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Research Article

USE OF PYROLYSIS DISTILLATE RAW MATERIALS FOR OBTAINING BENZENE

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ABSTRACT

The process of obtaining benzene and its homologues based on pyrolysis distillation has been implemented, the quantitative and qualitative composition of pyrolysis distillate samples and the processing of their fractions have been studied. Qualitative analysis was carried out by IR spectroscopic method, quantitative composition was studied by gas chromatograph with mass spectroscopy.

KEYWORDS

Pyrolysis distillate, benzene, toluene, xylene, methylethylbenzene, propylbenzene qualitative and quantitative analysis.

INTRODUCTION

In the Republic of Uzbekistan, the presence and expansion of pyrolysis production makes it possible to produce pyrolysis benzene by pyrolysis of gas condensate and catalytic reforming of oil products, followed by extraction separation of catalysts and pyrocondensates with selective solvents [2].

To date, universal extractants have not yet been found that combine high separation selectivity with a sufficiently high dissolving ability and fully meet the requirements of modern technology. Therefore, the search and study of the extracting properties of effective polar solvents for the production of benzene in Uzbekistan is an extremely important and urgent national economic task.

Benzene is the most important raw material of the petrochemical industry, on the basis of which large-scale organic synthesis products are produced. According to Rosstat, the volume of benzene production (including from pyrolysis products and petroleum) amounted to 1,200 thousand tons.

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According to experts from the Industrial Information Agency, global demand for benzene will grow by an average of 5.2% per year and will amount to 41 million tons. The fastest growth will be observed in Asia (excluding Japan) - an average of 7.5% per year - and in other regions of the world - 13.6% (mainly in the Middle East and South America). The main increase in benzene production volumes will occur due to the introduction of new capacities, as well as due to an increase in the production of pyrolysis benzene [1].

In different countries, the production of benzene is based on different processes. The main sources of benzene production in Uzbekistan are pyrolysis distillate produced by Uz-Kor Gas Chemical LLC JV and reforming catalyst produced by Bukhara Oil Refinery LLC.

One of the main points affecting the efficiency of the extraction process is the efficiency of the extractant, which determines the ratio of solvent to raw material. Reducing this ratio is one of the promising ways to improve the technical and economic indicators of the process.

The literature [2,4] describes in detail the requirements for selective solvents. An industrial extractant must have high selectivity and dissolving ability, easy regenerability, a sufficiently high density difference with the raw materials being separated, low viscosity, etc. When selecting an extractant, consideration should be given to solvent resources and the ability of the selected solvent to be used beyond extraction processes and for other industrial purposes. Currently, more than 200 solvents have been proposed for the extraction of aromatic hydrocarbons, of which about ten are used in industry. However, each of them, in addition to positive technological characteristics, also has a number of disadvantages. Therefore, research is widely carried out in the field of synthesis of new effective solvents and improvement of technology based on existing extractants [5-9].

The most common extractant for $C6 – C8$ aromatic hydrocarbons is diethylene glycol, used in the Judex process [5,6,7]. Its widespread use is explained by its high selectivity, comparative cheapness, availability, high thermal stability and low toxicity. Diethylene glycol provides high recovery and purity of aromatic hydrocarbons. The Yudex process has been intensively improved by improving technology and replacing diethylene glycol with higher polyglycols - tri- and tetraethylene glycol, which have greater capacity compared to diethylene glycol and almost the same selectivity [2, 3, 4].

Sulfolane is one of the most effective modern selective solvents, as evidenced by the rapid introduction of the sulfolane process into industry abroad. So, if the first installation was launched in 1962, then in 1970 the process was already used in 40 installations. Disadvantages of the process include difficulties in removing solvent from separation products and the need to use reduced pressure when regenerating the solvent. Sulfolane has a relatively high melting point (27.8°C) [lo], which can be reduced by adding water, but this leads to a significant decrease in the solubility of sulfolane. Dramatic changes in process conditions compared to the Yudex process and the relatively high cost of sulfolane require significant investment.

