Restructuring of oil of Zhangurshi deposit

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The article describes the results of applying a new technology of pre-cracking processing of the feedstock. The method was called the cavitation hydrogenation (***CH***) or the restructuring of raw hydrocarbons. The restructuring of hydrocarbon mixtures is illustrated by the example of oil from Zhangursi deposit, one of the Kazakh deposits. The article presents unusually high results of the technology application and describes the development trends of this technology.

(Keywords: oil refining, innovation, cavitation, hydrogenation, hydrocarbon restructuring)

Introduction

Feedstock for oil refining has its own genesis and characteristics. Their transformation requires new approaches to learning process innovation. Therefore, the facilities expands, but with slow evolution of the methodological base. Using traditional notion of feedstock operational transformation slightly "alloying" the variety of methods used but does not brings their radical improvement. With the current state of applied technologies, the development of the world economy is limited by the lack of fundamental knowledge in the physics of matter transformation processes. This, in particular, one could see in the oil refining, although it was previously experience spasmodic development.

Prior Art

Known are close and distant analogues of this technology. To better understand the article, pay attention to publication [5], where the foregoing is fully enough substantiated. There are presented references to more than 2.5 thousand works, which partly reveal the basis of the method. The unsuccessful or ineffective application of cavitation technologies is illustrated by numerous reports, and the most typical ones are listed in publication [6-12],

Features of the investigations and the hardware

The essence of the technology of cavitation hydrogenation (***CH***) is the weakening of intramolecular bonds and in the forced saturation of heavy hydrocarbons with active particles of atomic hydrogen or particles of light hydrogen-containing radicals. These organic compounds are produced by a liquid-phase generator of atomic hydrogen located in a closed reactor of the plant. The reactor operates in three hydrodynamic modes: linear mode, bypass mode and conservative mode.

Fig. 1. Appearance of the laboratory installation "Potok-7M", which was used for the restructuring of Zhangurshi oil.

In the experiments with Zhangurshi oil, linear and bypass modes are used in which oil is pumped into the reactor and saturated with light hydrogen-containing radicals, maintaining the optimum values of the thermodynamic and hydro acoustic parameters (preset values of reactor control parameters) and, at the rate of the process, the processed feedstock is evacuated from the reactor cavity. The oil processed in this way represents the output or refinement product.

From the reactor it enters to a tank, and, from the parallel outlet channel through the manifold, it is taken to a sealed measuring container, closured, labeled and a sample is prepared for further investigation of its physicochemical characteristics. A multibubble cavitation effect is used to process feedstock, which provides a continuous cavitation process (boiling) of feedstock saturated with hydrogen-containing radicals in a limited area of the reactor space, as well as phase transitions (from the liquid state to the vapor-gas bubble state and back).

All these effects are well studied, traceable and registered processes. For each new feedstock, it is necessary to conduct experimental studies of cavitation hydrogenation, analyze the results to determine an area of optimal control parameters and, subsequently, use them as settings for the system of process equipment automatic control.

Figure 1 shows the appearance of the laboratory installation "Potok-7M", which we used to research the restructuring of various feedstock. The installation is transportable. Reactor, pump with electric motor, tools controlling hydrodynamic, acoustic and thermal parameters are disposed in the light tubular frame. Operator's control panel is mounted on the front surface of the installation, and inside of it there is monitoring and control system. Measuring appliance and tools for control and select the processing modes are placed on the surface of the control panel. Power consumption of the installation does not exceed 7 kW. The heating of the reactor and pipe fitting does not exceed 90°C. The pressure in the hydraulic system does not exceed 0.5 MPa. Consumption of feedstock is not more than 22 l/min.

Control system of the installation provides the possibility for changing the technological modes of operation. Two operators manipulate the installation. It is not recommended to displace the installation or operate it outside the laboratory because of the fragility of the equipment elements comprising piezoceramic and elements of microelectronics.

