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Recovery of Anthracene from Coal Tar by Solvent Extraction

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Abstract

A method of anthracene purification by extraction of impurities with a methanol-benzene solvent mixture is proposed. In the first stage the anthracene cake is dissolved in the solvent mixture at the boiling temperature of the system. Subsequently the precipitation of the great part of anthracene takes place by cooling the system to room temperature. The solid phase is removed by filtration while the liquid phase is arranged in the last stage by stripping. After this operation the solvent can be reused in the anthracene recovery process. In this paper the results obtained on the recovery of anthracene from anthracene cake are reported. The influence of solvent mixture composition, solvent mixture volume/anthracene cake weight ratio, and operation time are studied. According to the experimental results, 90% of the anthracene from the anthracene cake can be recovered. The anthracene purity attained is close to 90%.

INTRODUCTION

In the coke industry, coal tar is obtained as a subproduct which is later subjected to distillation which leads to, among other products, a residual fraction known as "anthracene oil." The subsequent filtration of anthracene oil results in "anthracene cake" with a 20-50% weight anthracene (AN) content. The main impurities of anthracene cake are carbazole,

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phenanthrene, and, in lesser proportions, fluorene, fluoranthene, pyrene, and 2-methyl-anthracene.

Of worldwide anthraquinone (AQ) production, 85% is obtained from catalytic gas-phase oxidation of AN with air. Recovery of AN from anthracene cakes has become important because of an increase in AQ demand. Following Holton (*1, 2*), AQ is used as a redox additive catalyst in alkaline wood pulp production processes. The addition of small amounts of AQ to the chips digester increases the pulp yield and at the same time the delignification degree is improved. AN recovery provides the benefit of an economically limited subproduct as well as reducing toxic waste disposal.

AN purification methods can be physical or chemical. Physical methods which demand lower capital investments have become much more commonly used than chemical ones, mainly due to the fact that AN with sufficient purity for oxidation to AQ (85–95%) is obtained. Chemical methods are only employed in the latest purification stages, when a high degree of purity is required. In physical operations, solvent extraction is most frequently performed. In some cases, supplementary steps are necessary in order to purify the recovered AN. Several articles involving a wide variety of pure solvents such as acetic acid (*3*), acetone (*4*), propylene carbonate (*5*) and other organic polar solvents, hydrocarbons, and derivatives (*6–9*) have been found in the literature. Various results related to both AN recovery efficiency and purity deal primarily with different polarities and volatilities of the solvents used as well as to different anthracene cake compositions.

In order to select the most suitable solvent, it is necessary to consider its recovery from the waste stream, which results in an improvement of the process economics. Therefore, solvent volatility has to be such that its separation from dissolved impurities is easily carried out. A highly volatile solvent simplifies recovery but, at the same time, the operation temperature is limited and, consequently, so is the anthracene cake dissolution rate.

In this paper an industrial procedure for the recovery of AN from anthracene cakes is proposed. The method is based on the selective dissolution of impurities with respect to the AN in the solvent at its boiling point. The process utilizes a solvent mixture of methanol and benzene. The dissolved AN differential precipitation takes place by cooling the system to room temperature. An optimal methanol/benzene ratio for the treated anthracene cake composition is established. The influence of the solvent volume/anthracene cake weight ratio on the recovery efficiency was studied. The minimum operating time required for complete recovery of AN was also determined.

EXPERIMENTAL

All the experiments were carried out using 250 or 500 cm^3 agitated and refluxed vessels provided with temperature measurement and electric heating controls. Solids were fed into the vessel together with the solvent mixture. At that moment the heater was activated until the mixture's boiling point was reached. The quantity of anthracene cake used in all the experiments was 50 g. The AN precipitation took place by cooling the system to room temperature. Afterward the solids were removed by vacuum filtration and dried at 105°C until constant weight was achieved. Simultaneously, the liquid phase, which contained most of the impurities and dissolved AN, was evaporated, and the resultant solid was dried and weighed. A sample of each obtained solid was dissolved in cyclohexanone for analysis. An HPLC analytical procedure was employed in order to identify the components of the anthracene cake and to determine quantitatively the solids composition. Analysis was performed using a Perkin-Elmer series 2 liquid chromatograph. Because of the nonpolar nature of the hydrocarbons studied, separation by reverse phase partition was employed. The most suitable packing was a nonpolar bonding phase using a polar mobile phase. The analytical conditions are summarized in Table 1.

