

Study of purification of phenanthrene from phenanthrene waste

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Abstract

Isolation and purification of phenanthrene from phenanthrene waste has been studied by fractionation and acid wash with sulphuric acid. Experimental results showed that the purity of phenanthrene was increased from 50.29% to 86.06%. Commercial grade phenanthrene was obtained by purification, the melting point of the product was 96~103°C and the yield of phenanthrene was 26.58%.

Keywords: Phenanthrene waste, phenanthrene, purification.

Introduction

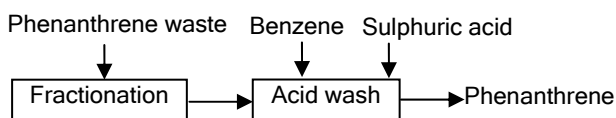
Next to naphthalene in terms of quantity, phenanthrene at the concentration of 4~5% is the most abundant constituent in coal tar. Phenanthrene can be oxidized to 9,10-phenanthrenequinone and 2,2'-diphenic acid. It can also be used to prepare anthracene (Handrick *et al.*, 1983). Electrically conductive substances e.g., for use in batteries and solar cells, liquid crystalline, used for optical-electronic applications and resins (Robinson & Barnes, 1983; Robinson & Riemer, 1986) such as a polyamide-polimide resin (Kishore *et al.*, 2003), which is suitable for use in high temperature insulators, printed circuit boards and laminates, can be produced from phenanthrene. It has also been proposed as a plasticizer for plastics, molding compounds, stabilizers for mineral oil products and water reducing agents (Zuyu *et al.*, 2005; Zuyu & Zhizhong, 2007). Phenanthrene waste, which is a residue/by-product after isolation of anthracene and carbazole from crude anthracene, contains mainly phenanthrene (about 50±5%) and a small quantity of fluorene, anthracene, carbazole etc. These impurities are difficult to remove thus very pure phenanthrene has been unavailable commercially. The study described the isolation and purification of phenanthrene from phenanthrene waste by fractionation and acid wash. Commercial grade phenanthrene was obtained by purification. This work had the advantages of simple procedure, environmental protection and economy.

Experimental procedures

Materials: Phenanthrene waste was obtained from a local market. For acid wash, commercial grade chemicals were used.

Procedure: The Isolation and purification of phenanthrene was carried out by fractionation and acid wash with sulfuric acid. The procedures were as follows (Fig. 1):

Fig. 1. Separation flow chart.



1. Fractional distillation: At first 100 g of phenanthrene waste was subjected to fractionation. The cut was distilled in the range of greater than 300°C wherein distillation phenanthrene was obtained.

2. Acid wash: Followed, 10 g distillate phenanthrene was added to a stirred reactor filled with 100 ml benzene (solvent) and was completely dissolved. Then 1 ml-2.5 ml of sulphuric acid (80%-95%) was introduced and the distillate fraction was sulfonated at 30°C-60°C for 0.5 h-2 h. After acid wash, acid layer was removed, and organic layer washed to neutrality with water. Finally, by evaporating off the solvent, commercial phenanthrene was obtained. The melting point of the product was determined by a melting point apparatus (X-4, Beijing, China). The quantitative analysis of phenanthrene was performed by means of gas chromatography (GC-2010, Shimadzu, Kyoto, Japan).

Chromatograph conditions: Column: fused silica capillary column (US1355961H, J&W Scientific Incorporation, USA), liquid phase: DB-1(100% Dimethylpolysiloxane), film thickness: 0.25 µm, Column dimensions: 30 m x 0.254 mm, detector: FID, temperature: injector 310°C, column 180°C, detector 240°C, flow control mode: pressure, column inlet pressure: 100 kPa, split ratio: 50, carrier gas: N₂, solvent: acetone.

Results and discussion

Phenanthrene waste contains mainly phenanthrene. From the waste chromatogram (Fig. 2), the qualitative and quantitative analysis of phenanthrene waste was obtained by comparison of the standard and sample retention times and calculating area percent of chromatograph peak. The results are shown in Table 1. It indicates that main impurities are fluorene (14.81%), anthracene (7.87%) and carbazole (3.47%) in the waste.

Fractional distillation: 100 g of phenanthrene waste was subjected to fractionation and a phenanthrene fraction boiling in the range >300°C was obtained. Fluorene, at the concentration of 14.8%, is the most abundant impurity in the waste and stable in chemical properties. Since the boiling point of fluorine is 295°C, Whereas, the boiling