In [5], a description and a list of the operational characteristics of the installations are given, as well as the appearance of some pilot installations of the "Potok" series designed for processing 50, 100, 200 and more cubic meters of feedstock per day. They are capable of increasing the content of light ends up to gas products, as well as realizing nucleon desulfurization or forced isomerization of feedstock as well as task-oriented improving the quality of motor oils. The installation and ***CH*** technology can be used to synthesize unusual inorganic and organic substances, such as NH_3, H_2O_2, H_2O_3 and the like.

Process description

Oil is processed in a toroidal reactor in order to study the influence of process conditions on the oil restructuring indicators. The purpose is to compulsory create (synthesize) new hydrocarbons, which previously were absent in the feedstock. Analysing the processed samples we get information on the transformations in the feedstock that occurred under the influence of hydrogenation and other less significant factors. Here we omit the sequence of operations for controlling the installation in the experiments. The analysis determines the necessary standardized indicators of the feedstock state in normal (laboratory) conditions. The effectiveness of restructuring was determined as the volume ratio of obtained distillates to distillates in feedstock.

Feedstocks

It is known that the feedstock of Zhangurshi deposit provided for experiments possesses a number of remarkable properties. Mangystau sedimentary basin [1 - 4], inclosing Zhangurshi deposit, plays a leading role, supplying almost 30% of Kazakhstan's oil production. Oil deposits of adjacent areas provide extraction of low-sulfur, high-paraffin (from 10 to 20%) and high-tar oils.

Distillate fractions in the group hydrocarbon composition have an exclusively paraffin base. Because of the excessive content of high-molecular paraffinic and naphthenic aromatic compounds (including polycyclic compounds entering in the tarry-asphaltene part of the oil), these oils are highly curing. The content of aromatic hydrocarbons even in highly solidified oil fractions is only 5-7%.

Based on this oil, industrial batches of 100-index base lube oils were obtained. The study of the oil lube fraction showed that the industrial mixture represents valuable feedstock for production of high-index paraffin base lube oils. The oils of Mangyshlak region in Buzachinskiy arch (Tyubezhik, Zhangurshi deposits) obtained from perforation intervals 293-311 m and 445-455 m respectively, contain 0.47-0.52% sulfur, 3.96-9.38% paraffin, and the yield light fractions is 14.79 - 28.08%. According to other sources, the oil of the Zhangurshi deposit, taken from depth 445-455 m of the Albian horizon, is sulfurous, paraffinic and highly resinous. It has a low yield of gasoline fractions and high density 0.922 (0.9218) g/cm^3 or 21.97 (22)°API. The pour point is 10°C, the viscosity is moderate. But according the passport, the viscosity of the oil was estimated at 3277 mm^2/s at 20°C.

High-index (121, 100, 82) lube oils were obtained from Zhangurshi oil. The yield of lube basestock was considerable. The residual lube basestock has a viscosity index 98 and a pour point -11°C. The yield of lube oil is 18.01%. The total yield of distillate and residual lube basestock from this oil is 40.11%. According to the petroleum certificate, the yield of fuel distillates is 6.5% at a temperature of 300°C and 23% at 360°C.

Research results

Because of hurry or for other reasons we were provided with unprepared oil, right from the well. Frankly, because of this we had to "suffer" a lot analyzing the processed products in the conditions of the existing modest laboratory. Instead of short distillation sessions, we expended 4-5 hours for slow warming up each sample and then exposure at the evaporation temperature of water and carbohydrates for their dehydration. In the Engler flask, because of the mixture watering, hydraulic impacts took place, incl. destructive. Only after a long warm-up was it possible to carry out the distillation of samples in accordance with the requirements of GOST 2177-99, variant B.

When making distillation of high-viscosity low-sulfur **watered** oil, we used the technology ***CH*** in the new laboratory installation "Potok-7M". Processed oil samples were placed in measuring containers (8 samples of 0.5 liters). Then, the initial oil and the said 8 samples were distilled in ARN-1M apparatus.

