and a decrease in the aromatic content of the product oil. Furthermore, increasing aluminium addition resulted in a marked decrease in PAHs [19]. PAH may also be formed from combustion of PVC. Wang et al. [20] investigated the sub-stoichiometric combustion of PVC at temperatures between 500 to 1000 °C. They reported that the PAHs from PVC combustion decreased from >4000 μg g^{-1} to <2000 μg g^{-1} with increasing temperature of combustion. Additionally, a decrease of fluorene, phenanthrene, and anthracene was reported.

At present, there are few reports investigating the formation of PAHs during PVC pyrolysis under different reaction conditions. Here we report on the influence of the process conditions of pyrolysis temperature and the influence of fast and slow heating rate on the formation of 2-ring to 4 ring PAH. The results are expected to contribute to the future process design of pyrolysis technologies for processing MSW, regarding the emission of PAHs derived from PVC, which is a significant fraction in the plastics fraction of MSW.

2. Materials and methods

3

2.1. Materials

The PVC sample was obtained from Sigma-Aldrich. Proximate analysis of the PVC sample shows that the sample has a volatile content of 94.8 wt.% and the content of fixed carbon is about 5.1 wt.%. Element analysis of the PVC shows that the sample contains about 38.34 wt.% C, 4.47 wt.% of H, 0.23 wt.% N, 0.61 wt.% S and 56.35 wt.% Cl. The PVC was obtained in the form of granules of about 1mm ID and used as received. For the elemental analysis and TGA tests, a portion of the sample was crushed to <125 µm before use. Pure PVC was used for this work in order eliminate the potential influence of contaminants or additives that may be found in real-world PVC waste.

2.2. Pyrolysis of PVC

Figure 1 shows the pyrolysis reactor system used for the investigation of the role of process conditions on PVC pyrolysis. The reactor was manufactured from stainless steel and was 640 mm long and 10 mm diameter and was continuously purged with N_2 with a gas residence time of 2.6 s. The reactor heated with a 0.95 kW furnace with a maximum temperature of 1200 °C, manufactured by Carbolite, UK. Two types of pyrolysis including fast and slow pyrolysis were studied in this work. For the fast pyrolysis experiments, the reactor was initially heated to the temperature set point of 500, 600, 700, 800, or 900 °C. The PVC plastic sample (1 g) was placed on a sample spoon and inserted into the reactor where fast pyrolysis occurred. The sample was quickly heated to the set pyrolysis temperature at an estimated heating rate of 350 °C min^{-1}. For the slow pyrolysis experiments, the sample spoon containing the PVC was pre-loaded into the reactor and heated from room temperature at a heating rate of 10 °C min^{-1} to the final temperature of 800 °C, and held for 30 min.

The exhaust pyrolysis gases exiting the reactor were quickly condensed in air and dry ice cooled condensers to collect the condensable hydrocarbon tar product, the condensers were weighed before and after to determine the mass of tar. The gaseous HCl was absorbed into water using a bubbler and the non-condensed gases were passed into a Tedlar™ gas sample bag. The amount of HCl was determined by the difference in weight of the scrubber system before and after the experiments. This method of HCl collection was shown to be efficient enough to capture all of the HCl, as identical results were obtained when water was replaced by NaOH solution.

2.3. Gas analysis

Gas chromatography was used to analyse the product gases from the pyrolysis of the PVC with two different Varian 3380 GCs. The concentration of H_2, N_2 and CO in the gas sample bag was determined on a molecular sieve column (60-80 mesh size) with Ar carrier gas and TCD. C_1-C_4 hydrocarbon concentrations were determined on a 80–100 mesh HayeSep column, N_2 carrier gas and FID. Knowing the N_2 gas flow, experimental time and gas concentration in the gas sample bag, the mass of other gases could be calculated. Therefore the total gas yield could be determined by mass rather than 'by difference'.