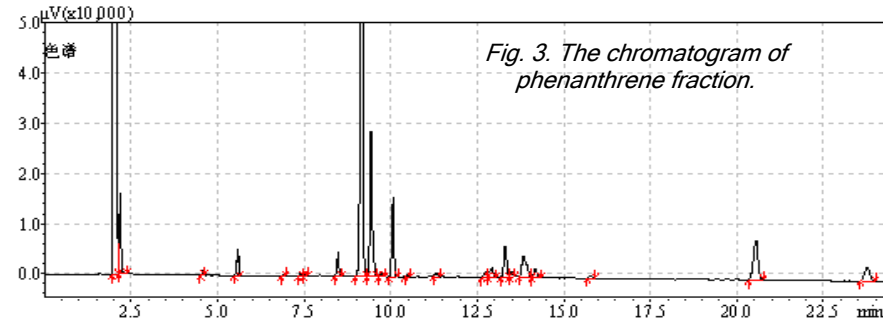
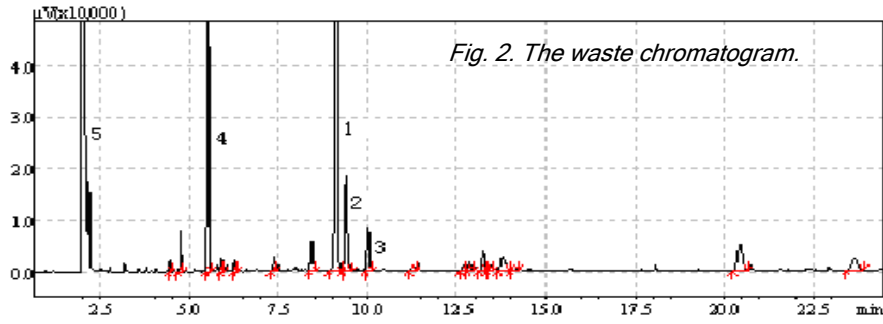


Fig. 4. Effects of H₂SO₄ concentration on purity & yields.

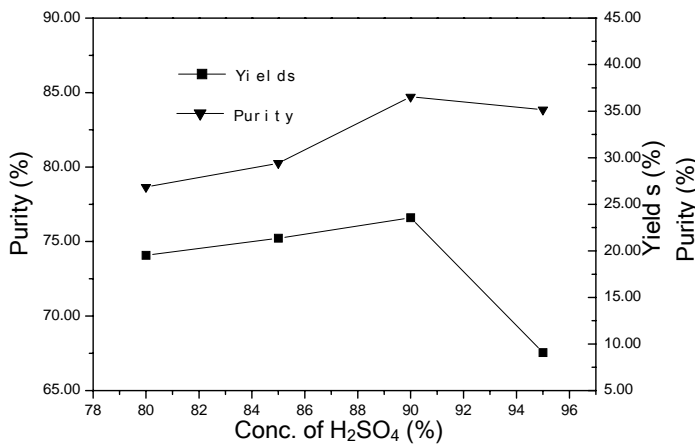


Fig. 5. Effects of amount of H₂SO₄ employed on purity & yields.

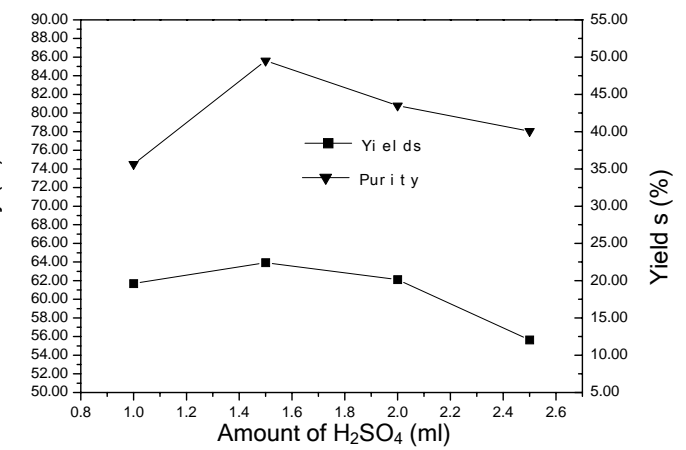


Fig. 6. Effects of temperature for acid wash on purity & yields.

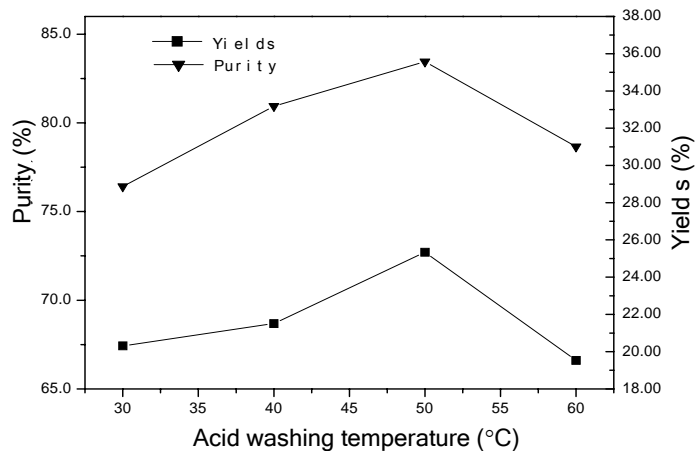
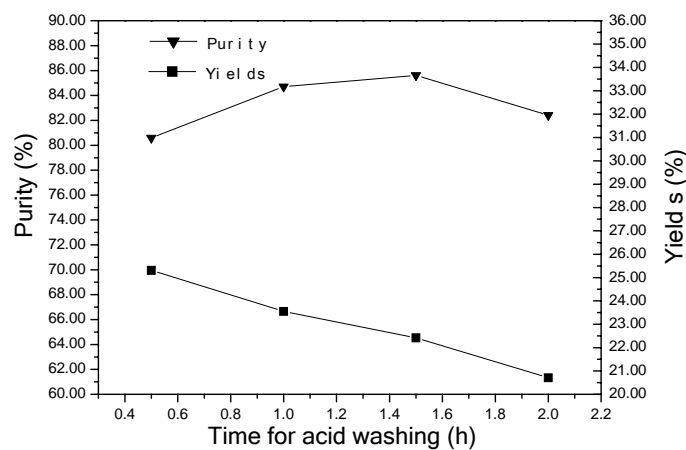