The French Petroleum Institute proposed using dimethyl sulfoxide as an extractant. Its main advantages as an extractant for aromatic hydrocarbons are as follows: due to the low viscosity of the solvent, a fairly low melting point with a low water content and a fairly high density, the process can be carried out at low temperatures of 25-40°C; under process conditions, the solvent does not cause corrosion of equipment; non-toxic; allows the isolation of aromatic hydrocarbons from any oil fractions [7-8].

The disadvantages of dimethyl sulfoxide include the fact that it has relatively low thermal stability (heat resistant up to 140°C), which makes its regeneration by rectification difficult. To obtain pure aromatic hydrocarbons, a second solvent (butane or pentane) is fed down the extraction column to displace 3-5% of non-aromatic hydrocarbons from the extract phase [8-9]. The solvent is separated from the extract phase by re-extracting aromatic hydrocarbons with butane or pentane. The use of a second solvent complicates the technological scheme [10]. In addition, dimethyl sulfoxide is hygroscopic, and the presence of water in the solvent reduces its dissolving ability.

Thus, none of the selective solvents discussed above is ideal for isolating low molecular weight aromatic hydrocarbons. These disadvantages of solvents in technological and economic terms force researchers to search for new, more effective solvents, including mixed ones, obtained from substances already available in the chemical industry [30].

The most widely practiced is the addition of water [9, 10], in order to increase the selectivity of the extraction process and increase the concentration of extracted components in the extract. However, the use of water leads to an increase in solvent consumption, a decrease in its dissolving ability, and an increase in energy costs. The introduction of water into the extractant is accompanied in some cases by hydrolysis of the solvent, leading to corrosion of the equipment and a decrease in the stability of the solvent.

Modern researchers believe that the use of mixed solvents that do not contain water is one of the promising ways to improve the extraction process of low molecular weight aromatic hydrocarbons.

The above literature review allows us to draw the following conclusions. Currently, in industrial practice, the liquid extraction process using selective solvents has become widespread in industrial practice for the extraction of low molecular weight aromatic hydrocarbons from petroleum feedstocks. Improvement of the process is associated with the selection of new selective solvents that are more effective than those currently used. An analysis of the literature shows that among the new selective solvents currently proposed, dimethyl sulfoxide and diethylene glycol are of practical interest. Benzene extraction with DMSO + DEG system can be carried out at low temperatures, atmospheric pressure and low ratio of solvent to raw material. DMSO+DEG meets the requirements for selective solvents and has a cheap and accessible raw material base.

Experimental part. The purpose of the work is to study the possibility of increasing the efficiency of the process of benzene extraction from pyrolysis distillate produced by JV Uz-Kor Gas Chemical LLC and reforming catalysts produced by Bukhara Oil Refinery LLC by using dimethyl sulfoxide (DMSO) and its mixtures with diethylene glycol (DEG) as an extractant.

To achieve this goal, the following tasks are required:

1. Study of the mutual solubility of aromatic hydrocarbons, n-paraffins, benzene and the mixed solvent DMSO + DEG.

2. Study of the influence of the main process factors on benzene extraction performance.

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The scientific work investigated the dissolving and selective abilities of the mixed solvent DMSO + DEG during the extraction of benzene from an artificial hydrocarbon mixture and pyrolysis distillate. The relationships between extraction indicators and technological parameters have been established.

Table 1. Physicochemical properties of DMSO

№	Indicator name	Reference data
1.	Molecular weight, g/mol	78,13
2.	Density, g/cm3	1,1004 g/sm^3
3.	Boiling point, °C (at 760 mm Hg)	189
4.	Melting temperature,°C	18,5
5.	**Acid dissociation constant pKa**	35,1
6.	Dynamic viscosity at 25°C, Pa s	0,001996
7.	Refractive index of dimethyl sulfoxide at 20°C:	1,4778-1,4790

To determine the mutual solubility of dimethyl sulfoxide and n-paraffins, n-hexane n-paraffins and n-octane were used. For the work, we used DMSO, DEG, benzene and n-paraffins, the physicochemical constants of which corresponded to the literature data (Tables 1 – 2).