2.4. Analysis of PAHs

The tar condenser system was washed with ethyl acetate to collect the condensed liquid. Any water formed during pyrolysis was removed by passing the condensed liquid through a

mini- column of anhydrous Na_2SO_4. The eluted sample containing the PAHs and other hydrocarbons were analysed by coupled gas chromatography-mass spectrometry (GC-MS) (Varian CP-3800 GC and Varian Saturn 2200 MS. The analytical methodology involved a 30 m DB-5 GC column, a sample injection volume of 2 μl and 2-hydoxyacetophenone as internal standard. The analytical methodology has been described before [21]. Table 1 shows the PAHs identified in this work and represent 2-ring, 3-ring and 4-ring PAHs. 1-methylnaphthalene and 2-methylnaphthalene were also included in the analyses. Benzo[a]anthracene and chrysene were difficult to separate with the GC column and methodology used and consequently these two PAH are reported together.

3. Results and discussion

3.1. Influence of pyrolysis temperature on pyrolysis of PVC

3.1.1. Mass balance and gas products in relation to temperature

The fast pyrolysis of PVC was carried out at pyrolysis temperatures between 500 and 900 °C. The mass balance is shown in Fig. 2. The mass balance of each experiment was between 91.8 and 102.5 wt%, indicating reliable results were obtained for this work. As shown in Fig. 2, the HCl yield was reduced from 54.65 to 30.23 wt.% as the pyrolysis temperature was increased from 500 to 900 °C. There was an increase in tar yield with the increase of temperature. The total gas yield also increased, particularly at the higher temperature of 900 °C, there was a consequent increase in all of the individual, H_2, CH_4 and C_2-C_4 hydrocarbon gases. The ten-fold increase of H_2 from 11.2 to 114.1 ml g^{-1} PVC was the most significant change. The amounts of CH_4 and C_2-

6

C_4 were also increased slightly with temperature. Ma et al. [22] compared the fast pyrolysis of PVC at 600 and 800 °C, and found that more CH_4, C_2H_4, C_2H_6, C_3H_6, and C_3H_8 were generated at 800 °C, which was consistent with the results in this study. The enhancement of gas production with the increase of pyrolysis temperature has been attributed to the promoting of C-C cracking reactions [23, 24].

3.1.2. PAHs formation in relation to temperature for the fast pyrolysis of PVC

Fig. 4 shows that, 2-4 ring PAHs were quantitatively detected in the tar from pyrolysis of PVC. Naphthalene was the simplest PAH, which decreased from 1780 to 755 µg g^{-1} PVC when the pyrolysis temperature was raised from 500 to 600 °C, but then increased to 7960 µg g^{-1} PVC as the pyrolysis temperature was raised from 600 to 900 °C. The 1-methylnaphthalene and 2-methylnaphthalene concentrations in the tar were increased in terms of yield with the increase of pyrolysis temperature from 500 to 700 °C, but were reduced in the tar when the pyrolysis temperature was raised from 700 to 900 °C; this might be due to demethylation reactions, which was consistent with our previous study of the pyrolysis of lignin [25]. There was an increase in 3-ring PAHs yield with increased pyrolysis temperature from 500 to 900 °C. In particular, the increase of phenanthrene was the most significant from 365 to 4240 µg g^{-1} PVC. 4-ring PAHs also increased with temperature from 500 to 900 °C, and the increase of benzo[a]anthracene + chrysene was the most significant from 210 to 6140 µg g^{-1} PVC. The yield of total 2-4 ring PAHs increased from 4070 to 26510 µg g^{-1} PVC with the increase of pyrolysis temperature from 500 to 900 °C. Williams and Williams [26] used a fast pyrolysis reactor in the form of a fluidised bed to study the pyrolysis low density polyethylene. They reported that the amounts of benzene, naphthalene, and methylnaphthalene were increased as the temperature of the fluidized bed was

raised from 500 to 700 °C; the increase of PAHs with the increase of temperature was attributed to the promoting of secondary reactions of tar

The vacuum pyrolysis of PVC has been conducted in a batch reactor under different pyrolysis temperature conditions [27]. The amount of naphthalene in the product oil increased as the temperature of the vacuum pyrolysis reactor was raised from 260 to 520 °C [27]. Gui et al. [28] also reported for PVC pyrolysis that the average tar yield was increased from 6.13 to 27.79 wt.% when the pyrolysis temperature was raised from 500 to 800 °C. There was also a significant increase of 2-ring group aromatic compounds in the product oils between pyrolysis temperatures of 600 to 800 °C.

