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EFFICIENCY IMPROVEMENT OF THE AROMATIC HYDROCARBONS EXTRACTION PROCESS FROM CATALYSATE OF REFORMING AND CO-PRODUCTS OF AROMATIC SECTIONS AT A REFINERY

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The issues of relevance of the production of aromatic hydrocarbons and, accordingly, the intensification of the extraction of aromatic hydrocarbons by selective solvents are considered. The performance characteristics and physicochemical properties of various extractants are compared. The optimal component for TEG was determined to obtain a mixed solvent. The effectiveness of the usage of such an extractant in the intensification of the aromatic hydrocarbons extraction by selective solvents is estimated.

Introduction.Proclivity by UN human rights activists and environmental activists to the idea of abandoning fossil fuels are gradually gaining popularity both among some countries and among automobile concerns, and oil companies carry out unitary reorientations of their refineries to zero fuel production, as it is supposed, to search the economic efficiency of such an operating mode of oil refineries in the current global market and the possibility of transition to a policy of companies to completely refuse to produce fuel. In addition, the existing environmental zones and the policy of banning certain types of internal combustion engines in some cities, as well as the production of cars with low fuel consumption, coupled with the policy of updating an outdated fleet, actually set the volume of fuel output at oil refineries, the need for which is constantly decreasing in Europe.However, in general, an increase in demand for petroleum fuels for the next 20 years is forecasted throughout the world [1].

The reorientation of refineries is possible in the direction of reducing production capacity or with an increase in the production of raw materials for petrochemistry or its final products.

Demand for petrochemicals in the world continues to grow rapidly, far outstripping global GDP growth.Therefore, from the point of view of maintaining the profitability of the enterprise and the guaranteed return on investment projects, the priority direction of the development of the oil refinery is to increase the production of the feedstock for the petrochemistry or its finished products. This policy can be seen in the "Strategy of the petrochemical complex until 2030" of the Belarusian State Concern for Oil and Chemistry, in China, measures are being taken to accelerate the development of petrochemistry; in Russia, the aim is to increase non-resource exports.

Task formulation. Aromatic hydrocarbons are the basic substances used in industry for the production of a variety of chemical products.The global growth in demand for low molecular weight aromatic hydrocarbons is, on average, 3-5% per year. This is due to the increasing demand for aromatic hydrocarbons produced, primarily paraxylene [2, 3].

Currently, the main source for the production of monocyclic aromatic hydrocarbons (benzene, toluene, xylene) are catalysts for the reforming of gasoline fractions [4]. Catalytic reforming products represent a mixture of aromatic, naphthenic and paraffinic hydrocarbons mixed with unsaturated hydrocarbons.It can be either narrow fractions containing, respectively, benzene, toluene or xylenes, or wide fractions containing a mixture of aromatic hydrocarbons. In addition to catalytic reforming products, by-products of the aromatic section of the refinery are also used to produce monocyclic aromatic hydrocarbons. The separation of high purity individual aromatic hydrocarbons (99 - 99.9%) from these blended products is a complex task associated with the usage of a number of processes [5].

Monocyclic aromatic hydrocarbons are recovered from these mixtures by liquid extraction with selective solvents. Refinery process units using 90–95% glycol solutions (DEG, TEG, and tetraethylene glycol) are widely used [6].The disadvantages of the existing process used at most refineries in the CIS countries, using the LG-35-8 / 300B unit as an example, are mainly due to the imperfection of the technological scheme of the extraction unit designed by Lengiproneftekhim (Lengiprogaz in the 1960s) according to the extraction laboratory of VNIIneftekhim.One of these is the high consumption of risicle (100–110% for raw materials), which leads to a decrease in the extractor productivity and a decrease in the actual concentration of extractant in the system and its selectivity.

For the successful realization of the separation of hydrocarbon raw materials, the used extractant must satisfy a number of requirements, the most important of which are high selectivity and solvent ability. However, an extractant that fully complies with the requirements of modern technology hasn't been found yet. The solvent triethylene glycol (TEG), currently used in the domestic industry, has a good capacity in relation to aromatic hydrocarbons for the separation of aromatic hydrocarbons, but it has low selectivity and solvent ability, which forces the process to be carried out at high extractant ratios to raw materials and elevated temperature and pressure, which leads to additional material and energy costs. In addition, it has a high viscosity and heating capacity, which contributes to a decrease of coefficient of efficiency of contact devices; it is necessary to maintain a high mass ratio of solvent to raw materials and a large consumption of recycle stock and high costs for the separation of the extract with the solvent [2, 7].All these disadvantages are associated with the fact that TEG is a strongly associated solvent due to the existence of two hydroxyl groups and the formation of stable intermolecular hydrogen bonds. Besides, triethylene glycol has strong toxic properties.By the degree of impact on the human body, triethylene glycol is a moderately dangerous substance, it belongs to the 3rd substance hazard category. The maximum allowable concentration (MAC) of technical triethylene glycol in the air of the working area of industrial premises is 10 mg / m^3.