Once the solids composition was determined, a mass balance for each anthracene cake component was performed. The recovery efficiency and the AN purity were derived from the results. The weight losses due to experimental manipulation were lower than 3% in all cases.

RESULTS AND DISCUSSION

Anthracene Cake Characterization

Figure 1 shows a chromatogram corresponding to the anthracene cake used in the experimentation. Its composition and the elution times of

TABLE 1
Analytical Conditions

Column	Spherisorb ODS-2, 25 × 0.46 cm i.d. Particle size of packing: 10 μm
Mobile phase	Water/methanol: 18/82
Flow (cm^3/min)	1.5
Loading (μL)	5
Wavelength (nm)	254
Temperature (K)	313

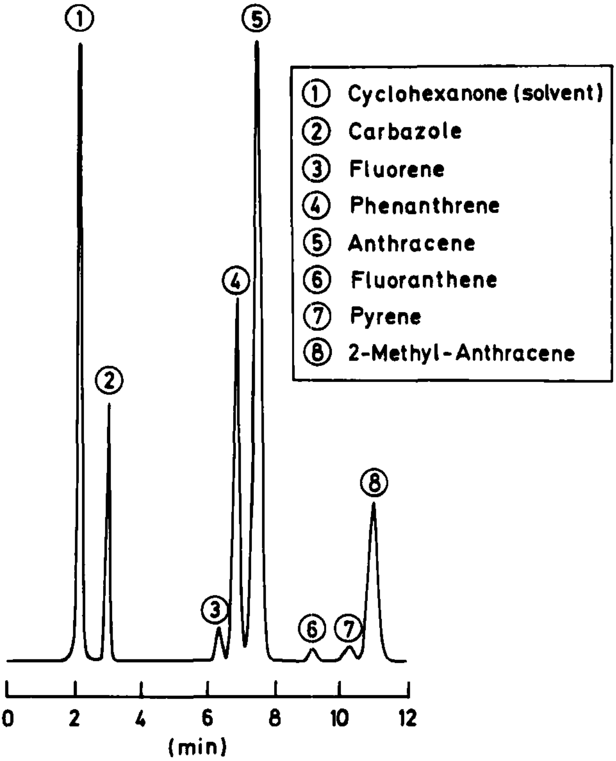

FIG. 1. Anthracene cake chromatogram.

their components are detailed in Table 2. This composition corresponds to a typical anthracene cake obtained from a medium volatile bituminous coal coking process. When anthracene cake from other coal coking is used, compounds such as naphthalene, acenaphthene, and chrysene could also appear as a consequence of the feedstock composition and coking conditions (mainly operation temperature).

Solvent Selection

Solvent selection was accomplished by taking into account the following criteria:

Chemical inertia with respect to anthracene cake

TABLE 2
Anthracene Cake Characterization

Component	Composition (w/w)	Retention time (min)
Anthracene	32.0	7.42
Phenanthrene	24.2	6.80
Carbazole	22.3	2.99
Pyrene	7.1	10.20
Fluoranthene	5.4	9.13
2-Methyl-anthracene	4.9	10.83
Fluorene	4.1	6.36

Selective solubility of impurities against AN at room temperature
Adequate volatility
Availability
Cost

These criteria and the literature (*10*, *11*) suggested the use of a methanol–benzene mixture as the most appropriate solvent. All of the components arranged in Table 3 are partially soluble in methanol and more than that in benzene. The AN solubility in the selected solvent is lower than the other components' solubilities over the solvent mixture composition range assayed. The solvent volatility has to be high in order to facilitate its regeneration. However, a very high solvent volatility limits the operation temperature and consequently the dissolution process rate.