The ***CH*** technology was tested twice under different process conditions by changing the settings of feedstock processing in the reactor. First - during the presentation 18 - 20 July this year, and then recently (23.10.2017). The work was carried out in the day-time and in a continuous mode. The entire test and taking of samples proceeded quickly, about 25 minutes. Modes were retargeted manually on the operator panel in accordance with the prepared experiment plan. Retargeting took several minutes. Then, the installation hydraulic system was rinsed with solvents and dried with gas.

Here basically described is the second test at a "finer" setting-up of the installation elements and subsystems. In the course of these tests, the installation worked stably, satisfactorily, without failures and irregularities. Insufficiencies of arrangement and malfunction were absent.

Analysis of the initial (untreated) oil showed that it contains only 6.5% of distillates being heated to 300°C. Boiling begins at 234°C and complete at 360°C. According the oil certificate, the initial oil totally contains 23% of distillates, but, please note, only when reaching 360°C. This is confirmed by the "Test Report" conducted by the “Saybolt Inspection Services Kazakhstan” laboratory on November 14, 2014. The additional heating of oil in the Engler's flask only by 60°C provided 16.5% of additional yield of distillates and reached a level of 23.0%. Making fractional distillation of the processed oil, we did not reach this temperature because of the limited capabilities of our ARN-1M. This is the clue of the low yield of distillates from the charge stock on our apparatus. As a result of the ***CH***-treatment of the original oil, it acquired completely different properties. It was successfully converted into a mixture of hydrocarbons, which contains a larger number and a wider range of fuel gasoline fractions. The boiling of oil began to occur at lower temperatures. In the first experiment, naphthenic-gasoline fractions began to boil out began to boil in the range (73-170) °C, and in the second experiment, they begin to boil in a more narrow temperature range (69-79.8) °C (naphthene-solvents).

The following figure 2 graphically illustrates the results of the experiment.