Dimethyl sulfoxide (DMSO) is a chemical substance with the formula – $(CH_3)_2SO$. A colorless, odorless liquid with a specific sweetish taste (an insufficiently pure product has a characteristic odor of dimethyl sulfide). An important bipolar aprotic solvent. It is widely used in various fields of chemistry, as well as as a medicine [4].

Table 2. Physicochemical properties of DEG

№	Indicator name	Reference data
1.	Molecular weight, g/mol	106,12
2.	Density, g/cm3	1,118
3.	Boiling point, °C (at 760 mm Hg)	244-245
4.	Melting point, °C	-7.8
5.	Flash point, °C	124

The system containing pure DMSO is characterized by a small area of the heterogeneous region, which indicates the high mutual solubility of the components of the system, the high dissolving ability and low selective ability of DMSO.

Thus, the addition of DEG to DMSO leads to a decrease in solubility and an increase in solvent selectivity. Given the nature of the solubility curves, the content of DEG in a mixed solvent above 50% is impractical.

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According to the above optimal technology condition, benzene was extracted from the pyrolysis distillate produced by JV Uz-Kor Gas Chemical LLC in a mixed solvent DMSO + DEG in a mass ratio of 1:1 and the resulting benzene was purified and analyzed on a GCMS device.

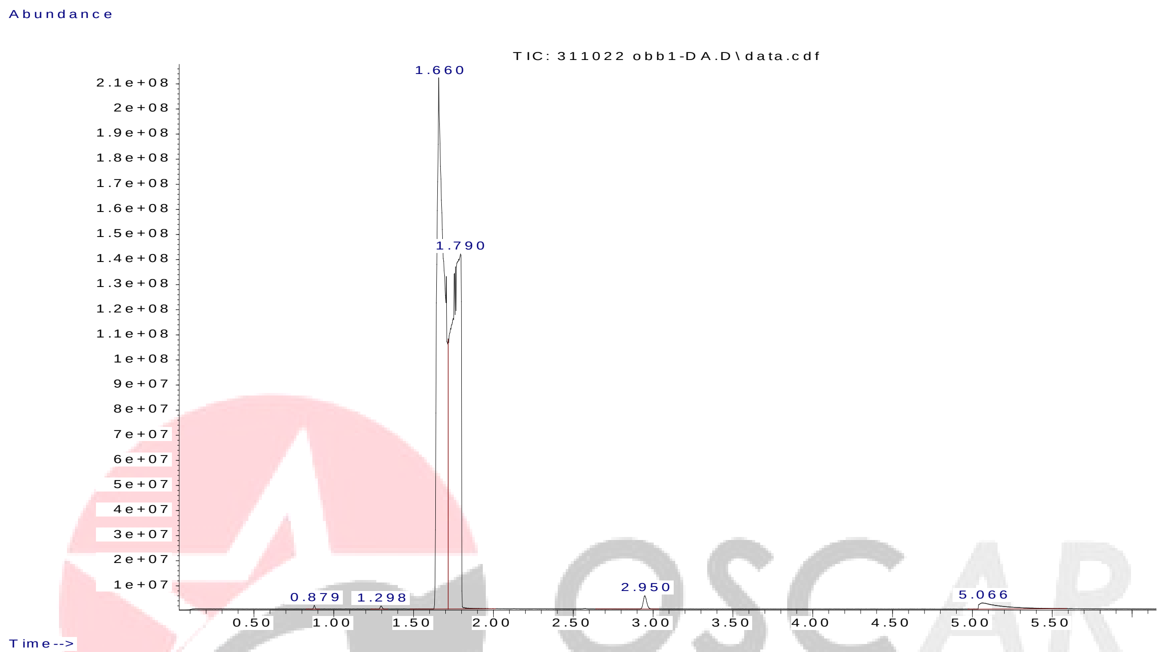

Fig.2. Chromatogram of extracted benzene from pyrolysis distillate.

