

Sh.K.Amerkhanova, R.M.Shlyapov, A.S.Uali

*Ye.A.Buketov Karagandy State University  
(E-mail: amerkhanova\_sh@mail.ru)*

## **Influence of various factors on productivity of distillation column in distillation process of oil**

It is obtained the generalized equation, reflecting the influence of each factor on the output fractions. The optimum parameters of the distillation process are established. It is revealed that increasing the flow rate lead to increase of the rate constants. The results of IR spectral studies show that all fractions of gasoline contain large amounts of saturated alkyl, unsaturated and aromatic compounds.

*Key words:* oil, distillation process, distillation column, gasoline, IR spectral study, kinetics, rate constants, alkyl and unsaturated compounds, series of aromatic compounds.

Oil is a mixture of chemical compounds on the basis of hydrocarbons generated from a source of organic matter resulting from prolonged interaction with the environment occurrence influenced by many factors. Oil is an oily liquid, complete chemical composition of which determines modern instrumental methods is almost impossible.

The main chemical elements forming part of oil are carbon, hydrogen, sulfur, nitrogen and oxygen. Carbon and hydrogen are contained in different oils in an amount of 82–87 % (by weight) and 11–14 % (by weight) respectively. They are an integral part of all chemical compounds of oil. The minerals (except petroleum gas) crude oil has the highest heat of combustion, as it contains the greatest amount of hydrogen. In this regard, fuel oil properties to characterize the ratio of hydrogen to carbon (H: C) in %. Sulfur is included in the composition of heteroatomic compounds. Sulfur content of oil are classified into three classes: a low-sulfur crudes, it is up to 0.5 % in sulfur — 0.51 to 2.0 %, and sour — from 2.01 %. Nitrogen and oxygen in the oil are from 3.0 to 0.8 % (wt), respectively. In the oil ash was found 30 metals of which the most common are V, Ni, Fe, Cu, Mg, Al [1].

Paraffinic hydrocarbons from pentane to hexadecane under normal conditions in a liquid state. They are part of the light distillate oil fractions. According to their structure, they are divided into the normal structure of alkanes and branched alkanes (isoalkanes). Typically, when the same number of carbon atoms per molecule of branched-chain hydrocarbons differ from the normal structure of hydrocarbon lower density, pour point and boiling point. Paraffin hydrocarbons with branched provide high quality gasoline, whereas normal paraffins adversely affect the behavior of fuel in the gasoline engines, as they being the least resistant to oxidation are the lowest detonation resistance.

The presence of normal alkanes in aviation kerosene is almost unacceptable due to deterioration in the low-temperature properties of the fuel, as the normal structure of the hydrocarbons have high pour point, and in these fuels is unacceptable formation of crystals at temperatures down to  $-60\text{ }^{\circ}\text{C}$ .

In diesel fuel, the presence of normal alkanes is desirable, since they have good ignitability (maximum ratio H:C), but at the same time increase the pour point of fuel. Therefore, in diesel fuels the allowable number of normal paraffins is by the temperature of solidification on the state standard. Liquid normal paraffins derived from petroleum fractions, are widely used as: processing and household solvents, raw materials for the production of protein-vitamin concentrate, a raw material for chlorinated paraffins are used as the polymeric composition, and plasticizers for synthetic carbon, films, coatings; raw materials for the production of SAW, medicines [2].

Paraffinic hydrocarbons  $C_{17}$  and above under normal conditions are solids whose melting point with increasing the molecular weight increases. Solid hydrocarbons included in the composition, and ceresin wax. Paraffins characterized lamellar crystals or belt structure, their melting point ranges from 40 to 70  $^{\circ}\text{C}$ , the number of carbon atoms in the molecule, — from 21 to 32, molecular weight — between 300–450 g/mol. Paraffin waxes are present mainly in the oil fraction boiling at a temperature of 350–500  $^{\circ}\text{C}$ , which is one of the reasons for high pour point of the fractions.