In this work, the PVC pyrolysis experiments showed that significant quantities of soot and benzenes were formed, and it may be suggested that benzene and soot were formed together during the chain scission process. In PAH were generated from benzenes via hydrogen abstraction acetylene addition (HACA) [29]. As the temperature of pyrolysis was raised, secondary reactions would be promoted, thus more PAHs would be formed [30], as shown in Fig. 4. In addition, the yield of methylnaphthalenes was reduced with the increase of reaction temperature from 700 to 900 °C due to demethylation reactions, thus methylnaphthalenes began to dealkylate to naphthalene.

3.2. Influence of heating rate

To investigate the influence of heating rate on PAHs formation, the results of fast pyrolysis at a heating rate of ~350 °C min^{-1} and a fixed reactor temperature of 800 °C was compared to slow pyrolysis where the PVC was heated at 10 °C min^{-1} to a final temperature of 800 °C.

3.2.1. Mass distribution and gas products

Fig. 5 shows the mass distribution for the fast and slow pyrolysis of PVC. Compared to the fast pyrolysis, the slow pyrolysis generated more HCl (52.7 wt.%), which was close to the chlorine content of PVC (Table 1) and similar to the slow pyrolysis of PVC at the heating rate of 25 °C min^{-1} in a fixed bed reactor (52.9 wt.%) [31]. In addition, the total gas and tar yields from the slow pyrolysis decreased compared to that from the fast pyrolysis. The residue content from fast or slow pyrolysis was similar (~17 wt.%). The H_2, CH_4 and $C_2 - C_4$ gas production from PVC pyrolysis in relation to fast and slow pyrolysis is shown in Fig. 6. Hydrogen production was reduced from about 74.9 to 36.4 (ml g^{-1} PVC), when the experiment was changed from fast pyrolysis to slow pyrolysis. In addition, the CH_4 and C_2-C_4 productions were reduced as well from 27.7 to 9.6 (ml g^{-1} PVC) and from 19.0 to 6.5 (ml g^{-1} PVC), respectively, when the pyrolysis of PVC was carried out at a slow heating rate. It was also due to the secondary reactions in the fast pyrolysis process. In the secondary reactions, heavier tar was generated with the generation of non-condensed gases [32].

3.2.2. PAHs analysis in tar products with different heating rates

The 2, 3, and 4-ring PAHs produced from PVC pyrolysis are shown in Fig. 7. As shown in Fig. 7(a), less 2-ring PAHs were formed from the slow pyrolysis compared to the fast pyrolysis. In particular, the naphthalene yield from the slow pyrolysis (290 μg g^{-1} PVC) was much lower than that from fast pyrolysis (5420 μg g^{-1} PVC). The influence of heating rate was similar on 3-ring and 4-ring PAHs which suggests that formation of PAHs was inhibited under slow pyrolysis conditions. The total 2-4 PAHs from slow pyrolysis (2330 μg g^{-1} PVC) were approximately one-tenth of the total 2-4 PAHs of fast pyrolysis (18010 μg g^{-1} PVC). Gui et al. compared the fast

pyrolysis of PVC in a vacuum reactor (heating rate 100-1000 K s^{-1}) and slow pyrolysis of PVC in a vacuum furnace (heating rate 10 K min^{-1}) at the temperature of 500 °C with the same holding time of 20 min. The condensed ring aromatic compounds for fast pyrolysis was 45.17 area%, while that for slow pyrolysis was only 2.4 area% [28, 33]. For the pyrolysis of lignin in a fixed bed reactor, the PAHs generation from fast pyrolysis has also been reported to be much more than the PAHs yield produced from low pyrolysis [25].

