### THEORETICAL BASES OF CHEMICAL TECHNOLOGY ТЕОРЕТИЧЕСКИЕ ОСНОВЫ ХИМИЧЕСКОЙ ТЕХНОЛОГИИ

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## Improvement of high-viscosity oil production technology via the effective redistribution of energy resources

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**Objectives.** The synthesis of high-viscosity oils is a fundamental aspect of oil refinement and contributes toward improvements in their production technologies. However, current methods of oil extraction are characterized by the inefficient use of energy resources. Therefore, refinement costs continue to increase. Furthermore, high production emissions affect the environment. For example, the Duosol-type process uses a large quantity of gas used in solvent recovery units in existing furnaces, and excess heat is wasted. Additionally, oil dewaxing plants use water steam, whose condensate can be contaminated with petroleum products or ketone-aromatic solvents. The purpose of this study was to identify ways of improving the efficiency of high-viscosity oil production technologies for energy efficiency and environmental safety as well as prove the feasibility of computational methods of oil production plants' improvement.

**Methods.** The heat quantity required for high-viscosity oil production is calculated using a thermal equation and data obtained from industrial equivalents, empirical dependencies, and reference data. The heat capacities and heat quantities of Duosol and dewaxing plants are calculated using conventional methods based on the heat recovery principle.

**Results.** At the solvent regeneration unit of a Duosol plant, excessive heating of the cube in one of the distillation columns was measured, leading to excessive heat consumption. This may result in contamination of the low boiling distillation component with water—one of the still bottom mixture components. Calculations show that the furnace should be divided into two chambers to lower the temperature of the column cube to help solve this problem. Water steam is currently used in the raw material preparation unit of the dewaxing plant. It has been found, however, that the quantity of heat carried away by the flue gases of the furnaces is sufficient to heat the raw material preparation unit of the oil dewaxing plant if water steam is completely excluded from this operation.

**Conclusions.** Technology improvement at Duosol and dewaxing plants, which are part of the process of obtaining high-viscosity oils at refineries, is possible through the effective redistribution of energy resources.

**Keywords:** Duosol, base oils, energy carriers, dewaxing, solvent regeneration, water steam, flue gases, production optimization.

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# Совершенствование технологии получения высоковязких масел с помощью эффективного перераспределения энергетических ресурсов

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**Цели.** Производство высоковязких масел, как и совершенствование технологии их получения, является перспективным направлением нефтепереработки. Способы выделения масляных фракций из нефти экстракционными методами характеризуются малоэффективным использованием энергоресурсов и, как следствие, удорожанием процесса, а также относительно большим количеством выбросов, негативно влияющих на окружающую среду. Так, в процессе типа Дуосол используется большое количество природного газа, применяемого в печах на блоках регенерации селективных растворителей, избыточную теплоту которого возможно рекуперировать, а на установках депарафинизации масел используется водяной пар, конденсат которого может быть загрязнен нефтепродуктом или кетон-ароматическим растворителем. Цель данной работы заключалась в поиске путей повышения эффективности технологии получения высоковязких масел с точки зрения энергоэффективности и экологической безопасности, а также в доказательстве целесообразности вариантов улучшения установок масляного производства расчетными методами.

**Методы.** Количество тепла, необходимое для технологических операций, осуществляемых на установках получения высоковязких масел, определяли тепловым расчетом. Этот расчет был проведен на основании данных, полученных на промышленном аналоге; на основании эмпирических зависимостей, а также литературных справочных данных. Общепринятыми способами рассчитаны величины теплоемкостей и тепловых потоков установок селективной очистки Дуосол и депарафинизации. В основу тепловых расчетов положен принцип рекуперации тепла.

**Результаты.** На блоке регенерации растворителя установки Дуосол выявлен избыточный нагрев куба одной из ректификационных колонн, приводящий к перерасходу тепла. Это может приводить к загрязнению низкокипящего компонента перегонки (пропана) водой, которая является одним из компонентов кубовой смеси. Расчет показал, что для решения этой проблемы целесообразно разделение печи на две камеры и понижение температуры в кубе колонны. На блоке подготовки сырья установки депарафинизации используется водяной пар. Установлено, что количество тепла, уносимого дымовыми газами печей установки Дуосол, достаточно для обеспечения теплом блока подготовки сырья установки депарафинизации масел при полном исключении водяного пара из данной операции.

**Выводы.** Совершенствование технологии на установках Дуосол и депарафинизации, являющихся частью процесса получения высоковязких масел на нефтеперерабатывающих заводах, возможно путем эффективного перераспределения энергоресурсов.

