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## APPLICATION OF IN-PLASTIC CATALYSIS FOR EXTRACTION OF HARD-TO-RECOVER HYDROCARBONS

*The object of research is the catalytic effect (hydrocracking) for the production of hard-to-recover hydrocarbons, the subject of the study is the change in the physicochemical properties of hydrocarbons by partial gasification, and the lightening of the fractional composition of hydrocarbons. One of the most problematic areas is the lack of studies of the catalytic effect on hard-to-recover hydrocarbons in reservoir conditions. Although processes such as catalytic cracking, reforming, isomerization, aromatization and alkylation of hydrocarbons are known and used in petroleum refining.*

*The research used the methods of scientific knowledge – experiment and measurement. In the course of laboratory work, an effective catalyst was developed, the effect of temperature on the fractional composition and physicochemical properties of oil, oil products and gas condensate was investigated. To simulate formation conditions, hermetic metal retorts were used, in which oil and gas condensate samples were subjected to different temperature regimes. In the process of testing cores saturated with gas condensate, the dependence of filtration on physical parameters – temperature and pressure, fractional composition, specific gravity and viscosity was studied.*

*Laboratory studies have shown a decrease in density and viscosity of hydrocarbons, an increase in core permeability. The effect of catalysis on oil made it possible to increase the volume of light ends distillation from 30 to 60 %, for gas condensate – up to 50 %, which confirms the effectiveness of the method of catalysis of hard-to-recover hydrocarbons. This is due to the fact that the correct formulation and solution of the problem provided adequate results. In contrast to the existing processes of hydrocracking of petroleum products, the proposed method allows you to extract heavy and low-mobile hydrocarbons in reservoir conditions at lower temperatures of 120–150 °C. At the same time, the technology for catalytic hydrogenation of hard-to-recover hydrocarbons will be similar to a typical treatment of a formation with an acid or surfactants. This will make it possible to intensify the commercial reserves of hydrocarbons in the fields that are now classified as hard-to-recover and which account for more than 50 %.*

**Keywords:** *hard-to-recover hydrocarbons, catalytic hydrogenation, hydrocarbon conversion, fractional composition, kinematic viscosity, molecular weight.*

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### 1. Introduction

A significant number of oil and gas fields in the world are characterized as difficult to produce and most of them are not developed. These include high-viscosity, high-bitumen oils and fallen retrograde condensate, which is quite difficult or impossible to remove with modern technology. For example, in Ukraine, geological oil reserves from the category of hard-to-recover reserves are currently estimated at 500 million tons, which is approximately 57 % of all reserves. These oils are mainly associated with a high content of paraffins and asphalt resin components, the amount of which reaches 50 %, which leads to their high viscosity and low filtration properties. Therefore, as a rule, due to the lack of effective technologies, they are little developed, and most are not completion at all. Retrograde gas condensate during the operation of gas condensate fields is also

a significant resource base for heavy production reserves. For example, at the Kotelevske, Tymofiiivske (Poltava region, Ukraine) and Novotroitske (Sumy region, Ukraine) fields, such reserves of stationary condensate amount to more than 10 million tons.

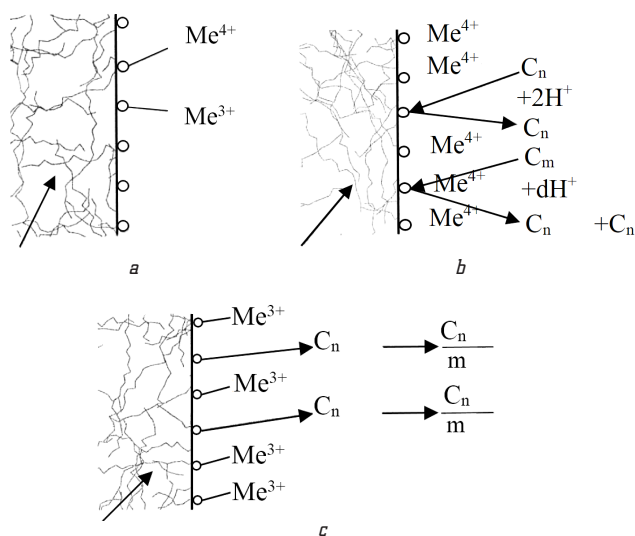
Therefore, the vital task is to involve these deposits in the development by intensifying their production. One of the methods is the method of catalytic action on oil and gas reservoirs. Due to this effect there is a change in the physicochemical properties of hydrocarbons by partial gasification, facilitation of the fractional composition.