The suggested mechanisms of PVC pyrolysis are shown in Fig. 8. Previous work has shown that the thermal degradation of PVC follows two routes, dehydrochlorination and chain scission [34]. The dehydrochlorination route is initiated at defects in the polymer chain [33]. Under slow pyrolysis conditions, it would be expected that dehydrochlorination is a slow process, releasing HCl into the gas phase which is later captured in the bubbler system [33]. But, for fast pyrolysis, polymer chain scission may occur before all of the HCl has been released into the gas phase, leading to incomplete dehydrochlorination and formation of chlorinated hydrocarbons such as illustrated in Fig. 8. Some of the possible chlorinated hydrocarbons have been reported by other researchers to include chlorinated ethylbenzenes, chlorinated phenylpropanes [35]. In this work the possibility of incomplete dehydrochlorination is supported by the investigation of reaction temperature which is related to heating rate (Fig. 2), where less HCl was obtained at higher reaction temperature.

4. Conclusions

In this work, the formation of 2-4-ring PAHs from the pyrolysis of PVC at different temperatures and heating rates was investigated in a fixed bed reactor. The PAHs in the product tar were quantitatively analysed using GC/MS/MS. The results suggest that;

1. With the increase of temperature from 500 to 900 °C, HCl yield decreased from 54.7 to 30.2 wt.%, while the yield of tar and all the non-condensable gases (H_2, CH_4, and C_2-C_4) were increased.

2. Compared to fast pyrolysis, slow pyrolysis generated higher HCl yield (52.7 wt.%), and lower gas and tar yield; in addition, the PAHs yield obtained from slow pyrolysis (2330 µg g^{-1} PVC) was much lower than that from fast pyrolysis (18010 µg g^{-1} PVC).

3. With the increase of reaction temperature, secondary reactions could be promoted, thus more PAHs would be formed. In the fast pyrolysis process, the dehydrochlorination process might be incomplete, thus some chlorine in PVC might present as chlorinated compounds.

11

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Table 1.
PAH analysed in this work

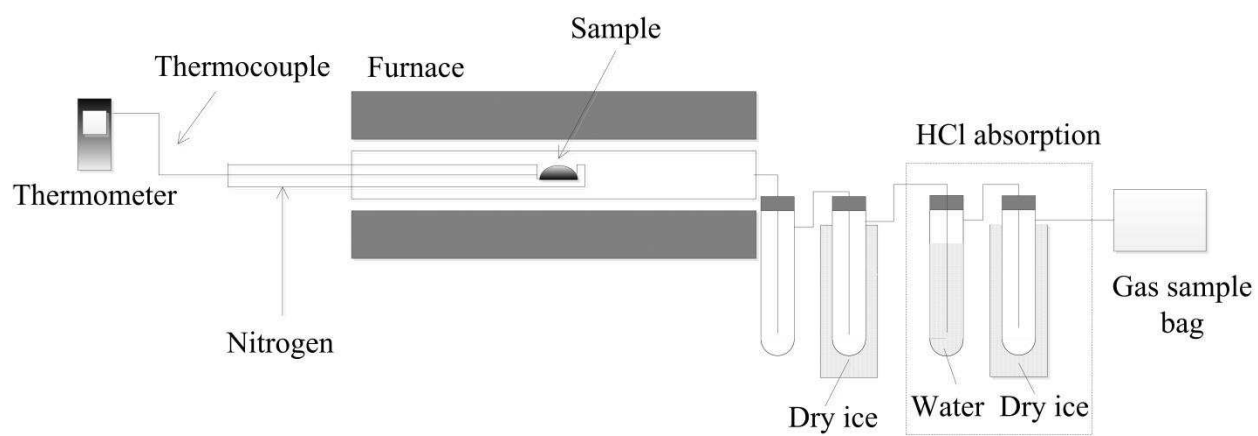| PAH	Number of PAH Aromatic Rings
Naphthalene	2
Acenaphthene	3
Acenaphthylene	3
Anthracene	3
Phenanthrene	3
Fluorene	3
Fluoranthene	4
Benzo[a]anthracene	4
Chrysene	4
Pyrene	4

Figure Captions

Fig. 1. Schematic of pyrolysis reaction system.