**Ключевые слова:** Дуосол, базовые масла, энергоносители, депарафинизация, регенерация растворителя, водяной пар, дымовые газы, оптимизация производства.

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#### INTRODUCTION

Although refineries are key producers of energy, they themselves are large energy consumers. Therefore, it is no surprise that a key motivation of refineries is increasing the efficiency of oil processing,

in Russia as well as worldwide [1]. The current trend in oil refinement is the elimination of water steam as a heat and energy carrier [2]. This has been driven by tighter environmental standards controlling emissions and effluents—the inevitable waste products of oil refinement. Notably, high-viscosity oil production

is the largest consumer of energy resources among refinery types.

High-viscosity oil is a mixture of base oil obtained from oil distillation and the purification of the oil fraction with additives that create and improve certain properties of the final product. Despite the ever-expanding market of additives [3], there are negative aspects of using them with oil products [4]. Therefore, improving the technology for the production of base oils is an imperative task.

The technology used to produce motor, aviation, cylinder, compressor, transmission, and other oils combines sequential physical processes of isolating (via extraction) hydrocarbons having high-viscosity indices, improved low-temperature properties, and low-coking properties from oil fractions. Subsequent to the vacuum distillation of fuel oil, distillate fractions undergo selective purification and dewaxing, and residual fractions (i.e., tar) undergo deasphalting, selective purification, and dewaxing.

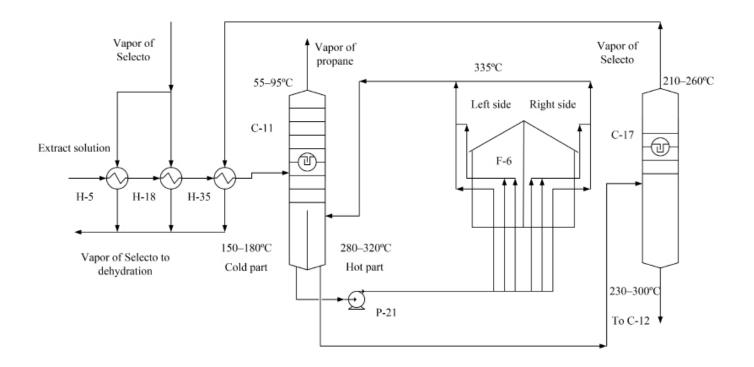
The Duosol process is a combined procedure of extracting oil fractions from tar. Subsequent to low-temperature solvent dewaxing, the fractions form the basis for highly viscous oils (e.g., MS-20) and insulating oils (e.g., KM-22). The Duosol process is based on the use of two mutually insoluble selective solvents. One of these selectively dissolves the desired

components of the feedstock, and the other dissolves the undesired ones. One of the solvents is propane, which exhibits deasphalting properties. The other is Selecto, a mixture of phenol and cresol. Thus, the Duosol process combines deasphalting and selective cleaning. As a result, a raffinate (target product) and a mixture of extract and asphalt (byproduct) are obtained [5].

#### MATERIALS AND METHODS

Solvents are sequentially regenerated from raffinates and extract solutions in distillation columns. The process of propane regeneration from the extract solution of a Duosol-type plant is conducted based on the technological scheme shown in Fig. 1.

The extract solution is mixed with the asphalt solution, and it sequentially passes H-5, H-18, and H-35 heat exchangers to enter the C-11 column. This column is designed to distil the main part of the propane contained in the extract solution. A vertical partition is installed at the bottom of the C-11 column. On one side of the partition, there is a suction pipe (cold part), and on the other side, there is an overflow to the C-17 column (hot part). The Selecto vapor from the C-17 column goes through the H-35 heat exchanger for dehydration, and the distillation



**Fig. 1.** Existing scheme of propane regeneration: H-5, H-18, H-35—heat exchangers; C-11, C-17—packed columns; F-6—furnace; P-21—pump.

residue goes to the C-12 column (not shown in the figure) and then further.

The heat required for propane evaporation is introduced by circulating the extract solution that enters the lower part of C-11 column through furnace F-6. The extract solution is obtained from the cold part of the bottom of the C-11 column using the P-21 pump and pumped in six flows through the F-6 furnace. The extract solution is heated up to 280–320°C.

The extract solution from the bottom of the C-11 column enters the C-17 column because of the pressure difference. Here, Selecto distillation takes place because of the excessive heat of the extract solution originating from the C-11 column. No additional heat supply is provided to the column.