The crystals have a needle-like structure ceresins. In addition to their composition includes solid paraffinic hydrocarbons, naphthenic and aromatic hydrocarbons with long side chains. At the same temperature, are characterized by high melting ceresins in alignment with paraffins density, viscosity and molecular

weight. Ceresin concentrated in vacuum distillation residues, causing an increase in temperature softening sludge. Low melting paraffin waxes are mainly hydrocarbons of normal structure, whereas in the more high-melting products — trade ceresins — get their isomeric forms.

Paraffin waxes are used as raw materials for production of synthetic fatty acids, detergents, chlorinated paraffins and olefins, as protective coatings, impregnating Crate packing products, pastes and Food Grease as an insulating material in electronics, as well as in the fragrance industry and for the preparation of suppositories. Ceresin widely used in industry and daily life as coatings, various ointments and pastes, basis of rope lubricants and etc.

### Experimental part

Rectifying distillation of hydrocarbons was carried by the procedure described in [3]. The oil of Kumkol field is used as the raw materials. Kinetic characteristics were evaluated on the output of light and medium fractions. IR transmission spectra were recorded using a Fourier transform spectrometer TERMO NICOLET AVATAR 360.

### Discussion of results

Research of the process of rectification of hydrocarbons in the sample of oil (Kumkol field) was carrying out in this paper. Thus the following factors were varied: the temperature 170–210 °C, the flow rate of from 0.8 to 4.0 ml/min, retention time of 30 to 90 min, number of plates is 2–9, the response function is served output light fractions. On the basis of a sample of obtained from the experimental data was obtained equation reflecting the impact of all factors on the yield of fractions [4].

$$W, \% = \frac{(0.04 \cdot T^2 - 1.31 \cdot T + 114.54) - (0.01 \cdot V_{pot}^2 + 0.07 \cdot V_{pot} + 11.14) - (7.44 / n + 13.51)}{1} \times \frac{(0.02\tau^2 - 0.27\tau + 16.70)}{11.6^2} \quad (1)$$

The optimal parameters are the feed rate 2.4 ml/min, the number of plates 5, retention time 90 min. Next rate constants of the process of fractional distillation of crude oil were calculated. The results are shown in Table 1.