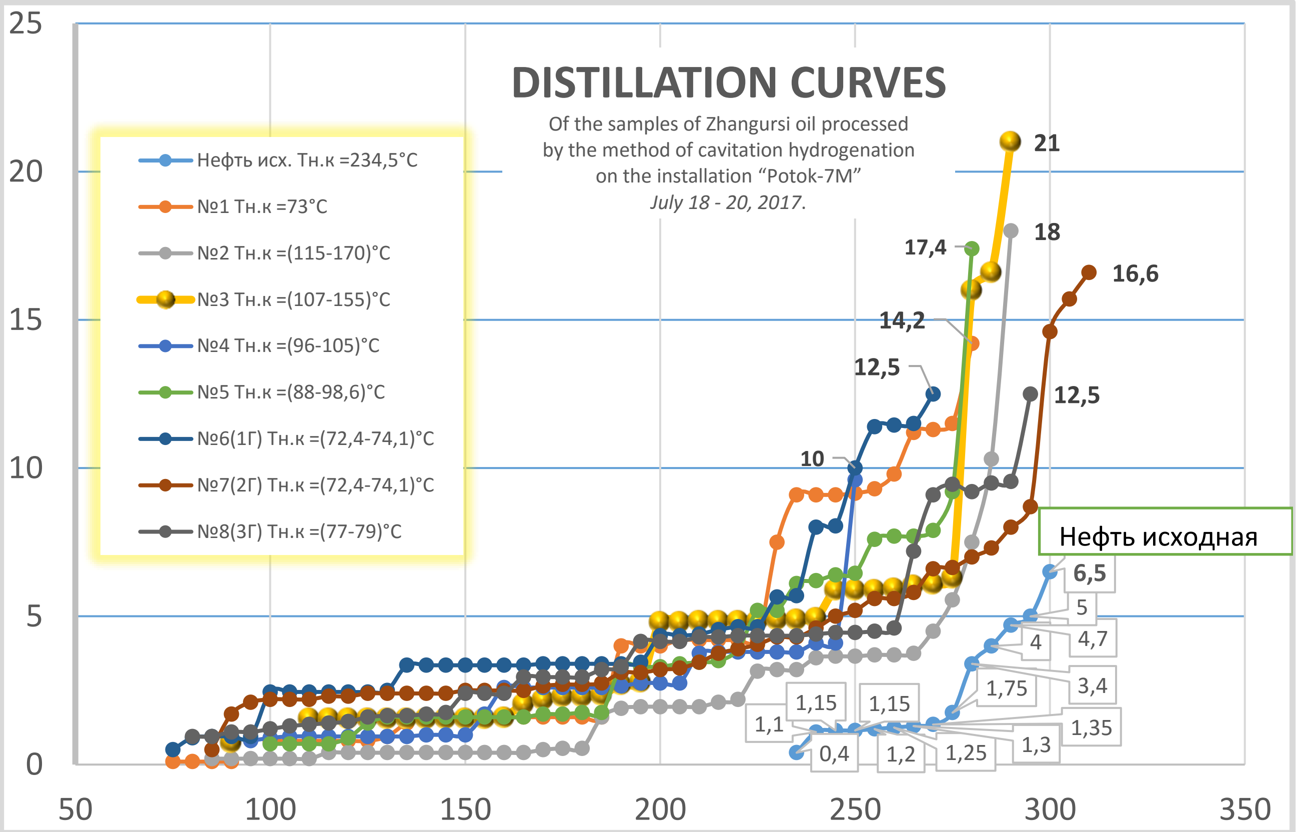

Fig. 2. Oil distillation curves for Zhangurshi deposit oil. Shown are 9 distillation curves of the oil processed by the ***CH*** *method (saturation of feedstock with atomic hydrogen) on the laboratory installation Potok 7M. The experiment was conducted on July 18 - 20, 2017.*

The data of the fractional distillation shown in Fig. 2 are displayed in the form of the following table. The table rows are ordered in the descending distillate content. The highest value of the distillate yield is for sample No. 7. All subsequent samples are demonstrative and correspond to the conditions under which the initial feedstock is restructured and the additional distillates grow up.

Table 1

Test №	T b.b. °C	235°C	240°C	250°C	260°C	270°C	280°C	290°C	300°C	T e.b.	Σ ,%	Δ
7	80-83	4,3	4,6	5,2	5,6	6,6	7	7,3	8,4	311,2	**24,5**	**18**
3	107-155	4,9	4,95	5,9	5,95	6,1	16	16,6		288,6	**21**	**14,5**
2	115 - 170	3,4	3,6	3,7	3,7	4,5	7,5	10,3		285,2	**18**	**11,5**
5	88-98,6	6,1	6,2	6,45	7,7	7,9				275,8	**17,4**	**10,9**
1	97,3-130	9,1	9,1	9,15	9,8	11,2	14,2			278,7	**14,2**	**7,7**
6	72,1-74,1	5,7	8	10	11,45					268,8	**12,5**	**6**
8	77-79	4,35	4,4	4,45	4,6	9,1	9,2	9,5	9,55	290,4	**12,5**	**6**
4	96-105	3,8	4,1	9,6						247,5	**9,6**	**3,5**
Feedstock	230	0,4	1,1	1,15	1,25	1,35	3,4	4,7	6,5	298,3	**6,5**	**0**