A certain amount of dissolved water accumulated on the column plates enters the C-11 column along with the extract solution. As the temperature of the column top is lower than what is required for water removal as a vapor phase (55–95°C) and the still bottom temperature is higher than the temperature at which water removal in the liquid phase occurs, water discharge through the column top (along with the oil product) periodically occurs. This results in propane contamination with asphalt.

Analysis of the technological scheme of the solvent regeneration unit of the Duosol process, as well as the analysis of methods for increasing the distillation columns efficiency at oil refineries [6, 7], allows us to propose a decrease in the temperature of the C-11 column still bottom to the temperature required for propane separation and simultaneously organize the heating of the extract solution flow before the C-17 column to enable water removal along with the extract solution. For this, we propose to divide the F-6 furnace into two parts. One part should be used to heat the C-11 column and the other one—to heat the extract solution flow from C-11 to C-17.

Calculation of the temperature required for the regeneration of most propane from the extract solution comes down to the calculation of the heat required to convert propane to its gaseous state at a given pressure

(1.9 MPa). It is known [8] that propane saturation temperature at 1.9 MPa is 50°C, and its evaporation heat is 514.96 kJ/kg [9]. The composition of the extract solution (extract + solvent) per 100 mass parts (percent) of raw materials (tar) directed to the regeneration of solvents is known based on the data for an industrial equivalent [5]. The composition for 100 mass parts of the extract solution is provided in Table 1.

Based on the data of Table 1, one ton of the extract solution contains an average of 21% or 210 kg of propane and its conversion to gas (regeneration from solution) requires 108 141.6 kJ (the specific evaporation heat is 514.96 kJ/kg). Considering the heat capacities of the extract solution components [10] and their content in the mixture, the heat capacity of the extract solution is  $c_p = 2.57 \text{ kJ/(°C} \times \text{kg)}$ .

We calculate the temperature required for propane evaporation as follows:

$$T = \frac{Q}{c_{\rm p} \times G},\tag{1}$$

where Q is the amount of heat required for the evaporation of 210 kg of propane at 1.9 MPa; T is the temperature of propane evaporation from the extract solution, °C;  $c_p$  is the average heat capacity of the extract solution, kJ/(°C×kg); and G is the average propane content in the extract solution, G = 210 kg.

The calculated minimal temperature for propane recovery from the extract solution is 201.16°C at 1.9 MPa. Thus, the C-11 column still bottom is heated to 280–320°C. This significantly exceeds the required temperature, and the main portion of propane can be distilled at a lower temperature. Reducing the temperature of the C-11 column still bottom would make it possible to remove water (along with the extract solution) and simultaneously organize the heating of the extract solution flow before the C-17 column. This can be done by dividing the flow from pump P-21 before furnace F-6 (the partition in the C-11

 Table 1. Components of the extract solution

Component of the solution	Quantity per 100 mass parts of tar, mass %	Quantity per 100 mass parts of extract solution, mass %	Mass per 1 ton of raw materials, kg
Extract	41	10	100
Propane	86	21	210
Phenol: cresol = 1:1	277	69	690
Total	404	100	1000

still bottom should be removed) and dividing furnace F-6 into two parts. One part should be used to heat the C-11 column still bottom, and the other one—to heat the extract solution flow to C-17. One stream should be directed back to C-11, and the other one—to C-17. The suggested flow separation scheme is shown in Fig. 2.

The proposed scheme would eliminate water discharge at C-11, thus reducing the probability of propane vapor contamination with the extract, reducing the corrosion of C-11 and its service lines, and reducing the probability of asphaltene cracking by shortening its residence time in the high-temperature zone. Moreover, the temperature decrease allows reducing the consumption of fuel (natural gas) upon combustion in furnaces, which could also result in reduced energy costs.

While analyzing the production of high-viscosity oils, we noticed that the regeneration of solvent pairs (i.e., propane and phenol-cresol mixture) at Duosol plants was performed in distillation columns using the heat of the flue gases from fuel combustion in furnaces. In typical plants for solvent dewaxing, we found that water steam was used for raw material preheating (80°C).