### 2. The object of research and its technological audit

*The object of research is the catalytic effect (hydrocracking) for the production of hard-to-recover hydrocarbons.*

Schematic diagram of hydrocracking of hydrocarbons in formation oil and gas conditions (Fig. 1) consists of three stages:

- I – adsorption of catalytically active substance in the porous structure of the formation;
- II – hydrogenation of unsaturated hydrocarbons, asphaltenes, bitumens;
- III – cracking and isomerization of paraffins and aliphatic compounds to obtain low molecular weight hydrocarbons, including gaseous.



**Fig. 1.** Schematic diagram of hydrocracking of hydrocarbons in reservoir oil and gas conditions: *a* – I stage; *b* – II stage; *c* – III stage

One of the most problematic points is that the above hydrocracking scheme is theoretical and has not yet been confirmed by either bench or field research in real formation conditions.

### 3. The aim and objectives of research

The aim of research is to increase the efficiency of extraction and connection to the development of heavy hydrocarbon resources, including retrograde condensate of spent gas condensate fields, by improving the rheological properties of the formation fluid by changing the chemical composition of hydrocarbons.

To achieve the aim of research the following scientific objectives are identified:

1. To develop an effective catalyst.
2. To investigate the change in the properties of hydrocarbons (oil, petroleum products and gas condensate) from thermobaric conditions and the catalyst.

### 4. Research of existing solution to the problem

Catalysis is the most effective and rational means of accelerating chemical processes. Many methods of oil refining are based on the use of catalysts: catalytic cracking, reforming, isomerization, aromatization and alkylation of hydrocarbons [1, 2]. Catalysts contain Cr, Fe, Co, Ni and other transition metals. They are elements with variable valence, and the transitions between different valence states are relatively easy. Related to this is the fact that oxides

and salts of these elements, especially Cr and Ni, are among the thermal catalysts for both homo- and heterogeneous processes of hydrogenation and cracking of hydrocarbon compounds [3]. The application of Nickel on  $Al_2O_3 \cdot SiO_2$  and other aluminosilicates (analogue may be formation rocks) significantly reduces the cracking temperature of various hydrocarbons. Therefore, nickel is often used as a component of catalysts for destructive hydrogenation and hydrogenolysis by C–C bond [4].

There is ground catalysis, which is used in refineries and which takes place at elevated temperatures – hydrocracking. Hydrocracking at temperatures of 170–280 °C on bifunctional catalysts (with acidic and hydrogenating properties) without coke formation produces products similar to catalytic cracking products. These products are less flavored, purified from heteroatoms (S, N, O) and do not contain large amounts of unsaturated hydrocarbons [5, 6].

An example of these processes are the following reactions:

- conversion reaction of heavy petroleum hydrocarbons ( $C_{22}–C_{41}$ ) using the viscosity of the catalyst of an alcoholic solution of  $MnCl_2$  or  $KMnO_4$ ; the result is a composition of hydrocarbons  $C_6–C_{16}$ , the process temperature in the range of 120–135 °C;
- gas oil dewaxing reaction (fractions 230–300 °C); product hydrogenesis (fractions 120–200 °C); catalyst – cobalt-aluminum-molybdenum (40 bar, yield – up to 80 % by weight) [7];
- destructive hydrogenation and hydrogenolysis with C–C bond break: hexomethyl cyclohexane NiS (5.3 % Ni) on aluminosilicate (contains 10 %  $Al_2O_3$ ),  $P_H=82$  bar, conversion of 87.5 %. The product contains  $C_3–C_7$  alkanes [8];
- reaction of processing of complex technical raw materials (desalination of oil) – at the exit products of destructive hydrogenation  $C_1–C_{16}$ ; catalyst – 5 % solution of  $NiCl_2$  in alcohol  $C_3H_7OH$ , the process is carried out at temperatures of 100–200 °C [9];
- coal, tar or heavy petroleum gas oils – at the yield  $C_1–C_6$ , gasoline fractions  $C_7–C_{14}$ , the process is carried out on a NiS catalyst, the temperature of hydrogenation reactions 150–250 °C [10].