1. Blue cells in Table 1 correspond to termination of the process of distillate formation in the samples of processed oil. It is subject to samples No. 3, 2, 5, 1, 6 and 4.
2. This table, as well as the following one, is built on the results of distillation of the samples selected in the first experiment. Here **T** $_{b.b.}$, **T** $_{e.b.}$ - temperatures of the beginning and end of the samples boiling, Σ - total yield of distillates from the sample and Δ - increment of distillates due to using new oil processing technology. And the formula Δ = Σ - **6,5** (where 6,5 is the yield of distillates from the initial oil at 300°C) reflects the effect of the restructuring.
3. The last column of the table shows the values of Δ. By arranging the table rows in Δ descending order, one can see the sequence of the sample numbers for which there was an increase in the volumes of feedstock converted into additional distillates. These are No. 4, 8, 6, 1, 5, 2, 3, 7. For this sequence, also indicative are the increasing boiling temperatures of distillates. From this, one can assume the relationship between the $T_{e.b.}$ and Δ. This supposed dependence can be represented by the following Fig. 3.
4. Samples No. 4, 8, 6, 1, 5, 2, 3, 7 reflect the growth of the volume of additional distillates, as well as the trend of increasing the restructuring coefficient. Due to incorrect choice of the process parameters, there was double decrease in the volume of additional fractions and in the boiling temperatures of these distillates.
5. Sequence of samples Nos. 7, 3, 2, 5, 1, 6, 8, 4 shows the tendency of decrease in the coefficient of oil restructuring due to improperly chosen process conditions. Therefore, the following possible experiments with Zhangurshi oil will require much more and correctly selected process conditions. It would be useful here to apply the methods of planning optimal experiments and other effective technique to improving the coefficient of restructuring and other characteristics of the process.

The same arguments can be applied to analyze the results of fractional distillation at the **second** experiment where we searched for the possibility of Zhangurshi oil restructuring by refining process conditions. First, we give a graph with distillation curves for 8 samples of processed oil and for initial oil.