A set of experiments was carried out to select the proper solvent mixture for AN recovery. The anthracene cake was treated with methanol–benzene mixtures in the range of 0.2–0.5 methanol molar fractions. This mixture exhibits a minimum homogeneous boiling azeotrope for a 0.58 methanol molar fraction value at 725 mmHg (*12*), thus a 0.5 molar fraction was chosen as the upper limit. A 20-min operation time was more than enough to achieve the dissolution equilibria at the operating conditions. Table 3 illustrates the set of results for a 100-g sample of anthracene cake. The total precipitated solid amount increases with the methanol molar fraction. This is due to the fact that all component solubilities diminish at high proportions of methanol in the mixture. In any case, AN is the more insoluble component. Both carbazole and phenanthrene are the impurities most affected by molar fraction variation. Thus, by increasing the methanol molar fraction from 0.4 to 0.5, there is a marked increase in carbazole and

TABLE 3
Extract and Precipitate Weight Versus Methanol Molar Fraction[a]

	Methanol molar fraction													
	0.20		0.25		0.30		0.35		0.40		0.45		0.50	
Component	Ext[b]	Prec[c]	Ext	Prec	Ext	Prec	Ext	Prec	Ext	Prec	Ext	Prec	Ext	Prec
Anthracene	11.8	19.9	8.5	23.1	5.7	25.6	3.7	28.0	1.5	29.8	1.1	30.5	0.4	31.2
Carbazole	17.6	4.4	16.9	5.0	16.2	5.4	15.8	5.7	14.8	6.8	11.9	9.8	6.2	15.5
Phenanthrene	23.7	0.1	23.2	0.2	22.9	0.4	22.5	1.4	20.8	3.0	19.7	4.1	17.5	6.1
Fluorene	3.1	0.7	3.0	0.9	2.6	1.2	2.6	1.3	2.4	1.5	2.3	1.6	2.0	1.9
Pyrene	6.2	0.3	6.6	0.3	6.6	0.3	6.6	0.4	6.4	0.4	6.3	0.5	6.1	0.6
Fluoranthene	5.2	—	5.3	—	5.3	0.1	5.1	0.1	5.0	0.2	5.0	0.3	4.9	0.4
2-Methyl-anthracene	4.5	—	4.7	—	4.8	—	4.8	—	4.6	—	4.7	—	4.5	0.2
Total	72.1	25.4	68.2	29.5	61.1	33.0	60.7	36.9	55.5	41.7	51.0	46.8	41.6	55.9

[a] Experimental conditions: Solvent mixture volume/anthracene cake weight ratio = 1.0 cm^3/g; operating time = 20 min.

[b] Extract in grams.

[c] Precipitate in grams.

phenanthrene amounts in the precipitate with respect to the remaining impurities. By increasing the molar fraction from 0.2 to 0.4, phenanthrene precipitation is favored. In this range the incremental increase of the rest of precipitate impurities is not significant. In any case, carbazole is the major precipitated impurity.

The selection of an appropriate solvent mixture composition will be a result of the greatest precipitate purity as well as the highest AN recovery yield attained. In order to determine this composition, the terms "AN recovery efficiency" and "nondissolved impurities ratio" are respectively defined as

$$E_{AN} = \frac{\text{AN weight in precipitate}}{\text{AN weight in anthracene cake}} \tag{1}$$

$$R_{IMP} = \frac{\text{total impurities weight in precipitate}}{\text{total impurities weight in anthracene cake}} \tag{2}$$

The E_{AN} and R_{IMP} values have been calculated from the experimental results and plotted against the methanol molar fraction in the solvent mixture (Fig. 2). The optimum methanol molar fraction should be the point where the difference between E_{AN} and R_{IMP} is a maximum. The optimum molar fraction can be derived from both analytical or graphical calculation. The analytical method involves the resolution of the equation

$$\frac{dE_{AN}(X_{MeOH})}{dX_{MeOH}} = \frac{dR_{IMP}(X_{MeOH})}{dX_{MeOH}} \tag{3}$$

The graphical procedure of resolution consists of the maximum difference determined between E_{AN} and R_{IMP} that corresponds to the methanol molar fraction in which both function tangent slopes are equal. Figure 2 shows that 0.4 is the optimum methanol molar fraction.

