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Hydrocracking of Highly Paraffinic Gas Condensate Residues

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Abstract

One of the possible variants of rational processing highly paraffinic gas condensate residues (HPGCR) with the maximum yield of low-sulphur medium-distillate fractions, *i.e.* hydrocracking in a fixed catalyst bed, was considered. Experiments were carried using a flow through plant. Home-made catalysts, such as KNT-442MNi (hydrorefining catalyst) and KNT-442NiY (hydrocracking catalyst) manufactured at the LLC Ishimbayskiy SKhZK, were used. Process temperature that ensures the maximum yield of diesel fraction was pre-selected. Considering the unique composition of HPGCR, the hydrocracking of initial raw materials, and also 350+ °C and 350–500 °C fractions, was investigated without their pre-preparation. As demonstrated by analysis of diesel fractions of hydrocracking products (180–350 °C), various variants of raw materials, regardless of their fractional composition and recirculation of residues, their key parameters meet the requirements for the commercial diesel fuel of environmental K-5 class. At the same time, regardless of the quality of initial raw materials, the products from variants with the recirculation of residues have somewhat improved characteristics. As demonstrated by analysis results for gasoline fractions (IBP – 180 °C), products have similar characteristics, regardless of the composition of initial raw materials and the residue recirculation mode. These fractions do not require preliminary hydroforming and may be directed to isomerisation and reforming plants. Among the variants considered, the hydrocracking of the initial HPGCR ensuring the maximum yield of diesel fraction and not requiring the preliminary fractionation of initial raw materials and the secondary processing of the primary distillate fractions and the residue is preferable.

Key words: fuel environmental indicators, gas condensate, hydrocracking, catalyst, highly paraffinic gas condensate residues, hydroforming

INTRODUCTION

The improvement of environmental indicators of engine fuels and the deepening of oil refining are the major trends that determine the development of the modern world and domestic oil processing. Highly paraffinic gas condensate residues (HPGCR) are prevailing in the total volume of processing for a number of companies in our country. Unlike traditional residues of oil origin, little attention has been paid to selection issues of the efficient processing of gas condensate ones.

Among likely variants of processing oil residues, the hydrocracking process that allows producing low molecular weight products upon insignificant coke yields is of greatest interest. The use of hydrocracking technology facilitates a significant increase in the yield of light oil products upon heavy oil and gas residues, and also heavy gas oils processing and guarantees the maximum output of diesel fraction, with good quality indicators that meet modern environmental requirements.

TABLE 1

Physicochemical properties of highly paraffinic gas condensate residues (HPGCR) and their fractions

Indicator	Method	HPGCR	Fraction of HPGCR	
			350+ °C	350–500 °C
Density at 20 °C, kg/m^3	GOST 3900–85	850.7	905.4	838.4
Kinematic viscosity at 50 °C, Ost,	GOST 33–2000	7.24	26.87	16.17
Chilling temperature, °C	GOST 20287–91	+26	+37	+33
Water content, mass %	GOST 2477–65	Traces	Traces	Traces
Total sulphur content, mass % (mg/kg)	GOST P 51947–2002	0.089 (890)	0.123 (1230)	0.112 (1120)
Metal content, ppm by weight				
Fe	MARK Spectroscopy		Traces	Traces
Pb				
Ni				
Mn				
V		~1	~(1–2)	~1
Zn		Traces	Traces	Traces
Mechanical impurities content, mass %	GOST 6370–83	0.090	0.12	0.1
Chlorine salts content, ppm	GOST 21534–76	47	–	–
Cokeability, mass %	GOST 19932–99	0.2	1.0	0.3

TABLE 2

Fractional HPGCR composition (GOST 2177–99)

Fraction, vol. %	Temperature, °C
IBP	127.3
10	228.8
20	284.3
30	316.5
40	341.9
50	361.0
60	375.7
70	389.2
80	389.2
85	388.1

TABLE 3

Fractional HPGCR composition (GOST 11011–85)

Fraction, mass %	Temperature, °C	
	Fraction 350+ °C	Fraction 500+ °C
IBP	347	348
10	358	367
20	372	377
30	395	394
40	418	422
50	424	431
60	438	439
70	443	446
80	481	455
90	513	470
98	-570	495