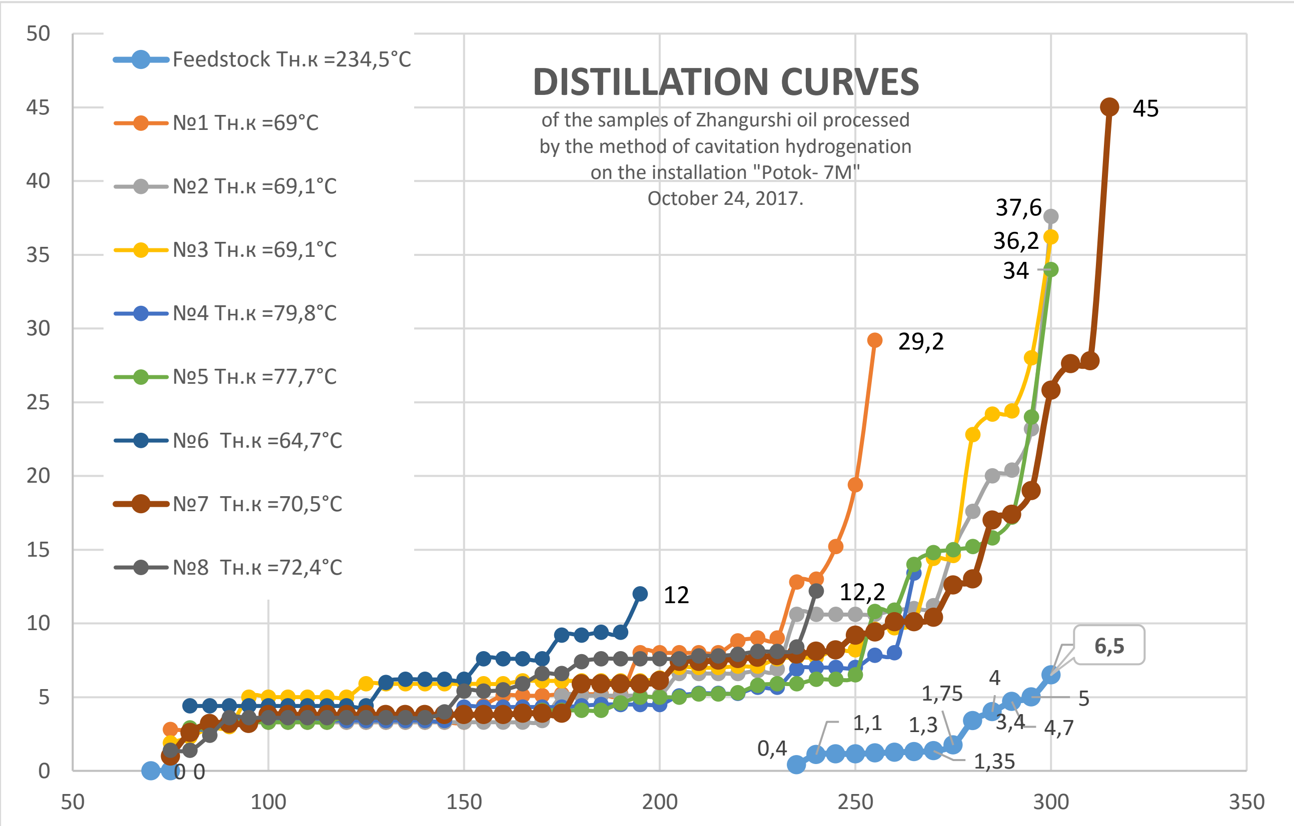

Fig.3. Oil distillation curves for Zhangurshi deposit oil. Shown are 9 curves of oil distillations processed with CG method (saturation of feedstock by atomic hydrogen) on the laboratory installation "Potok 7M". The experiment was carried out on October 23 - 24, 2017.

Here we note some features of the technology, observed in the second experiment. To do this, we plot Table 2 with the distillation data of the corresponding samples. In this case, we order the table rows in descending order of the distillate content.

Tab.2

Test №	T н.к. °C	235°C	240°C	250°C	260°C	270°C	280°C	290°C	300°C	T к.к.	∑ ,%	Δ
7	70,5	3,95	4,05	4,6	5,05	5,2	6,5	8,7	12,9	310	**45,0**	**38,5**
2	69,1	5,3	5,35	5,4	5,45	5,6	8,8	10,2	12,9	301,5	**37,6**	**31,1**
3	68,0	3,85	3,9	4,15	4,85	7,2	11,4	12,2	19,2	302,2	**36,2**	**29,7**
5	77,7	3,0	3,1	3,25	5,45	7,4	7,6	8,6	12,0	298,8	**34,0**	**27,5**
1	69,0	6,4	6,5	9,7	--	-	-	-	-	251,9	**29,2**	**22,7**
4	79,8	4,15	4,2	4,45	4,8	-	-	-	-	262,5	**13,4**	**6,9**
8	72,4	4,2	-	-	-	-	-		-	237,5	**12,2**	**5,7**
6	64,7	-	-	-	-	-	-		-	190,2	**12,0**	**5,5**
. Feed-stock	**230**	**0,4**	**1,1**	**1,15**	**1,25**	**1,35**	**3,4**	**4,7**	**6,5**	**298,3**	**6,5**	**0**

1. Blue cells in Table 2 correspond to absence of boiling of the samples of processed oil. It is subject to samples No. 1, 4, 8 и and 6.
2. The table shows the results of distillation of the samples selected in the second experiment. Here **T** $_{b.b.}$, **T** $_{e.b.}$ - temperatures of the beginning and end of the sample boiling, Σ - total yield of distillates from a sample and **Δ** - increment of distillates due to using new oil processing technology. At that, Δ = Σ - **6,5**, where 6,5 is the yield of distillates from the initial oil at 300°C.
3. Samples No 7, 2, 3 and 5 show not only maximum volume of additional distillates, but also a tendency to reduce the restructuring coefficient. Due to improper choice of parameters, both the volume of additional fractions and the boiling temperature of these distillates are reduced.
4. Samples No 1, 4, 8 and 6 denote a tendency of critical reduction in the oil restructuring ratio due to improperly selected process conditions.
5. Sample No. 6 deserves attention. Boil-off occurred almost in double volume, and the boiling point temperature is the lowest among all the samples - 64.7°C, the end boiling point is 190.2°C. Additional distillates were by nature of naphthenic and gasoline fractions of almost equal volumes, and ligroin fractions were absent. Such unusual combination of operating parameters gave notable results.