Table 1

**The influence of feed rate and temperature of process on the rate constants of rectification of hydrocarbons**

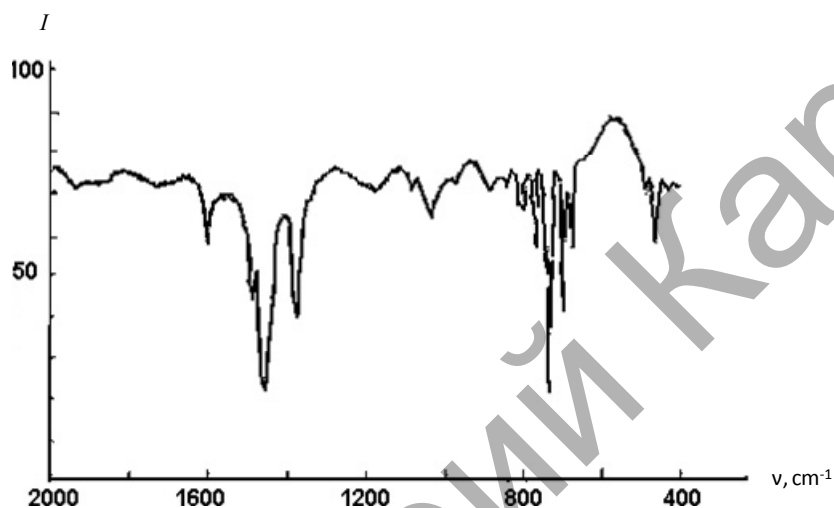
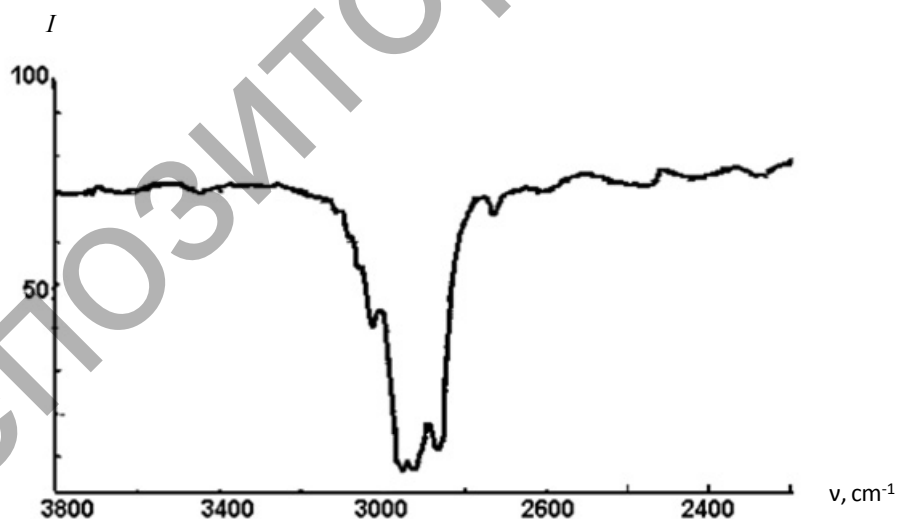
T, K	-lgk				
	0.8	1.6	2.4	3.2	4.0
443	17.51	6.55	6.54	6.54	6.57
453	5.44	5.41	5.40	5.41	5.43
463	2.86	2.85	2.85	2.85	2.86
473	6.76	11.36	11.33	11.35	11.42
483	1.80	1.80	1.81	1.80	1.80

It was established that the increase in flow rate leads to an increase in first order rate constant [5]. Low values of the rate constants for the 443 K at 0.8 ml/min associated with the occurrence of evaporation and condensation directly in the alembic in which light fractions have low vapor pressure. Increasing temperature promotes stabilization processes, i.e. dependence on the flow rate is not observed at 473 K due to lower vapor pressure of the factions, as well as increasing their molecular weight. Consequently, a higher temperature in order to intensify the process of evaporation is necessary. The next increase in temperature also leads to equilibrium. Also values of the enthalpy of activation were calculated (Table 2) [6].

From the data in Table 2 shows that the maximum observed for the activation enthalpy flow rate of 0.8 ml/min, i.e. fractional distillation process is almost no oil flows at a given flow rate. This is supported by the fact that in this case the evaporation products of oil condense and form associates with the evaporation products heavier fractions. Minimum value of activation energy is observed at a flow rate of 2.4 i.e. process occurs at maximum speed. Consequently, the separation process is determined by the stability associates forming feedstock. Next IR-spectra of gasoline were obtained (Fig. 1, 2).

Change of the thermodynamic characteristics of catalytic cracking of diesel

T, K	$\Delta H^\ddagger$ , kJ/mol				
	0.8	1.6	2.4	3.2	4.0
443	541.83	59.05	58.93	58.99	59.25
453	541.79	59.01	58.89	58.95	59.21
463	541.74	58.97	58.84	58.91	59.17
473	541.70	58.93	58.8	58.87	59.13
483	541.66	58.89	58.76	58.83	59.09
lnA	309.73	23.57	23.52	23.54	23.65

Figure 1. IR spectrum of gasoline in the frequency range from 400 to 2000  $\text{cm}^{-1}$ Figure 2. IR spectrum of gasoline in the frequency range from 2000 to 3800  $\text{cm}^{-1}$ 