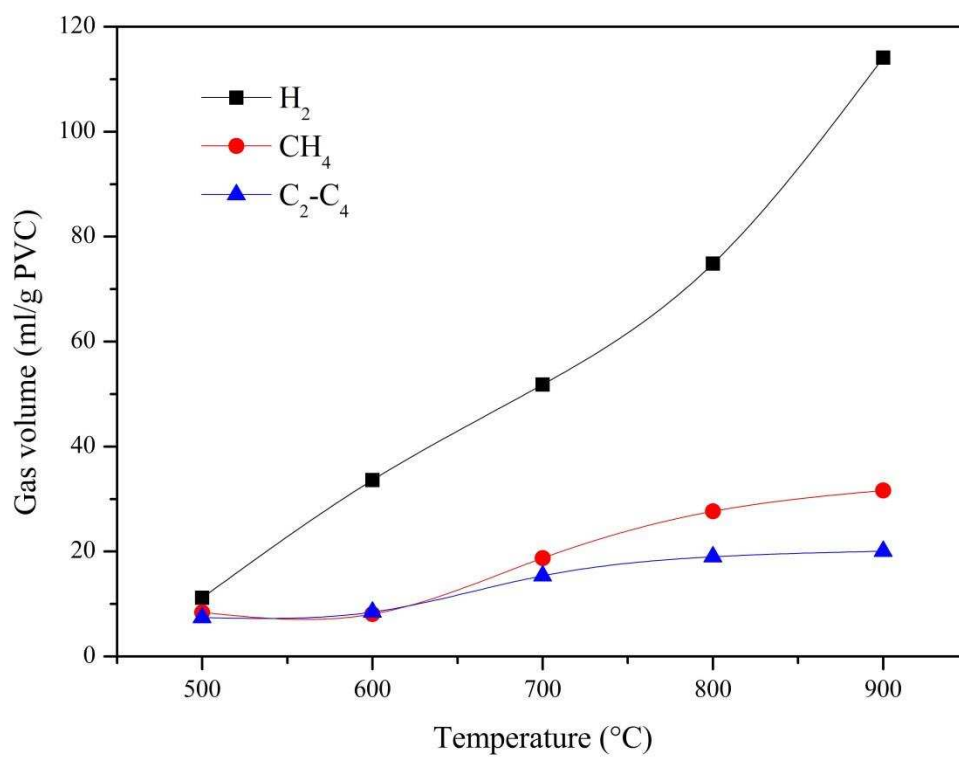**Fig. 2.** Mass balance for the pyrolysis of PVC at different temperatures.

Fig. 3. Gas release from the pyrolysis of PVC at different temperatures.

Fig. 4. PAHs formation from the pyrolysis of PVC at different temperatures.

Fig. 5. Mass distribution of PVC at different heating rates.

Fig. 6. Gas release from PVC at different heating rates.

Fig. 7. PAHs formation from PVC at different heating rates.

Fig. 8. Proposed mechanism of PAHs formation from pyrolysis of PVC.

Fig. 1. Schematic of pyrolysis reaction system.

Fig. 2. Mass balance for the fast pyrolysis of PVC at different temperatures.