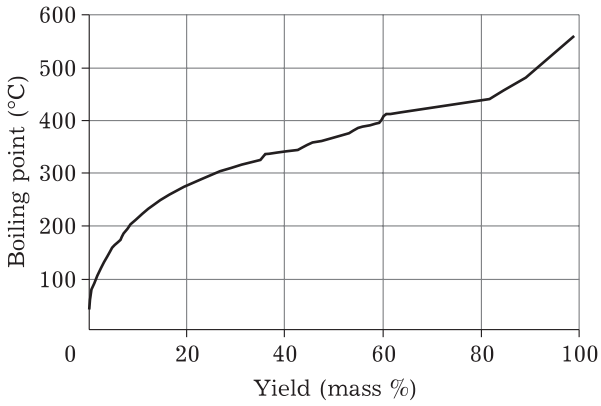
HYDROCRACKING OF HIGHLY PARAFFINIC GAS CONDENSATE RESIDUES

Table 1 gives the physicochemical properties of a standard sample of HPGCR and their fractions. Figure 1 presents a true boiling point (TBP) curve for the initial sample. It can be seen (see Table 1) that HPGCR and their fractions differ from similar portions of oil origin by a much lower content of heavy metals, sulphur, and a high chilling temperature. High contents of light fractions in HPGCR should also be noted: the total content of those boiling out before 360 °C, for example, is 44.4 mass % (Tables 2 and 3).

Table 4 presents the group hydrocarbon composition of the residue and its fractions. For comparison purposes, similar indicators for the vacuum gas oil of West Siberian oil that is one of the common similar fractions of oil origin are listed here too. Thus, for example, the content of paraffin-naphthene hydrocarbons in the 350–500 °C HPGCR fraction is more than twice higher than that in a similar portion of West Siberian oil, whereas the concentration of arene compounds is 2.5–5 times lower.

Owing to the flexibility of the process and an opportunity to produce a wide variety of high-quality and highly liquid oil products, hydrocracking is currently one of the dynamically developing processes of residue processing [1, 2].

Various procedures for hydrocracking of oil residues have been implemented in modern oil processing. According to the type of the reactors



Fraction yield, mass %:

< 180 °C	6.5	
180–270 °C	10.9	37.9
270–360 °C	27.0	
360–420 °C	15.6	44.4
420–500 °C	28.8	
500+ °C	11.2	

Fig. 1. True boiling point (TBP) curve for GC.

used, there distinguish the following varieties of the process: in fixed, moving, fluidized, and suspension catalyst beds. Selecting process type mainly depends on the content of metals and asphaltenes in raw materials. For example, depending on the content of metals (Ni + V), the authors of [2] recommend the following process parameters: 200–250, 50–400, 100–600, and 300 g/t and higher for fixed, moving, fluidized, and suspension catalyst beds, respectively. Various variants of pre-demetallization of raw materials have been suggested [5, 6] in addition to a suspension layer [3, 4] upon high contents of metals.

The layer-by-layer loading of the catalyst is also recommended for a process with a fixed bed of a catalyst depending on the contents of metals. For example, upon the metals content below 25 g/t, it is recommended to use narrow pore catalysts with high activities, upon metal content of 25–50 g/t; a two-layer catalyst bed with a catalyst that has a good resistance towards metal deposition located in the front layer of the bed should be used. In order to process raw materials with a metals content of 50–100 g/t, it is recommended to use a three-layer system with a highly metal-resistant hydrodemetallization catalyst located in the front protective layer.

Considering peculiarities of the examined raw materials, the research paper considered a variant of hydrocracking HPGCR with a fixed bed of the catalyst. The process was carried out using a pilot plant designed to investigate processes that proceed under elevated pressure conditions, in the flowing mode, at a maximum pressure of 20 MPa and a temperature of 650 °C. The maximum volume of the reactor is 450 cm^3. The manufacturer is RTI Engineering Co. (South Korea).

Domestic catalysts for hydrogenation processes (KNT-442MNi hydrotreatment catalyst and KNT-442NiY hydrocracking catalyst) were used in the process. Catalyst loading was carried out layer by layer: hydrotreatment catalyst volume of 200.0 cm^3, hydrocracking catalyst volume of 100.0 cm^3. An inert material with a volume of 50 cm^3 was loaded from the bottom and at the top of catalytic layers. Preliminary sulphidation of the catalyst was carried out with dimethyl sulphide.