The most important information obtained fractions shown in the absorption region of 800–1850  $\text{cm}^{-1}$ . Strong absorption of below 1850  $\text{cm}^{-1}$  (methylene and methyl groups) indicates a significant amount of the alkyl groups. Also vibrations  $-\text{CH}_3$  and  $-\text{CH}_2$  groups correspond to absorption bands near 1075 and 1150  $\text{cm}^{-1}$  [7]. At the same time, the absorption at 1200  $\text{cm}^{-1}$  relating to aromatic hydrogen, a relatively strong (Fig. 1). Strips of 900–700  $\text{cm}^{-1}$  correspond to the vibrations of the CH bonds of methyl and alkyl groups. Most pronounced band at 870  $\text{cm}^{-1}$  (stretching vibrations C–C in the conformation  $\text{GTn} > 5\text{G}$ ) and peak around 765  $\text{cm}^{-1}$  (stretching vibrations C–C mixed with fan  $-\text{CH}_2$  fluctuations). The strong absorption

in the region of  $3000\text{ cm}^{-1}$  belongs to the aromatic ring (Fig. 2). Strips of  $1280\text{--}1050\text{ cm}^{-1}$  related to the grouping Ar–O ether groups. The band at  $1375\text{ cm}^{-1}$ , apparently, is responsible to carbonyl group.

In general, the results of IR spectral studies show that all fractions of gasoline contain a large amount of aliphatic saturated and unsaturated series of aromatic compounds.

Thus, the optimal parameters of the distillation process is determined; generalized equation, which allows to carry out a qualitative and quantitative forecast of fractions yield any values of the studied parameters, and which opens the possibility of a wide variation in terms of the production of light oil fractions, was obtained.

The rate constants of the distillation process under the impact of the flow rate of raw materials were calculated based on these equations. It is shown that increases the yield of light fractions at a flow rate of  $2.4\text{ ml/min}$ , which promotes more complete separation of the mixture, the absence of accumulation of high boilers in the lighter fractions.

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### References

- 1 *Dobriansky A.F.* Chemistry of oil. — Leningrad: Gostoptekhizdat, 1961. — 320 p.
- 2 *Bogomolov A.* Modern methods of research oils. — Leningrad: Nedra, 1984 — 140 p.
- 3 *Sokolov V.A.* Workshop on chemical technology. — Moscow: Khimiya, 1985 — 78 p.
- 4 *Malyshev V.P.* Mathematical planning of metallurgical and chemical experiment. — Alma-Ata: Nauka, 1977. — 37 p.
- 5 *Panchenkov G.M., Lebedev V.P.* Chemical kinetics and catalysis. — Moscow: Nedra, 1973. — 311 p.
- 6 *Ospanov J.C.* Thermodynamics and kinetics of heterogeneous (non-equilibrium) chemical processes. — Almaty: Complex, 2006. — 328 p.
- 7 *Kazitsyna L.A., Kupletskaya N.B.* Application of UV, IR and NMR spectroscopy in organic chemistry. — M.: Vysshaya Shkola, 1971. — 264 p.

Ш.К.Әмірханова, Р.М.Шляпов, А.С.Уәлі

### Мұнайды айдау процесіндегі ректификациялық бағананың өнімділігіне әр түрлі факторлар әсерін бағалау

Фракциялардың шығымына әсер ететін әрбір фактордың ықпалын сипаттайтын жалпыланған теңдеу алынды. Ректификациялау процесінің оңтайлы параметрлері анықталды, ағын жылдамдығының артуы жылдамдық константаларының жоғарылауына әкелетіні көрсетілді. ИҚ-спектралды зерттеулер нәтижелері бензиннің барлық фракцияларында қаныққан және қанықпаған қатардың алкилді қосылыстарының, ароматты қосылыстардың көп мөлшерін барын көрсетті.

Ш.К.Амерханова, Р.М.Шляпов, А.С.Уали

### Оценка влияния различных факторов на производительность ректификационной колонны в процессе перегонки нефти

Получено обобщенное уравнение, отражающее влияние каждого из факторов на выход фракций. Определены оптимальные параметры процесса ректификации; установлено, что возрастание скорости потока приводит к увеличению констант скоростей. Результаты ИК-спектрального исследования показывают, что все фракции бензина содержат большое количество алкильных соединений насыщенного и ненасыщенного ряда, ароматических соединений.