The low dissolving capacity of TEG leads to the necessity to increase the temperature of the extraction process to 150 ° C, however, this reduces the stability of π-complexes with arenes and the selectivity of the extractant.The high selectivity of TEG by molecular weight is also due to the strong association of its molecules. In the transition from benzene to xylenes, the energy expenditure sharply increases when the arene molecules dissolve to form a cavity in the solvent structure, as a result, the critical solution temperature increases sharply, and the distribution coefficients and the degree of extraction decrease.

The high viscosity of the TEG leads to a decrease in the efficiency of the plates of extraction columns, which is much lower than for plates of columns of extractive distillation.

Therefore, improving the technology for the separation of complex hydrocarbon mixtures in order to reduce energy costs by reducing the solvent to feed ratio and the process temperature is an urgent scientific and technical task.

Methods of research. One way to solve this problem is to use mixed-type extractants.Their use allows more flexible implementation of extraction processes for the separation of hydrocarbon mixtures during processing of raw materials of variable composition due to changes in the extraction and physicochemical properties of extractants [4].

There are solvents that are devoid of the above drawbacks, however, a complete replacement of the solvent would lead to a partial or complete replacement of technological equipment, which, given the growing costs of reorienting to the course of petrochemicals, does not have a high profitability.

Therefore, the best of the methods of intensification of extraction, which avoids significant material costs, and especially reconstruction / change of the technological scheme, is the use of mixed solvents [2, 8].

Results, their discussion and perspectives. Currently, there are many options for additions to TEG: sulfolane, N-methylpyrrolidone, diglycolamine, dimethyl sulfoxide, N-formyl morpholline, ethyl alcohol, etc. [2, 9-11]. Their comparison, presented in [11], defines N-methylpyrrolidone as the most suitable.

Table 1 shows the comparative characteristics of selective solvents used in industry, where $\left(\frac{\gamma_h^0}{\gamma_b^0}\cdot\frac{1}{\gamma_b^0}\right)$ – is the efficiency criterion.

Table 1. – The selectivity and dissolving capacity of aromatic hydrocarbon extractants

Extractant	T, °C	γ_h^0	γ_b^0	$\frac{\gamma_h^0}{\gamma_b^0}$	$\frac{\gamma_{ch}^0}{\gamma_b^0}$	$\frac{\lg(\gamma_{oct}^0)}{\gamma_{hp}^0}$	$\frac{1}{\gamma_b^0}$	$\left(\frac{\gamma_h^0}{\gamma_b^0}\cdot\frac{1}{\gamma_b^0}\right)$
Triethylene glycol	30	60,6	3,86	15,7	7,24	0,168	0,259	4,1
	80	30,4	3,02	10,1		0,126	0,331	3,3
Tetraethyleneglycol	30	37,7	2,46	15,3	7,54	0,171	0,407	6,2
	70	24,8	2,48	10,0		–	0,403	4,0
Sulfolane	30	72,0	2,43	29,6	13,9	0,154	0,412	12,2
	80	38,4	2,49	15,4		0,112	0,402	6,2
Dimethylsulfoxide	20	92,0	3,83	24,0	11,4	0,169	0,261	6,3
	60	48,0	3,03	15,8		0,126	0,330	5,2
N-formylmorpholine	30	34,6	2,03	17,1	10,0	0,133	0,493	8,4
	61,7	24,7	1,99	12,4		0,115	0,503	6,2
N-methylpyrrolidone	30	14,2	1,08	13,1	7,90	0,086	0,926	12,1
	60	9,9	1,08	9,17		0,057	0,926	8,5

According to the efficiency criterion, when separating the model system "hexane-benzene", sulfolane and N-methylpyrrolidone are at the same level, and when separating the system "cyclohexane-benzene" N-methylpyrrolidone should be more effective even in comparison with sulfolane. When comparing the physicochemical properties of the extractants (Table 2), the following conclusions can be drawn: sulfolane has a high melting point, which may limit its use; N-methylpyrrolidone has the lowest dynamic viscosity, which will increase the efficiency of the contact steps; N-methylpyrrolidone is less toxic than sulfolane.

Table 2. – Physico-chemical properties of arene extractants

Extractant	ρ_4^{20}	B.P.,°C	M.P.,°C	η^{20}, MPa·s	C_p^{20}, $\frac{kJ}{kg \cdot K}$	H_{vap}^{25}, $\frac{kJ}{mol}$	σ^{20}, $\frac{mN}{m}$	MAC, $\frac{mg}{m^3}$
Triethylene glycol	1,1242	285	-4,3	49,0	2,17	71,6	45,57	10
Tetraethyleneglycol	1,1247	327,3	-6,2	61,3	2,14	88,8	45 (20 °C)	10
Sulfolane	1,2604 (30 °C)	285	28,4	10,0 (30 °C)	1,34 (30 °C)	61,5 (30 °C)	60,33 (40 °C)	50
Dimethylsulfoxide	1,0960	189	18,45	2,473	2,05	57,28	43,49	20
N-formylmorpholine	1,1528	244	20…21	9,37	1,97	46,06	–	–
N-methylpyrrolidone	1,0328	202	-24	1,65	1,97	53,06	39,91	100