The flue gases of the Duosol furnaces are directed into the chimneys with the outlet temperature of up to 350°C. On average, the temperature is in the range of 250–260°C. If we consider that 60–100 m<sup>3</sup>/h of natural

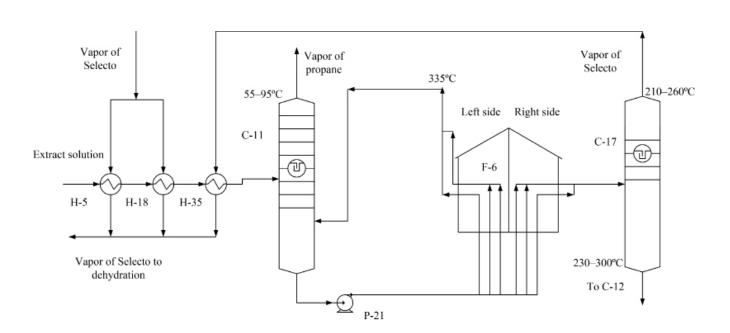
gas is burned (on average) every hour per one ton of the raw materials, it is clear that the recovery of this amount of heat is possible.

Water steam is used in dewaxing plants as a working fluid in ejectors of columns used for solvent regeneration from final products and for raw materials' preheating. This is required to obtain a true oil solution, from which pure paraffin crystals are separated at a later stage.

In recent years, there has been a trend of not using water steam as a working fluid in vacuum devices or as a heat transfer agent in oil refineries owing to the possibility of contaminated effluents' formation. Moreover, there is an efficient method [11] of solvent regeneration in nitrogen. Therefore, the complete repudiation of using water steam at the stage of raw material preheating is of practical interest, if water steam could be replaced by an efficient and economical energy carrier.

#### RESULTS AND DISCUSSION

We have proposed the redistribution of energy resources for the production of oil products at Duosol and dewaxing plants, which are often located near oil refineries. Furthermore, we have shown that it is possible to rationally design process pipelines from furnaces to heat exchangers. Using the heat of the flue gases of Duosol furnaces will allow the reduction of water vapor, and fuel gases with lower temperatures will have less impact on the environment.



**Fig. 2.** Proposed scheme of propane regeneration: H-5, H-18, H-35—heat exchangers; C-11, C-17—packed columns; F-6—furnace; P-21—pump.

During the Duosol process, solvent pairs are used to extract the raffinate. The latter is subsequently subjected to low-temperature dewaxing using a ketone-aromatic solvent, and the extract serves as a raw material for producing oxidized bitumen. It is known that prior to leaving the unit, the main product (raffinate) and the byproduct (extract) of the Duosol process undergo solvent regeneration because of the heat of the flue gases produced by the combustion of gaseous fuels in furnaces [12].

To support the feasibility of using the heat of flue gases, a thermal calculation was presented. The amount of heat required to heat the dewaxed raw material was determined. The calculation used the initial data of the material balance of the Duosol plant. In accordance with it, 3.36 parts of propane and 3.52 parts of Selecto solvent corresponded to 1 part of tar (i.e., the raw material of the Duosol plant). The phenol-cresol ratio was 1:1.04, or 49 and 51%, respectively.

The evaporation heat of propane, phenol, and tricresol (components of Selecto) are 431800, 446200, and 438800 kJ/t, respectively [13]. Therefore, we calculated the amount of heat required for the regeneration of solvent pairs with a specific productivity of one ton of raw material per hour (100 mass %) (Table 2). Hereinafter, calculations are performed for this specific productivity.

Typically, the furnaces of refinery plants use gas of their own production or natural gas from nearby pipelines. In addition to methane, fuel gases contain a certain amount of ethane (up to 0.7%), propane (up to 0.1%), butane (up to 0.1%), nitrogen (up to 2.8%), acidic CO<sub>2</sub> gases (up to 0.2%), and traces of sulfur compounds. Therefore, the calculation considers the composition of the energy carrier, which affects the specific heat of combustion (35.13 MJ/m³) [14]. Moreover, fuel gases contain compounds that can cause corrosion of the heat exchange equipment. When using conventional natural gas for the calculation, its specific consumption was 84.56 m³/(t<sub>raw mat.</sub>×h), which is typical at Duosol refineries.

The volume  $V_{cp}$  of the combustion products of 1 m<sup>3</sup> of natural gas (with a given composition) and

the volumetric heat capacity of these products were calculated using conventional methods [15]. In typical Duosol furnaces,  $10.85 \, \text{m}^3$  of combustion products are obtained from 1 m³ of natural gas. The heat capacity of the flue gases at the outlet of a Duosol furnace pipe and accordingly, at the heat exchanger inlet is  $1.4191 \, \text{kJ/(m³} \times \text{K)}$  at  $t_{in} = 260 \, ^{\circ}\text{C}$ .

The heat capacity of the flue gases at the heat exchanger outlet (at a permissible temperature of  $170^{\circ}\text{C}$ ) is  $c'_p = 1.4037 \text{ kJ/(m}^3 \times \text{K)}$ . The permissible temperature is chosen such as to prevent the condensation of water vapor and avoid the formation of corrosive compounds that results in equipment wear.