In the formation catalysis takes place at temperatures of 100–200 °C. The working reactor is an oil and gas reservoir, which is saturated with heavy hydrocarbons ( $C_5$  and above), which break down into smaller ones. In a porous medium, they are destructed.

Thus, the results of the analysis of the hydrocracking process allow us to conclude that in order to convert hydrocarbons by chemical composition (increase in light compounds) to enhance their extraction from oil and gas condensate fields, which contain high paraffin, high bitumen compounds, it is possible intralayer catalysis.

### 5. Methods of research

The essence of the method is that the productive layer is treated with a catalytically active mixture, a thermal effect on the layer at a temperature of 120–150 °C is created to emit autocatalysis of hydrocarbon molecules into radicals and their subsequent recombination, disproportionation, substitution and isomerization. As a result of these processes, simple hydrocarbons such as alkanes  $C_1–C_4$  appear in the formation fluids, the yield of light gasoline fractions  $C_6–C_{10}$  and more mobile fractions of

light gas oil C<sub>11</sub>–C<sub>16</sub> increases. The fractional composition of hydrocarbons changes, density, dynamic viscosity, average molecular weight decrease. There is an increase in the permeability of hydrocarbons due to changes in the chemical composition, which in reservoir conditions will lead to an increase in the flow of oil and gas condensate wells while improving the composition of hydrocarbons. The proposed method differs from classical cracking in that the processes of hydrogenation and cracking occur exclusively in the liquid phase with the use of a hydrogen donor; that is, the use of hydrogen gas and associated high pressures (up to 25 MPa) is excluded.

## 6. Research results

In the course of laboratory research, a catalyst was developed, which is a mineral porous structure with pore sizes of 0.5–1.8 μm (channels mainly capillary type), modified with acid and hydrogenating elements, which to some extent mimics a productive reservoir with a porosity coefficient of 2.5–3.5 %.

A formulation of a hydrogen donor has been developed, which allows to provide the process of preliminary hydrogenation of heterogeneous compounds (resins and asphaltenes) with atomic water without the use of its atomic form.

In order to determine the influence of the composition of hydrocarbons on the depth and efficiency of hydrogenation processes, oil samples of the Ashtanske (Crimea), Seliukhivske and Yablunivske fields (Poltava region, Ukraine), liquid samples of pyrolysis processes of rubber waste, petrolatum produced by Ukratnafta (Kyiv, Ukraine) were used. The research results are presented in Table 1.

From the results presented in Table 1, it is seen that the processes of transformation of hydrocarbons occur with varying degrees of hydrogenation destruction in almost all cases.

The fractional composition of hydrocarbon samples changes (in the direction of relief), the density, kinematic viscosity decreases, the total volume of the distilled sample increases at distillation temperatures up to 370 °C. That is, all this indicates that in the microporous projector of the catalytically active material, processes similar to hydrogenation cracking, which is used in oil refining.

A number of studies have been conducted in conditions close to reservoirs. For this purpose, sealed metal retorts at different temperatures were used. The results of these studies are presented in Table 2.

In the course of research, it was found that up to 50 % of the raw material is the gas phase, and the liquid formed was 50–60 % of the initial sample volume.

Based on the obtained previous laboratory studies, it was found that the best in its activity is a catalytic mixture of metal salts of amphoteric groups. The process temperature is determined by the activity of the catalytic mixture and for its various ratios of these metals is in the wide range from 90 to 200 °C. The Mo catalyst on halogenated zeolite type U is effective in the temperature range from 120 to 170 °C. The catalyst with the new formulation shows its activity starting from 90 °C, at 150 °C the stage of stable autocatalysis is observed. Liquid catalysts show their activity in the same temperature range, but without a solid carrier – zeolite type U. Conversion of hydrocarbons by their catalysis is manifested in the facilitation of fractional composition, reducing density, and increasing the formed gaseous products of the process.