Anthracene Recovery

In order to establish the influence of operating time on the precipitate composition, a set of experiments—arranged in Table 4—was carried out. As can be seen, the weight and composition of the solids obtained stay constant up to 15 min. Consequently, a 20-min operation time was used in all the experiments.

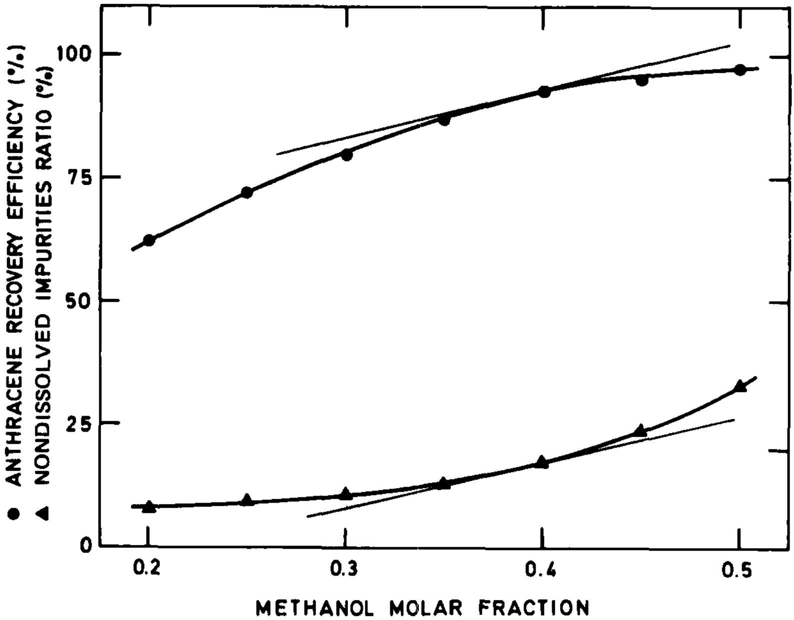

FIG. 2. Anthracene recovery efficiency and nondissolved impurities ratio versus methanol molar fraction.

Once both an adequate solvent mixture and the precipitation conditions were established, an AN recovery procedure based on impurities selective extraction was studied. Table 5 lists the results obtained in the recovery process referred to different solvent mixture volume/anthracene cake weight ratios. Analysis of the results indicates that precipitated AN purity is improved by increasing the solvent mixture volume/anthracene cake weight ratio. Contrarily, the AN recovery efficiency decreases when the solvent volume is raised. Figure 3 shows the AN purity obtained and the operation efficiency, and the trends can be clearly seen. The most appropriate solvent/anthracene cake weight ratio is obtained in a similar way to the optimum methanol molar fraction by using the abovementioned graphic method. Therefore, starting from the E_{AN} and R_{IMP} function representations, a solvent volume/anthracene cake weight ratio of 1.5 cm^3/g was established. This ratio gives sufficient AN purity for vapor-phase catalytic oxidation with air. If higher solvent/anthracene cake ratios were employed, then the AN purity would be greater but, at the same time, the recovery efficiency would be reduced to less than the

TABLE 4
Effect of Operating Time on the Anthracene Cake Components Precipitation[a]

	Operating time (min)							
	10		15		20		30	
Component	Weight (g)	%	Weight (g)	%	Weight (g)	%	Weight (g)	%
Anthracene	31.0	64.9	30.6	70.2	29.8	71.5	30.4	72.0
Carbazole	7.5	15.7	6.9	15.8	6.8	16.3	6.2	14.7
Phenanthrene	3.7	7.7	2.5	5.7	3.0	7.2	2.9	6.9
Fluorene	2.8	5.9	2.1	4.8	1.5	3.6	1.8	4.3
Pyrene	1.3	2.7	0.8	1.8	0.4	1.0	0.6	1.4
Fluoranthene	0.8	1.7	0.5	1.1	0.2	0.5	0.3	0.7
2-Methyl-anthracene	0.7	1.5	0.2	0.5	—	—	—	—
Total	47.8	100.1	43.6	100.0	41.7	100.1	42.2	100.0

[a] Experimental conditions: Methanol molar fraction = 0.4; solvent mixture volume/anthracene cake weight ratio = 1.0 cm^3/g.