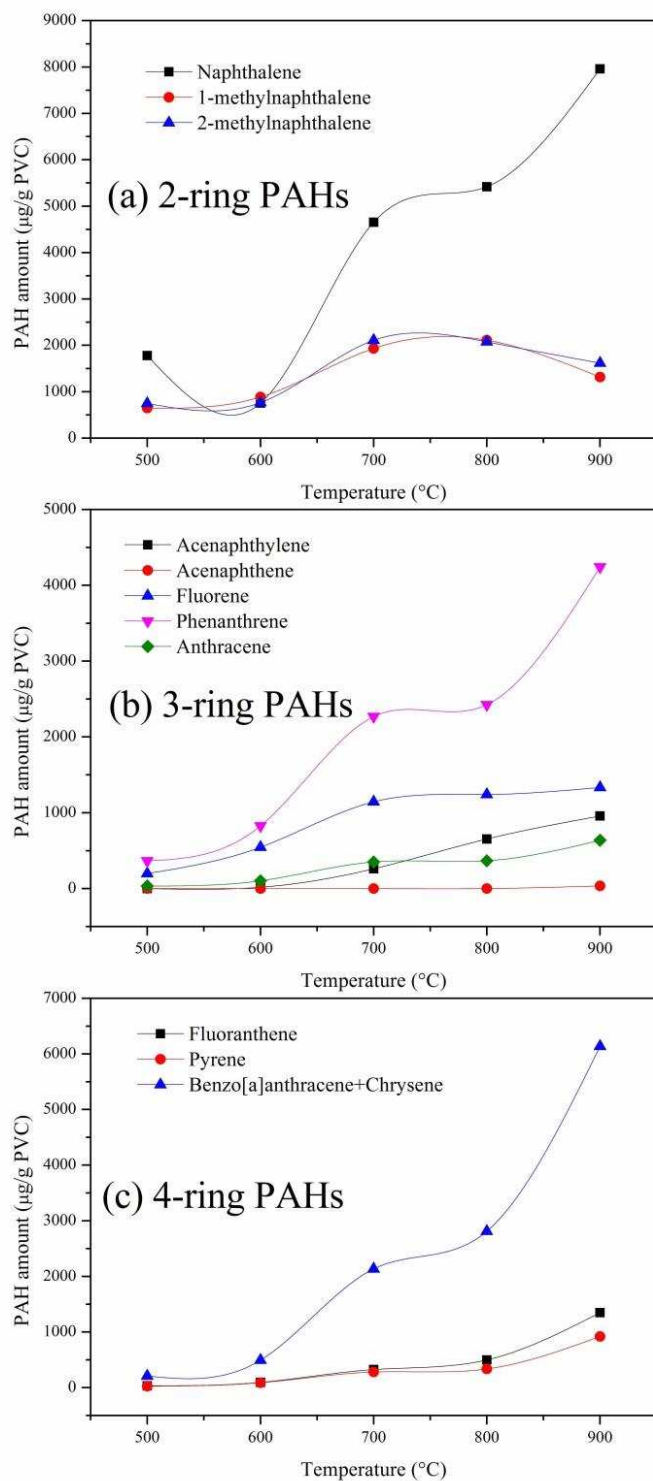**Fig. 3.** Gas release from the fast pyrolysis of PVC at different temperatures.

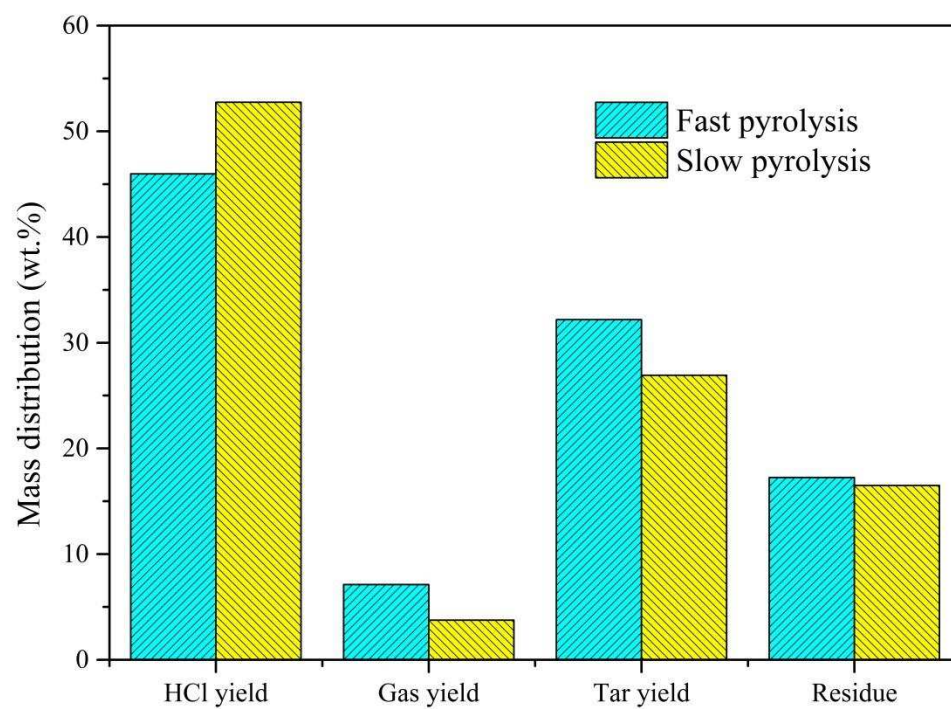**Fig. 4**. PAHs formation from the fast pyrolysis of PVC at different temperatures.