The heat  $Q_{ep}$  that can be obtained from the flue gases of the Duosol plant in the heat exchanger of the dewaxing unit is determined by the difference in the enthalpies at the heat exchanger inlet and outlet:

$$Q_{\rm cp} = H_{\rm in} - H_{\rm out} \,. \tag{2}$$

The enthalpy of the flue gases at the heat exchanger inlet at 260°C per one ton of raw material is

$$H_{out} = c'_p \times t_{out} \times V_{cp} \times V_{gas} = 1.419 \times 260 \times 10.85 \times 84.56 = 351690 \text{ kJ/t}_{raw mat}.$$

At the heat exchanger outlet at 170°C:

$$H_{out} = c'_p \times t_{out} \times V_{cp} \times V_{gas} = 1.4037 \times 170 \times 10.85 \times 84.56 = 224320 \text{ kJ/t}_{raw mat}.$$

Then the heat  $Q_{\rm cp}$  obtained from the flue gases in the heat exchanger (calculated per one ton of raw material) is 127 369 kJ/t<sub>raw mat</sub>.

Exhaust steam (130°C, 0.3 MPa) is typically used for the preparation of raw material at dewaxing plants [14]. The amount of heat required to heat the oil (the

Solvent		mass %, (ton/ton <sub>raw materials</sub> )		Amount of heat, kJ/ton <sub>raw materials</sub>	
Propane		336 (3.36)		1 450 848	
Selecto, of them:	Phenol	352 (3.52)	172 (1.72)	1519936	742 696
	Cresol		180 (1.80)		777 240
Total		788 (7.88)		2970784	

Table 2. Amount of heat required for solvent regeneration in the Duosol process

raffinate of the Duosol process and the raw material of the dewaxing unit) can be calculated by the following formula:

$$H_{lig} = \frac{1}{\sqrt{d_{15}^{15}}} \times \left(0.0015 \times T^2 + 0.726 \times T - 334.25\right),\tag{3}$$

where  $H_{\text{lig}}$  is the enthalpy of the liquid oil product, kJ/kg;  $d_{15}^{15}$  is the relative density of the oil product to be dewaxed; and T is temperature, K.

In this case, the relative density of the oil product to be dewaxed is 0.840, and the heating temperature is 80°C (or 353 K). On this basis, the amount of heat  $Q_{\text{heat}}$  required to heat the raw material to be dewaxed from 20 to 80°C is 122 650 kJ/t<sub>raw mat.</sub>

As seen from the calculation, the heat that can be obtained from the flue gases of the Duosol furnace at 260°C meets the demand for heating at the dewaxing units for raw material preparation:  $Q_{\rm cp} > Q_{\rm heat}$ .

Considering the heat-carrier properties of the flue gases of the Duosol process, we suggest that a one-way counter-flow shell-and-tube heat exchanger be used. In this heat exchanger, the intertubular space should be used to heat the selective purification raffinates or Duosol raffinates.

Heat transfer surface F required for heating the raw material to be dewaxed can be calculated using the following formula:

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$$F = \frac{Q_{\text{heat}}}{\Delta t_{\text{m}} \times K_{\text{T}}},\tag{4}$$

where  $\Delta t_{\rm m}$  is the average temperature difference in the heat exchanger, and  $K_{\rm T}$  is the average heat transfer coefficient over the heat exchange surface.

The required heat transfer surface F at  $\Delta t_{\rm m} = 220^{\circ}{\rm C}$  and  $K_{\rm T} = 70~{\rm W/(m^2 \times K)}$  (from the gas to the organic liquid), calculated for a specific productivity of one ton raw material per hour, is 8.27 m<sup>2</sup>.

#### **CONCLUSIONS**

- 1. To avoid propane contamination with water steam and reduce the probability of propane vapor contamination with the extract solution, we have suggested dividing the furnace of the propane regeneration unit at the Duosol plant into two chambers.
- 2. The heat of the flue gases leaving the Duosol furnaces, with a temperature of 260°C and above, is sufficient to preheat the raw material of the dewaxing unit.
- 3. For Duosol plants, we have shown the possibility of efficient redistribution of energy resources from oil production plants. For this purpose, it is necessary to partially (or completely, in the case of solvent regeneration in nitrogen) eliminate water steam. As a result, contaminated effluents at oil dewaxing plants could be avoided.

The authors declare no conflicts of interest.

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