It is obvious that both gasoline fractions (in a volume of 8 to 14%) and diesel fuel oil evidently appeared in all formed distillates. They were identified by boiling points as gasoline-kerosene and gas-oil fractions in volumes from 12 to 45%. This means that the cavitation hydrogenation allowed "to create" gasoline-kerosene-diesel fuel fractions in part of the volume of the processed feedstock.

At that, all experiments without exception gave positive results. We received unprecedented data on the influence of atomic hydrogen on the oil. The maximum values of fuel distillate content were: 21% (row No. 3 in experiment No. 1) and 45% (row No. 7 in the second experiment). These are unusual results, which many times exceed all known world achievements in the field of refining technologies. Thus, in the first experiment we succeeded to increase the distillate content by 3,23 times, and in the second one - by 6,92 times. We observed similar result earlier, experimenting with residual fuel M100 from one of Poltava mini refinery on the installation Potok-6 [5]. Then, we succeeded to receive a record transformation of fuel oil to solar oil: 41,3%, instead of routine 5,6%. %. The following diagram in Fig. 4 illustrates the same conclusions, applied to the samples of Zhangurshi oil.

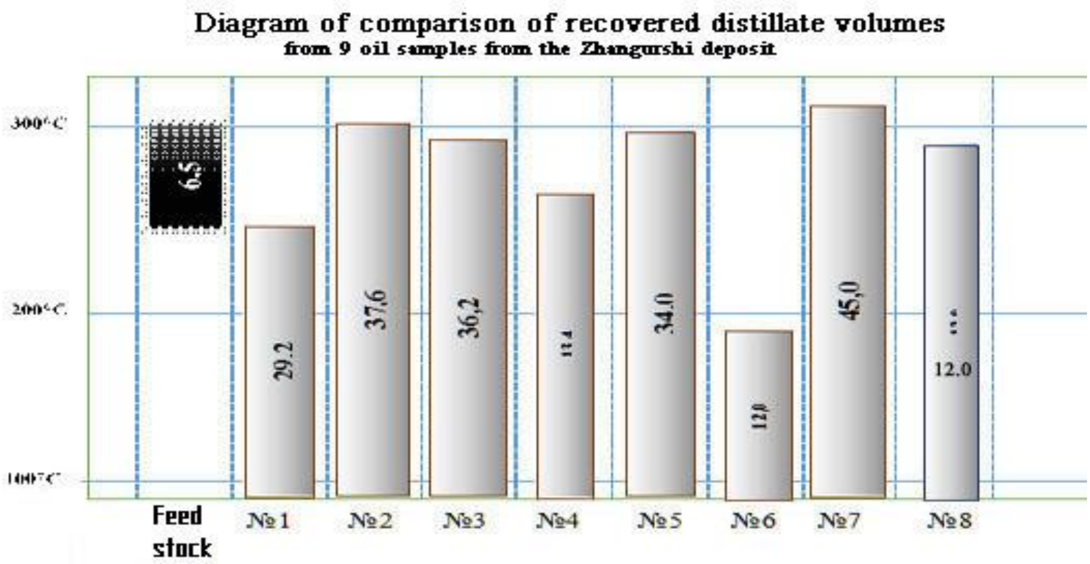

Fig.4. Diagram of comparing the distillate volumes recovered from 9 oil samples of Zhangurshi oil depending on distillate boiling point.

Analysis of tables and obvious conclusions does not pretend to perfection and comprehensive information. The analysis of the effect in question should not be taken as true in the last stage. But one cannot ignore what happened to the oil presented. Surely, the discussed phenomenon does not fit into the framework of traditional oil refining. This is something else.

Conclusions

A. Experiments have shown the effectiveness of the restructuring of high-viscosity Zhangurshi oil. Its properties have radically changed towards light fuel distillates. Instead of the available 6,5% (up to 23%) diesel fuel, we obtained more than 45% of marketable hydrocarbons (naphthene-gasoline-kerosene-diesel fuels).