TABLE 5
Anthracene Recovery. Experimental Results[a]

	Solvent mixture volume/anthracene cake weight ratio (cm^3/g)									
	0.5		1.0		1.5		2.0		2.5	
Component	Weight (g)	%	Weight (g)	%	Weight (g)	%	Weight (g)	%	Weight (g)	%
Anthracene	31.0	56.8	29.8	71.5	27.9	88.9	24.4	96.1	16.9	98.8
Carbazole	12.0	22.0	6.8	16.3	2.6	8.3	1.0	3.9	0.2	1.2
Phenanthrene	6.7	12.3	3.0	7.2	0.6	1.9	—	—	—	—
Fluorene	2.6	4.8	1.5	3.6	0.3	1.0	—	—	—	—
Pyrene	1.3	2.4	0.4	1.0	—	—	—	—	—	—
Fluoranthene	0.7	1.3	0.2	0.5	—	—	—	—	—	—
2-Methyl-anthracene	0.3	0.5	—	—	—	—	—	—	—	—
Total	54.6	100.1	41.7	100.1	31.4	100.1	25.4	100	17.1	100

[a] Experimental conditions: Methanol molar fraction = 0.4; operating time = 20 min.

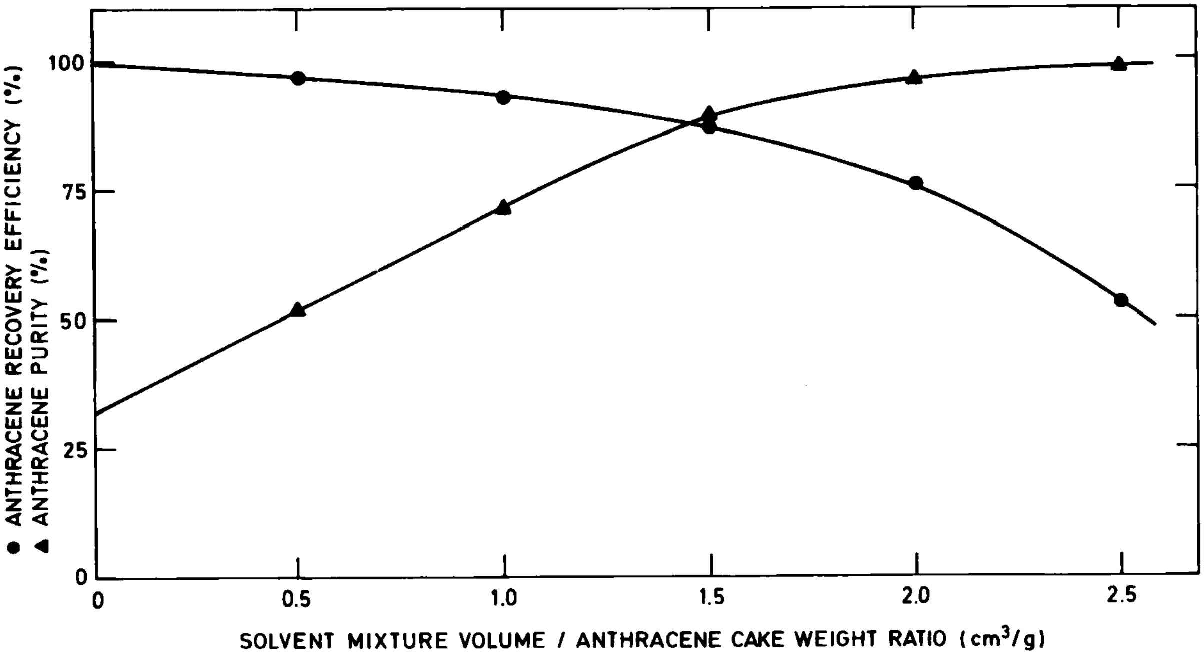

FIG. 3. Anthracene recovery efficiency and anthracene purity versus solvent mixture volume/anthracene cake weight ratio.