One of the determining factors of the hydrocracking process is temperature, therefore the value, upon which the maximum yield of diesel fraction was reached, was selected. The reactor pressure, volume feed rate, and a circulation ratio of VSG were 10 MPa, 0.65 h^{-1}, and 1100, respec-

TABLE 4

Group hydrocarbon composition of HPGCR, their fractions and vacuum gasoil of West Siberian oil, mass %

Moieties	HPGCR, 180+ °C	HPGCR fraction, °C			350–500 °C fraction of West Siberian oil
		350–500	350+	500+	
Paraffin-naphthenic					
Low-molecular-weight arenes	79.4	83.1	76.6	56.8	50.1
Medium-molecular-weight arenes	4.7	6.9	6.8	18.4	16.8
High-molecular-weight arenes	4.5	2.3	4.3	4.6	11.3
Resins I	1.7	0.8	1.5	2.3	1.1
Resins II	2.7	1.7	2.6	2.8	2.2
In total	100	100	100	100	100

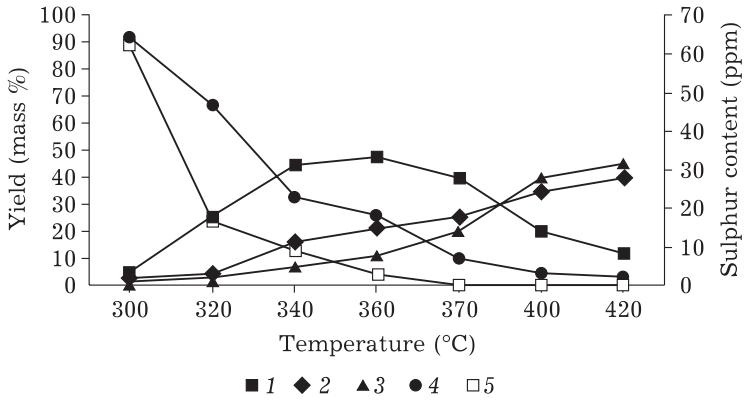


Fig. 2. Yields of products (1–4) and sulphur content in diesel fraction *vs* temperature, *T*, °C: 180–350 (*1*), IBP 180 (*2*), C1–C4 (*3*), 350+ (*4*), 180–350 (*5*).

tively. The taking of regime samples was carried out every 2 h followed by averaging values of their indicators.

Figure 2 presents the yields of the main products of the process and sulphur content in diesel fraction *vs* process temperature. It can be seen that there is a maximum yield of diesel fraction (47 mass %) at 360 °C. Upon higher temperatures, the yield is reduced; the yields of gases and gasoline are increased due to secondary reactions of cracking. It is worth noting that already at temperatures above 340 °C, the sulphur content in diesel fraction meets the requirements of Euro-5 (below 10 ppm by weight).

Although the majority of hydrocracking plants with a fixed catalyst layer operate using distillate (straight-run gas oil fractions), coking and catalytic cracking gas oils (350–500 °C factions) or residual raw materials of their corresponding preparation (deasphaltizing, demetallization, *etc.*), the research on hydrocracking of initial raw materials and the 350+ °C fraction was carried out without their preparation. Table 5 gives the material balance of the hydrocracking process using various types of raw materials.

As demonstrated by analysis of 180–350 °C diesel fractions produced using hydrocracking of various types of raw materials, regardless of their fractional composition and residue recirculation, the former correspond to regulations imposed on commercial diesel fuels of K-5 environmental class according to key indicators (Table 6). At the same time, products of variants with residue recirculation are characterised by somewhat improved indicators regardless of the quality of initial raw materials.

Diesel fuel was produced by HPGCR hydrocracking during research; the 140–320 °C fraction was isolated and compared it with diesel winter fuel in the major indicators according to GOST 305–2013. The yields of products were 49.51 mass % upon the variant of work for passage and 56.08 mass % when working with hydrocracking residue recirculation.