**Table 1**

The results of studies of the hydrogenation processes influence on the fractional composition and physicochemical properties of oil samples and waste oil products

Fractional composition		Density, g/cm <sup>3</sup> (before/after)	Viscosity, mm <sup>2</sup> /s (before/after)	Total volume distilled sample, % vol. (before/after)	Flash point in an open crucible, °C (before/after)
% vol.	°C (before/after)				
Oil of the Ashtanske field					
BB*	60/59	0.917/0.876	70/27	39/63	17.2/15.5
10	122/134				
20	189/176				
30	273/195				
40	342/210				
50	–/235				
60	–/255				
70	–/–				
80	–/–				
90	–/–				
EB*	342/257				
Oil of the Seliukhivske field					
BB	42/37	0.880/0.867	54/22	43/42	15.5/14.9
10	85/81				
20	195/158				
30	268/242				
40	315/275				
50	–/297				
60	–/319				
70	–/335				
80	–/–				
90	–/–				
EB	324/344				
Oil of the Yablunivske field					
BB	35/38	0.893/0.868	61/31	46/74	16.2/16.7
10	84/82				
20	183/154				
30	235/203				
40	312/257				
50	–/295				
60	–/324				
70	–/343				
80	–/–				
90	–/–				
EB	331/362				
The product of pyrolysis of tire waste					
BB	89/85	0.914/0.897	48/35	93/97	59/55
10	132/124				
20	205/192				
30	242/223				
40	258/247				
50	274/268				
60	297/289				
70	317/305				
80	–/321				
90	360/–				
EB	368/345				
Petrolatum selective purification of oils					
BB	229/168	0.885/0.861	102/27	8/43	235/75
10	>370/210				
20	–/254				
30	–/283				
40	–/331				
50	–/–				
60	–/–				
70	–/–				
80	–/–				
90	–/–				
EB	–/354				

**Note:** \* BB – the beginning of boiling; EB – the end of boiling

Table 2

Changing the properties of hydrocarbons from thermobaric conditions close to formation

Fractional composition		Density, g/cm <sup>3</sup>	Viscosity, mm <sup>2</sup> /s	Total volume distilled sample, % vol.	Molecular weight
% vol.	°C				
<i>Stabilized oil of the Matviyivsko-Legedovske field (Poltava region, Ukraine)</i>					
BB*	94	0.830	8.42	63	374
50	290				
63	325				
EB*	380				
<i>Matviyivsko-Legedovske oil treated with a liquid catalytically active mixture in a sealed retort at 130 °C</i>					
BB	75	0.780	1.80	90	262
50	150				
80	265				
EB	285				
<i>Matviyivsko-Legedovske oil treated with a liquid catalytically active mixture in a sealed retort at 150 °C</i>					
BB	50	0.760	0.94	93	244
50	132				
90	202				
EB	263				
<i>Stabilized gas condensate of Bobrytsky gas condensate field (Poltava region, Ukraine)</i>					
BB	60	0.774	5.53	92	276
50	148				
90	284				
EB	307				
<i>Bobrytsky gas condensate treated with a liquid catalytically active mixture in a sealed retort at 130 °C</i>					
BB	41	0.745	1.12	95	202
50	110				
90	172				
EB	246				
<i>Bobrytsky gas condensate treated with a liquid catalytically active mixture in a sealed retort at 150 °C</i>					
BB	37	0.739	1.02	97	185
50	104				
90	163				
EB	224				

Note: \* BB – the beginning of boiling; EB – the end of boiling

Data from laboratory studies on samples of natural core from the Zagorianske gas condensate field (Poltava region, Ukraine), which was treated with hydrocarbon material and aqueous solution of bifunctional catalytic mixture, and with the introduction of the promoter (2.5 % of the sample volume) are presented in Table 3.

The dependence of filtration on physical parameters – temperature and pressure, fractional composition, specific gravity and viscosity – was studied.

On samples of natural core untreated with catalytically active liquid and promoter, the properties of the condensate do not change under the same conditions ( $t$ ,  $p$ ). In experiments where the core sample was treated with a catalyst without the introduction of a hydrogen formation promoter, the properties of the condensate changed insignificantly, and in experiments with the introduction of a promoter such properties as fractional composition, density, molecular weight and permeability changed dramatically.