1.5 cm^3/g ratio and the AN purity would not be enough for later catalytic oxidation in spite of the improved recovery efficiency. Figure 4 shows chromatograms of both the precipitate and the extract obtained in an operation carried out with a 1.5 solvent/anthracene cake ratio. It can be clearly seen that a reduction of precipitate impurities with respect to the initial anthracene cake impurities is achieved.

In Table 6 the results corresponding to a 1.5 cm^3/g ratio are compared with those obtained under the same operating conditions but with longer treatment times. The data show no influence on operation results with varying time. Therefore, the separation process is unaffected beyond 20 min.

Finally, an AN recovery industrial method based on the experimental results is proposed. The flow sheet of the recovery system established is shown in Fig. 5. In the first stage the anthracene cake is subjected to a methanol–benzene mixture at the boiling temperature. In the second stage the greater part of the dissolved AN differential precipitation takes place by cooling the mixture at room temperature. Two flows are obtained from the separation unit: one solid, where the AN constitutes the major component, and the other liquid, corresponding to the solvent mixture contaminated with the impurities. In the last step the dissolved impurities are removed from the rich solvent by stripping with steam in a heated regenerator column. After this operation, the solvent is ready for reuse in the extraction stage.

CONCLUSIONS

An AN from anthracene cake solvent extraction procedure using methanol–benzene mixtures has been studied. A 0.4-methanol *M* fraction was found to be the most appropriate in order to obtain selective precipitation of AN against the companion impurities. For a 1.5 solvent volume/anthracene cake weight ratio, a 88.9% AN purity was obtained, giving a total recovery efficiency of 87.2%. The final product purity obtained enables it to be used as a feedstock in AN catalytic oxidation with air. Based on the experimental results, an AN recovery industrial procedure based on differential precipitation and subsequent liquid–solid phases separation is proposed. By applying this procedure, wastes derived from the anthracene oil fraction could be considerably reduced.