Fig. 7. Effects of time for acid wash on purity & yields.



point of phenanthrene is 340°C, therefore fractional distillation can be used for removing the impurity fluorene. The distillate fraction chromatogram is shown in Fig. 3 and content in Table 2. Fig. 3 shows that low boiling substances and fluorine are basically removed and the purity of phenanthrene reaches to 58.86%.

Table 1. Results of analysis of phenanthrene waste.

Peak No.	Components	Retention times (min)	Percent composition (%)
1	Phenanthrene	9.136	50.29%
2	Anthracene	9.387	7.87%
3	Carbazole	10.017	3.47%
4	Fluorene	5.518	14.81%
5	Acetone (solvent)	2.0	

Table 2. Content of components in distillate phenanthrene.

Peak No.	Components	Retention times (min)	Percent Composition (%)
1	Phenanthrene	9.136	58.86
2	Anthracene	9.387	12.59
3	Carbazole	10.017	6.27
4	Fluorene	5.518	3.12

Table 3. Concentration of products.

Peak No.	Components	Retention times (min)	Percent composition (%)
1	Phenanthrene	9.111	86.06
2	Anthracene	9.370	3.04
3	Fluorene	5.506	1.13
4	Impurity 1	13.236	1.88
5	Impurity 2	13.765	2.01
6	Impurity 3	20.448	5.25

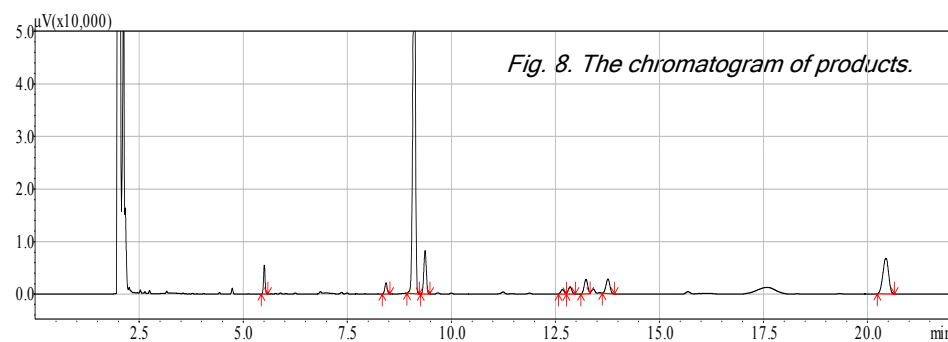


Fig. 8. The chromatogram of products.

Acid wash: Acid wash with sulfuric acid was for removing impurities of anthracene and carbazole. Since anthracene than phenanthrene is more easily sulfonated, and carbazole easily soluble in sulphuric acid, forming carbazole sulphate insoluble in organics, therefore, anthracene and carbazole can be removed by treating distillate phenanthrene with sulfuric acid. In the study, we investigated effects of concentration of sulfuric acid, the quantity of H₂SO₄ employed, time and temperature for acid wash on the purity and yields of phenanthrene. The results are shown in Fig. 4-7. They show that when the amount of 90% H₂SO₄ employed is 1.5 ml, time for acid wash was 1.5 h and when the temperature for acid wash

is 50°C, the purity and yields are greater. The experiment was conducted under these conditions for acid wash. A commercial grade product, whose freezing point was 96°C~103°C and yield 26.58% was obtained. The product chromatogram is shown in Fig. 8 and concentration Table 3. They show that impurities are basically removed. Sulphonate yielded in acid wash can be used for preparation of water reducing agents reaching the purpose of environmental protection (Zuyu *et al.*, 2005; Zuyu & Zhizhong, 2007). The products yielded in the work were further treated with DMF (Zuyu & Zhizhong, 2008) or maleic anhydride and purer phenanthrene could be obtained (Zuyu & Zhizhong, 2009).

Conclusion

From phenanthrene waste, phenanthrene was refined by fractional distillation and acid wash. The study showed that, by Isolation and purification, the purity of phenanthrene was increased from 50.29% to 86.06% and commercial grade phenanthrene was obtained, the freezing point of the product was 96°C~103°C, and the yield of phenanthrene 26.58%. This method had the advantages of simple operation, environmental protection and economy.

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