Table 7 gives the main characteristics of the fraction obtained compared to regulations ac-

TABLE 5
Mass balance of the hydrocracking process for raw materials of various types (yield, mass %)

Products	HPGCR		HPGCR fraction 350+ °C		HPGCR fraction 350–500 °C	
	For passage	For residue recycling	For passage	For residue recycling	For passage	For residue recycling
C_1	0.23	0.28	0.21	0.32	0.29	0.33
C_2	0.49	0.64	0.38	0.71	0.46	0.76
C_3	1.29	1.67	1.19	1.62	1.71	1.91
i-C_4	1.95	2.11	1.46	1.88	2.32	2.45
n-C_4	2.28	2.78	2.10	2.61	2.12	2.68
Gasoline fraction (<180 °C)	15.50	17.72	15.36	17.66	16.10	19.10
Diesel fraction (180–350 °C)	59.86	67.68	46.80	66.80	43.90	66.47
Residual fraction 350+ °C	18.40	7.12	32.50	8.40	33.10	6.30
Total	100.00	100.00	100.00	100.00	100.00	100.00

TABLE 6

Characteristics of diesel fractions of hydrocracking

Indicator	Standards for K5 class	GC		GC fraction 350 °C+		GC fraction 350–500 °C	
		For passage	With recycling	For passage	With recycling	For passage	With recycling
Density at 20 °C, g/mL	820–845	0.823	0.820	0.827	0.825	0.822	0.821
Content of total sulphur, mg/kg, not more than	10	6.0	3.0	8.0	2.0	3.0	1.0
Viscosity at 20 °C, mm^2/s	2.0–4.5	5.1	4.2	5.4	4.3	4.8	4.1
Flash point, °C, not less than	55	62	63	61	62	62	64
Chilling temperature, °C		−18	−30	−21	−31	−25	−34
Volume fraction of aromatic hydrocarbons, %, not more than	11	16	9	12	8	11	6
Content of mercaptan sulphur, %	–	–	–	–	–	–	–
Fractional composition:							
IBP		165	168	169	171	166	172
50 mass %		258	251	255	261	269	252
95 mass %		349	350	352	352	354	348
FBP		357	361	357	359	360	356

cording to the standard. It can be seen that 140–320 °C fractions of HPGCR hydrocracking correspond to GOST 305 – 2013 regulations of DT winter grade according to key indicators.

As demonstrated by the analytical result for gasoline fractions, regardless of the composition of initial raw materials, and also in passage mode or residue recirculation, products are characterised by similar indicators. These fractions may be forwarded to isomerization and reforming plants; moreover, they do not require pre-hydroforming.

As it follows from Table 6 data, the hydrocracking variant of total HPGCR is most desirable, making it possible to produce as high as 67.68 mass % of the product (or to 56.68 mass % of winter DT); herewith, the product is completely processed without pre-fractionation.

The yield of diesel fraction when processing the residual 350+ °C fraction HPGCR is somewhat lower; at the same time, its higher total conversion is reached. It is worth noting that this variant requires the pre-fractionation of raw materials using

TABLE 7

Characteristics of 140–320 °C diesel fractions

Indicator	GC		Standard for winter DF (GOST 305–2013)
	For passage	With recycling	
Density at 15 °C, kg/m^3	813.0	811.0	Not more than 843.4
Content of total sulphur, mg/kg, not more than	4.0	2.0	Not more than 10
Viscosity at 20 °C, mm^2/s	3.1	3.3	1.8–5.0
Flash point, °C, not less than	42	43	Not lower than 30
Cloud point temperature, °C	−28	−31	Not specified
Filterability limit temperature, °C	−39	−41	Not higher than minus 35
PAH mass fraction, mass % (GOST 32511–2013)	4	2	Not more than 8
Fractional composition, mass %:			
50	228	231	Not higher than 280
95	319	322	Not higher than 360

an atmospheric distillation unit and the solution of the issue regarding the secondary processing of the gasoline fraction, and also hydrotreatment and deparaffinization of diesel fractions.

The hydrocracking variant of the 350–500 °C fraction of HPGCR requires the pre-fractionation of raw materials using an atmospheric and vacuum distillation unit and the secondary processing of distillate fractions and the residue.

CONCLUSION

Thus, as demonstrated by integrated research, the most efficient variant of highly paraffinic gas condensate residues (HPGCR) processing is the hydrocracking process. In our view, hydrocracking of the initial HPGCR is most preferable, ensuring the maximum yield of diesel fraction with improved environmental indicators and not requiring pre-fractioning the initial raw materials and the residue.

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