The obtained analysis results show that the extraction of benzene from the pyrolysis distillate produced by JV Uz-Kor Gas Chemical LLC in a mixed solvent DMSO + DEG in a mass ratio of 1:1 benzene appeared in 1.660 and 1.790 minutes with a purity of 97.52%.

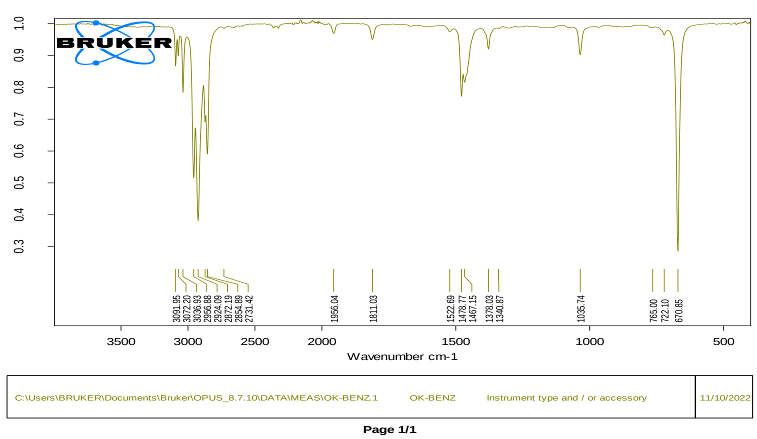

Fig.3. IR spectrogram of extracted benzene from pyrolysis distillate

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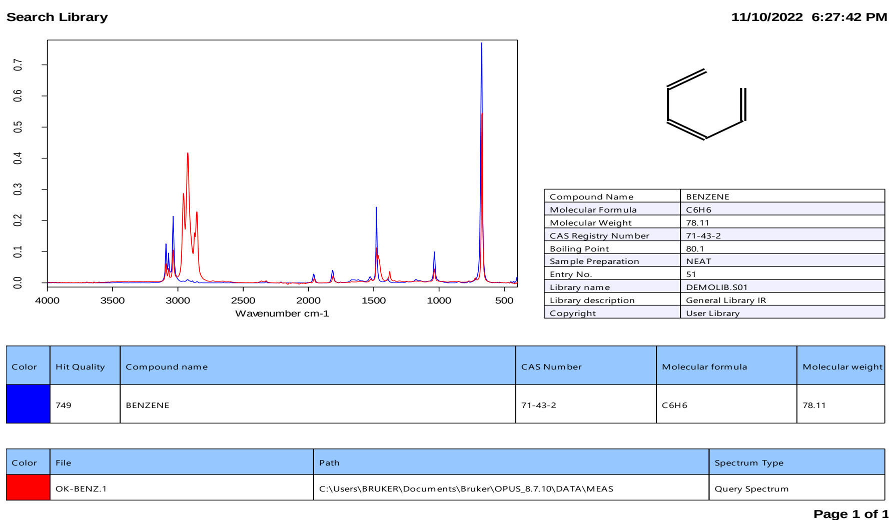

Fig.4. IR spectrogram of extracted benzene from pyrolysis distillate compared with the instrument database.

CONCLUSIONS

Based on the results obtained, the extraction of benzene from the pyrolysis distillate produced by JV Uz-Kor Gas Chemical LLC in a mixed solvent DMSO + DEG in a mass ratio of 1:1 makes it possible to increase the efficiency of the benzene extraction process expediently.

The optimal parameters of the benzene extraction process with a mixed solvent DMSO + DEG, necessary for the design of installations for the extraction of aromatic hydrocarbons, have been determined.

Based on the data obtained and their mathematical processing in laboratory conditions, optimal conditions for the extraction of benzene from model mixtures of hydrocarbons and pyrolysis distillate with a mixed solvent DMSO + DEG were established. The feasibility and effectiveness of replacing diethylene glycol with a mixed solvent DMSO + DEG was shown. The data obtained can be used in the design of installations for the extraction separation of benzene and the reconstruction of similar installations.

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