Table 3

The results of laboratory tests of the catalytic method of extraction of hydrocarbons

Fractional composition		Density, g/cm <sup>3</sup>	Viscosity, mm <sup>2</sup> /s	Total volume distilled sample, % vol.	Molecular weight	Permeability, mD
% vol.	°C					
<i>Condensate, well No. 3, <math>t=120</math> °C, <math>p=7.3</math> MPa. Sample of natural core, porosity – 15 % vol.</i>						
BB	72	0.829	42	90	249	2.76
50.0	170					
90.0	297					
EB	303					
<i>Condensate, well No. 3, <math>t=120</math> °C, <math>p=7.3</math> MPa. Sample of natural core treated with catalytically active liquid, porosity – 15 % vol.</i>						
BB	60	0.825	34	90	173	7.54
50.0	164					
90.0	282					
EB	287					
<i>Condensate, well No. 3, <math>t=120</math> °C, <math>p=7.3</math> MPa. Sample of natural core treated with catalytically active liquid, promoter supplement, porosity – 15 % vol.</i>						
BB	47	0.812	17	96	104	40.35
50.0	126					
90.0	249					
EB	261					
<i>Condensate, well No. 3, <math>t=150</math> °C, <math>p=7.3</math> MPa. Sample of natural core, porosity – 15 % vol.</i>						
BB	72	0.829	43	89	252	2.19
50.0	170					
90.0	297					
EB	302					
<i>Condensate, well No. 3, <math>t=150</math> °C, <math>p=7.3</math> MPa. Sample of natural core treated with catalytically active liquid, porosity – 15 % vol.</i>						
BB	56	0.823	34	90	169	8.04
50.0	154					
90.0	280					
EB	285					
<i>Condensate, well No. 3, <math>t=150</math> °C, <math>p=7.3</math> MPa. Sample of natural core treated with catalytically active liquid, promoter supplement, porosity – 15 % vol.</i>						
BB	43	0.81	15	96	94	42.64
50.0	121					
90.0	247					
EB	257					
<i>Condensate, well No. 3, <math>t=200</math> °C, <math>p=7.3</math> MPa. Sample of natural core, porosity – 15 % vol.</i>						
BB	70	0.822	40	90	235	2.75
50.0	168					
90.0	293					
EB	296					
<i>Condensate, well No. 3, <math>t=200</math> °C, <math>p=7.3</math> MPa. Sample of natural core treated with catalytically active liquid, porosity – 15 % vol.</i>						
BB	51	0.815	23	95	114	38.10
50.0	149					
90.0	277					
EB	292					
<i>Condensate, well No. 3, <math>t=200</math> °C, <math>p=7.3</math> MPa. Sample of natural core treated with catalytically active liquid, promoter supplement, porosity – 15 % vol.</i>						
BB	27	0.798	11	98	78	100.25
50.0	139					
90.0	266					
EB	275					

## 7. SWOT analysis of research results

**Strengths.** The technology of catalytic hydrogenation of hard-to-recover deposits in the well will be similar to the typical treatment with acid, surfactant and thermochemical. It requires a minimum number of technical means and staff. The chemical reagents that make up the solutions are available in Ukraine.

**Weaknesses.** The weaknesses of this study are that there are currently no bench trials to simulate reservoir filtration conditions for hard-to-recover hydrocarbons.

**Opportunities.** Potential for the application of the method may be fields with hard-to-recover hydrocarbon reserves, the production of industrial inflow from which through the use of other technologies are impractical from an economic point of view. In particular, Yablunivske, Chutivske (Dnipro-Donetsk basin) and a number of fields in Western Ukraine can be potential for the application of the method in Ukraine.

**Threats.** The proposed method of extraction of difficult-to-produce hydrocarbons has not yet been implemented in industrial conditions, and therefore there are risks of obtaining a different picture of hydrocarbon conversion during hydrocracking and different properties of hydrocarbons compared to laboratory tests.

## 8. Conclusions

1. Studies show that improvement of hydrocarbon filtration after treatment is observed in all cases (high-tar and bituminous oil, high-viscosity oil, high-paraffinic and retrograde condensate, etc.). For example, as a result of hydrogenation in the oil of the Yablunovske field (Poltava region, Ukraine), the following properties improved: the density decreased from 0.893 to 0.868 g/cm<sup>3</sup>, the viscosity decreased from 61 to 31 mm<sup>2</sup>/s; the volume of light hydrocarbons increased from 46 to 74 % vol. When studying the effect of temperature on oil and gas condensate in metal retorts, it was found that up to 50 % of the gas phase can be removed from the initial liquid. This suggests that the application of in-reservoir catalysis to wells that have opened deposits with substandard oil will help to obtain industrial inflows from them.

2. The application of this method of intensification of the inflow of heavy oil and retrograde condensate, depending on the physicochemical properties of the formation and fluid, will significantly increase the existing flow rates and connect the operation of the formation, which is not currently being developed.

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