When choosing the optimal extractant, it is also necessary to take into account their thermal and chemical stability and corrosion activity. Sulfolan is a chemically inert substance and is thermally stable up to 220 ° C. Sulfolan, both watercut and anhydrous, has insignificant corrosion activity even at 200 ° C. N-methylpyrrolidone is a corrosive substance. However, corrosion is caused by the corrosive activity not of N-methylpyrrolidone itself, but of the products of chemical transformation during its heating, hydrolysis and contact with air. N-methylpyrrolidone has almost the same comprehensive efficiency criterion with sulfolane, however, its operation is hampered by its corrosivity, which is easily leveled out by introducing a corrosion inhibitor into the system, lowering the process temperature, and maintaining the system under a slight overpressure. Upon that the main disadvantage of sulfolane is that under normal conditions it is a solid. Therefore, for its keeping and pumping, it is necessary to keep it in a heated state. Also, sulfolane has a maximum allowable concentration 2 times lower than that of N-methylpyrrolidone, which requires additional measures to protect people when using it.

However, with a logical attempt to add N-methylpyrrolidone to TEG to obtain a mixed extractant, it is not as effective.In the 1990s, studies were conducted at the St. Petersburg State Technological Institute in conjunction with Kirishinefteorgsintez LLC to develop a mixed extractant for the extraction of aromatic hydrocarbons from reformate of fraction 62 - 105 ºC, the results of which were implemented on the LG-35- 8 / 300Bunit LLC "PO" Kirishinefteorgsintez "in 1999 –2000.

To increase the dissolving capacity of TEG, it was proposed to use mixtures of it with various solvents: N-methylpyrrolidone, dimethylformamide, furfural, propylene carbonate, morpholine, acetone, dioxane. However, all these solvents, increasing the dissolving ability, reduce its selectivity.

The TEG-sulfolane mixture is devoid of this drawback, exhibiting both higher selectivity and increased dissolving capacity with respect to arenes.A complete replacement of TEG with sulfolane would lead to the need for a substantial reconstruction of existing extraction plants.When using sulfolane, the recycle stock and extract are stripped in separate columns, and in the process with TEG, in a combined column.The arenas are steamed from sulfolane in a larger diameter vacuum column; a vacuum-generating system is necessary (due to the low partial pressure of aromatic hydrocarbons over the solvent).

Effective mixed extractants, as well as individual solvents, should not be strongly associated.

The mixing of TEG with N-methylpyrrolidone, dimethylformamide, N-methylcaprolactam is accompanied by an exothermic effect ($\Delta H^E<0$)which can be explained by the formation of intermolecular hydrogen bonds. In contrast to these systems, the mixing of TEG with sulfolane occurs with an endothermic effect. Positive deviations from Raoul's law in the TEG – sulfolane system, taking into account close boiling points and pressures of saturated steam of the components, leads to the formation of an azeotropic mixture and a decrease in the temperature in the stripping column when arenes are distilled from the extract phase.Thus, the regeneration of the mixed extractant is facilitated in comparison with the regeneration of individual TEG and sulfolane.

The most important advantage of using the mixed TEG – sulfolane extractant is that the mass ratio to the feed is reduced from 8: 1 for TEG to 4.9: 1 when the sulfolane content in the mixture with TEG is 28-30% wt. At the same time, the transfer of the LG-35-8 / 300B installation to a mixed solvent with a sulfolane content of 28-30% wt. mixed with TEG was carried out without a significant change in the technological scheme.

The increase in the ratio of sulfolane: TEG to 60: 40% wt. would reduce the temperature of the extraction process, as well as the mass ratio of the mixed extractant to the raw material to 3: 1 and the recycle stock consumption from 80 - 100 to 30% wt. on raw materials. However, to reduce the temperature of the extraction process, it is necessary to install a heat interchanger for cooling the regenerated extractant discharged from the stripping column at 150 ° C [12, 13].

According to the research results, the amount of saturated hydrocarbons in the extract remains less, which is due to the increased selectivity of the extractant with a weight ratio TEG: sulfolane ratio of 1: 1, compared with 0.27 : 1 [13].

Reducing the water content in the mixed extractant is possible only to a level that ensures its boiling point at a normal pressure of not more than 150 ° C, which allows the use of water vapor with a pressure of about 1 MPa in the boiler of the stripping column. In this case, selective solvents (sulfolane and TEG) are thermally stable. An increase in the content of sulfolane in the mixed extractant with the same water content also leads to a decrease in the boiling point of the mixture. This can be explained by the greater degree of non-ideality of the water - sulfolane system compared to the water - TEG system. At the same time, an increase in the sulfolane content, as well as a decrease in the water content, leads to an increase in the solvent ability of the mixed extractant.

Conclusion.Thus, the use of such a mixed extractant allows not only to reduce the energy costs of the process, but also by reducing the weight ratio of the extractant to the raw material to increase the productivity of the plant, which affects the determination of design capacity and, accordingly, the cost of new extraction plants, if necessary for the modernized / new aromatic block.Both reducing energy costs and increasing plant productivity reduces the cost of production of aromatic hydrocarbons, which allows you to increase the profit of the enterprise.

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