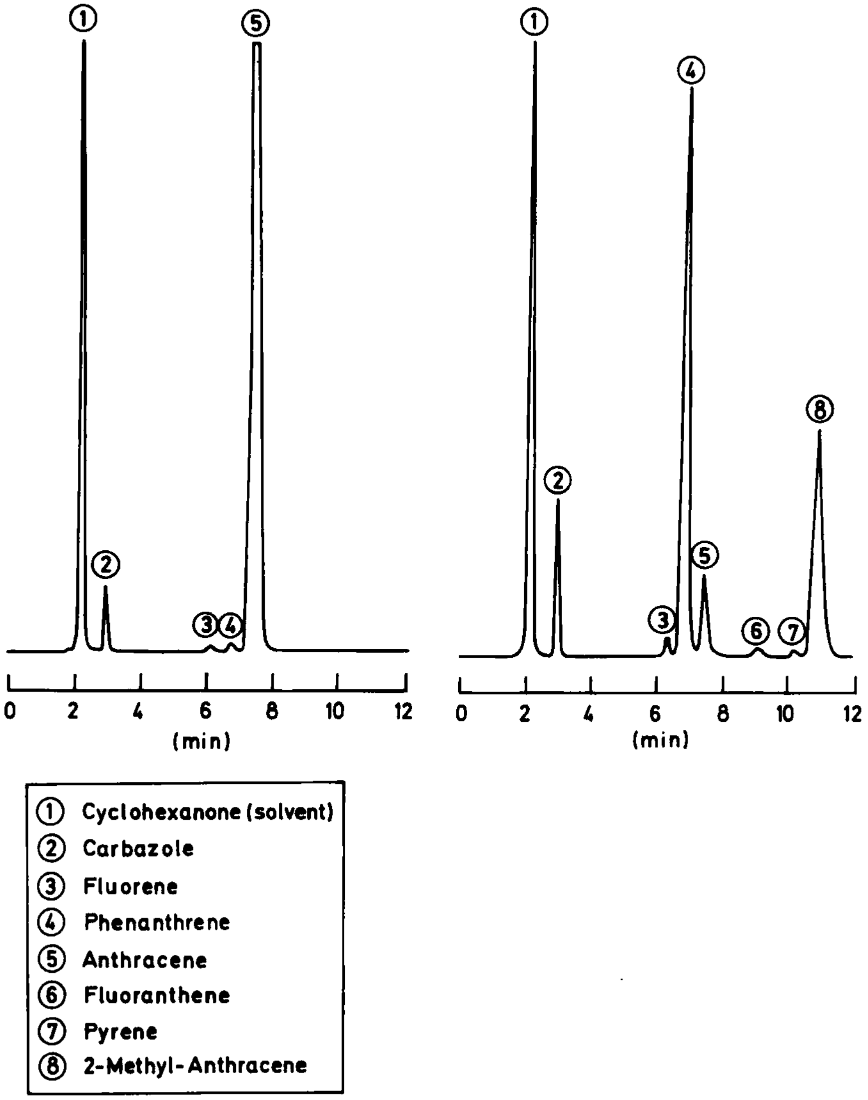

FIG. 4. Precipitate and extract chromatograms. Experimental conditions: Methanol molar fraction = 0.4; solvent mixture volume/anthracene cake weight ratio = 1.5 cm^3/g; operating time = 20 min.

TABLE 6

Effect of Operating on the Anthracene Cake Components Precipitation[a]

	Operating time (min)			
	20		30	
Component	Weight (g)	%	Weight (g)	%
Anthracene	27.9	88.9	27.2	89.2
Carbazole	2.6	8.3	2.4	7.9
Phenanthrene	0.6	1.9	0.7	2.3
Fluorene	0.3	1.0	0.2	0.7
Pyrene	—	—	—	—
Fluoranthene	—	—	—	—
2-Methyl-anthracene	—	—	—	—
Total	31.4	100.1	30.5	100.1

[a] Experimental conditions: Methanol molar fraction = 0.4; solvent mixture volume/anthracene cake weight ratio = 1.5 g/cm^3.

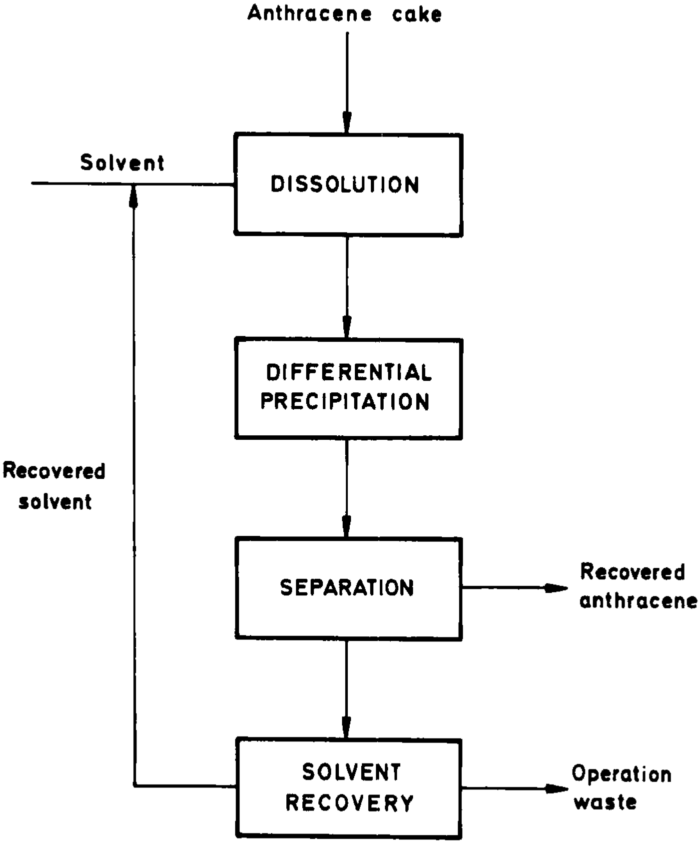

FIG. 5. Flow sheet of proposed anthracene recovery method.

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