B. The technology was tested not only for described here oil of 22°API density, but also for heavier mixtures such as residual fuel of 12°API and light oils with a higher °API density. Except for installation "Potok-7M", other installations of the Potok series were tested. In all cases, we succeeded to increase the feedstock restructuring coefficient. In this case, it reached in the first experiment by 3.23 times, and in the second experiment - by 6.92 times. The technology is ready for use in small and large oil-production enterprise and distilleries.

C. Process conditions can be adapted and adjusted to solve a variety of production tasks.

D. In view of simplicity and cheapness of the equipment, the technology can be easily implemented in practice.

I think, nobody surpassed the achievements presented here! No company in the world can now boast of such results. The effectiveness of the conducted transformations of feedstock can be criticized, questioned by reasons of using small amounts of feedstock for experiments or small containers for processed products collection, etc. But I am sure that technological inconveniences can be easily eliminated during pilot industrial experiments.

In addition to the above, I'd like to add some general comments to the text. I am convinced that because of unfinished research and experimental work, additional studies are necessary in order to structurally and parametrically identify statistical models of the process. And on their basis, automated control systems for the processes in the reactor should be developed. Models can be detailed. It is known that the general models of dynamic processes in the reactor are inertial. As a rule, they are represented in the form of systems of integro-differential equations with a system of closing relations, and initial and boundary conditions. These models have a complex dynamics of phase variables, caused by thermodynamic state transitions (vapor ↔ liquid). The dynamics of deterministic models of atomic hydrogen generation and its interaction with hydrocarbons in a multibubble cavitation zone has not been fully studied. There are difficulties with the organization of such works. Therefore, meanwhile, we shall rely on the statistics.

It is necessary to expand the possibilities of the technology application by varying the chemical composition of the used substances. The composition of various substances in the output product can be improved not only by searching for optimal parameters of process conditions, but also by searching for various additives. To optimize the wave characteristics of the cavitation processes in the reactor, one should select and model more diverse active elements stimulating cavitation processes in the reactor cavity. For this, it is necessary to conduct numerous experiments, changing structure elements and regimes, but at the moment there are no means for this. Therefore, to solve these problems of the technology development we shall continue to search for Customers / Partners.

It should be noted a lively interest shown to the new technology by top managers - swindlers from the friendly eastern republic. They were attracted by the novelty, but mostly, by the effectiveness of the method. We realized that they were "biased" when they began to lie about the obvious results. It is clear that falsification of indicators of oil restructuring will not bring them successful business in the field of oil refining. There was a lot of trouble in delivering raw materials, attracting tiny alien funds for the presentations and. But the presentation and discussion of what was seen aroused a natural intrigue. The ambiguity of carrying out generally accepted analyzes and voluntarism in their interpretation aggravated the intrigue. In this connection, we had, ignoring the criticism, to repeat the experiment and get even more interesting results of oil restructuring.

Acknowledgements

I have the pleasure to describe not only technological and other problems, but invigorating facts as well. The incredibly high results of Zhangursi oil restructuring were delivered with constant and incidental help of my near and dear ones, relatives, friends, colleagues, investors, my assistants and schoolers. I am deeply grateful to these people. Exhausting, full of hope, work nonetheless brings its own enjoyment. The products processed with this technology were verified by an independent laboratory, what has excluded all doubts about its effectiveness. It is a pity that the delay in the use of the technology will affect the economy of extracting and processing organizations in different countries.

I am happy with such achievements and admire my assistants, colleagues and friends!

I am very grateful to them for their help and for their deep understanding of the problem.

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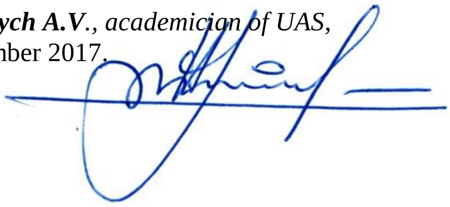

T, °C