Fig. 5. Mass distribution for fast pyrolysis and slow pyrolysis of PVC with the final temperature 800 °C.
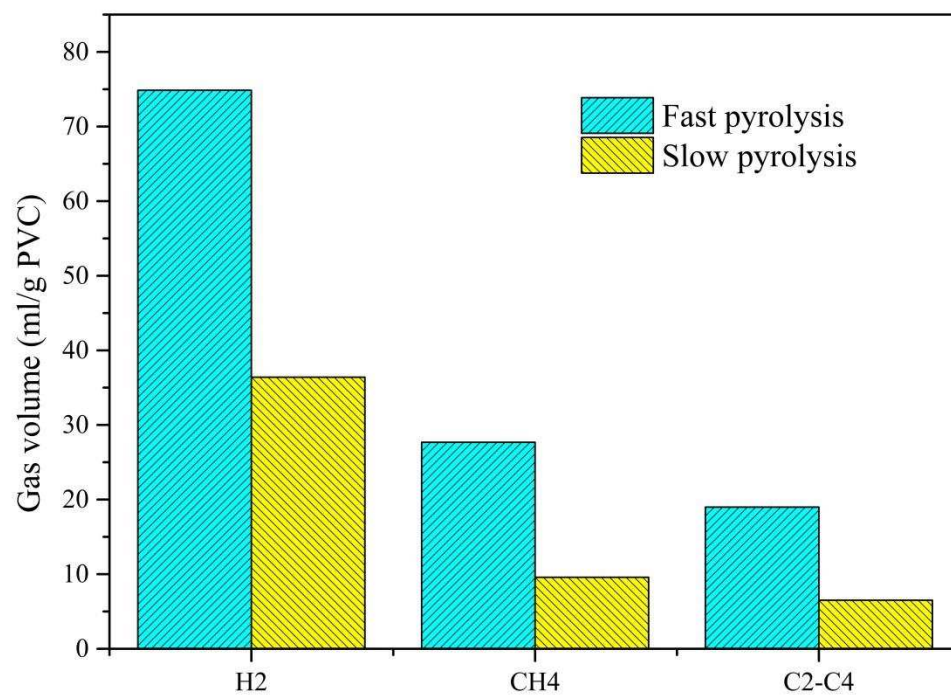
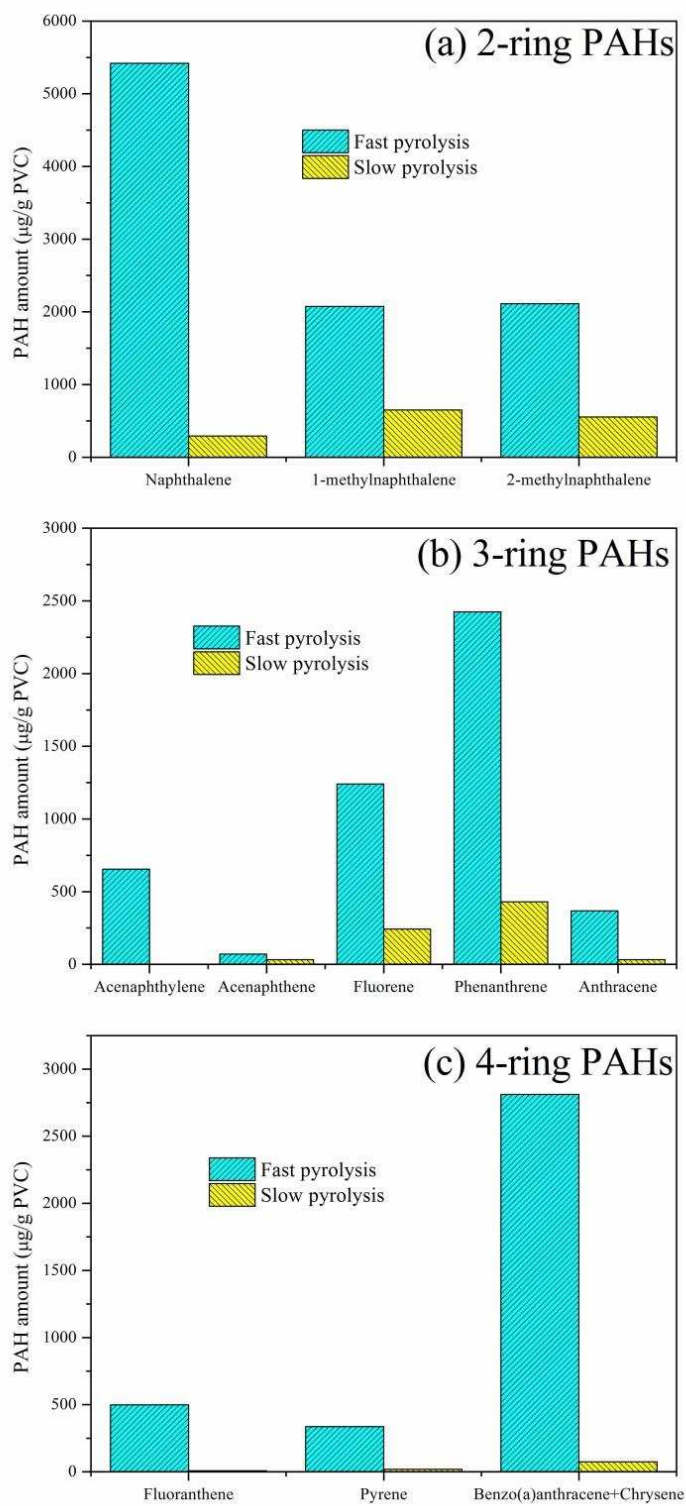**Fig. 6.** Gas release for fast pyrolysis and slow pyrolysis of PVC with the final temperature 800 °C.

Fig. 7. PAHs formation from fast pyrolysis and slow pyrolysis of PVC with the final temperature 800 °C.
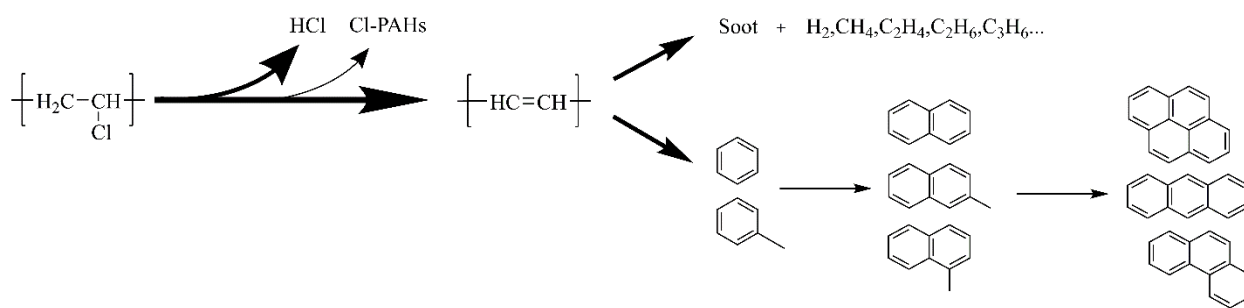
Fig. 8. Proposed mechanism of PAHs formation from pyrolysis of PVC.