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STUDY OF CHANGES IN THE HYDROCARBON COMPOSITION OF GASOLINE AFTER EACH STAGE REFORMING REACTOR

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ABSTRACT

This article presents the results of studies of individual hydrocarbon composition of the initial hydrogenation and reformate process of catalytic reforming of gasoline fraction high paraffinic petroleum.

Key words: Hydrocarbon composition, Gasoline, Reforming reactor.

INTRODUCTION

Study of various petroleum fractions Kazakhstana are given in a number of papers[1-8]. However, to determine chemism and mechanism of the process of reforming the study of physico-chemical properties and individual hydrocarbon composition of the starting gasoline and reformate obtained from the various stages of the reactor block catalytic reforming process are of particular interest. Study of physico-chemical properties and individual hydrocarbon composition of the starting gasoline and reforming catalysate obtained from different stages of the reactor are of particular interest to determine the chemistry and mechanism of the reforming process. The paper presents a study data of raw materials and catalysate. They obtained catalytic reforming of an industrial plant in the processing of virgin gasoline (fr.62-18°C) paraffin Kazakh oil.

EXPERIMENTAL

The process was carried out on an industrial aluminoplatinum catalyst Al_2O_3 + Pt (0.6%) + Cl_2 (1.0%) under the conditions: temperature I - II - III stage - 490-495°C,

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pressure - I - II - III stage-3.1-3.15 MPa, volumetric feed rate -1.5 hr^{-1}. The multiplicity of the hydrogen-containing gas circulation-1900 m^3/m^3 of feedstock.

Individual and group hydrocarbon and hydrogenation compositions were determined by catalysate chromatograph GS8000 FINONS INS, as described in[9,10].

RESULTS AND DISCUSSION

Table 1 shows the composition of the individual raw materials-hydrogenation and reformate. They are selected from various industrial reactor catalytic reformer unit.

Table 1: Comparison hydrocarbon composition of raw materials and reforming catalysate obtained from various commercial plant reactors oil refineries

Hydrocarbons	Catalysate of the individual stages of reactors			
	Raw material	After R-1	After R-2	After R-3
1	2	3	4	5
Normal paraffins:	34.98	24.36	16.61	15.81
Propane	-	0.93	0.12	1.13
N-butane	0.06	0.62	0.31	3.05
N-pentane	1.82	0.74	0.39	2.16
N-Hexane	6.12	1.74	1.94	3.71
N-heptane	10.91	4.91	0.56	0.28
N-octane	8.03	7.04	3.57	0.73
N-nonane	5.57	4.60	2.55	0.75
N-decane	2.0	3.49	4.08	3.90
N-undecane	0.48	0.22	0.26	0.10
Isoparaffins	20.59	24.29	25.36	28.09
Isobutane	-	0.60	0.18	1.60
Isopentane	1.02	1.67	1.22	1.10
2.2-dimethylbutane	0.24	0.24	0.26	0.46
2-methylpentane	3.16	1.66	2.01	4.38
3-methylpentane	0.99	1.40	1.62	3.63

Cont…

Hydrocarbons	**Catalysate of the individual stages of reactors**			
	Raw material	**After R-1**	**After R-2**	**After R-3**
1	**2**	**3**	**4**	**5**
2.2-dimethylpentane	0.22	0.12	0.59	1.16
2.2.3-trimethylbutane	0.48	0.23	-	0.33
3.3-dimethylpentane	0.06	0.12	-	0.13
2.3-dimethylpentane	4.92	0.82	-	1.46
3-methylhexane	2.12	3.18	2.42	3.27
Isoparaffins C8	0.30	0.19	0.59	1.13
2-dimethylhexane	2.96	2.64	3.59	1.42
4-methylheptane	1.17	1.19	1.44	2.44
3-methylheptane	1.99	2.74	3.11	2.12
2.2- dimetilgeptan	-	0.76	0.33	0.11
2.6-dimetilgeptan	0.26	-	0.86	-
2.3-dimetilgeptan	1.76	0.37	-	-
4-methyloctane	1.17	0.68	0.59	0.27
2-methyloctane	1.34	2.16	2.66	2.86
3-methyloctane	1.74	1.61	1.83	0.66
3.3-dietilpentan	0.20	0.08	-	-
2.6-dimetiloktan	-	0.43	-	0.82
4-methylnonane	-	0.38	0.75	1.23
3-methylnonane	0.69	0.43	0.98	1.56
2-methylnonane	-	0.30	0.39	0.99
C11 isoparaffins	0.54	0.68	0.20	0.37
Naphthenic:	23.61	9.21	7.87	5.54
Methylcyclopentane	1.91	0.91	0.72	0.75
Trans-1-methylcyclopentane	0.66	0.41	0.93	0.20
Cis-1. 3-methylcyclopentane	1.15	0.61	-	-
1-trans-2-methylcyclopentane	2.19	-	-	-
1.1.3-trimethylcyclopentane	1.07	0.74	0.49	-

Cont…

Hydrocarbons	Catalysate of the individual stages of reactors			
	Raw material	After R-1	After R-2	After R-3
1	2	3	4	5
Trans-1. 2-tsisbtri methylcyclopentane	0.54	0.19	0.28	0.40
C8 alkylcyclopentane	0.12	0.08	Следы	Следы
C9 alkylcyclopentane	0.90	1.14	-	-
Cyclohexane +2-methylhexane	0.62	1.49	1.74	2.70
methylcyclohexane	10.40	1.26	1.70	0.51
Trans 1. 4-dimethylcyclohexane	3.08	0.53	-	0.17
Trans 1.3-dimethylcyclohexane	1.82	0.47	0.29	0.13
Trans 1.2-dimethylcyclohexane	0.87	-	0.33	-
Ethylcyclohexane	0.54	0.43	-	-
1.1.3-trimethylcyclohexane	1.57	0.34	-	-
Alkylcyclohexane C_{10}	-	0.85	0.94	0.60
Butylcyclohexane	-	0.66	0.45	0.08
Aromatic	10.28	39.32	47.44	54.41
Benzene	1.78	2.90	3.25	3.75
Toluene	1.96	13.31	9.26	22.65
Ethylbenzene	0.50	2.64	2.26	2.68
1.4-dimethylbenzene	3.21	7.11	10.40	0.01
1.2-dimethylbenzene	0.64	3.96	4.85	4.35
Isopropylbenzene	-	1.89	1.23	2.28
Methyl-1. 3-ethylbenzene	0.46	0.19	7.34	4.73
N-propylbenzene	0.15	1.38	1.99	2.41
1.3.3-trimethylbenzene	-	1.60	1.65	1.08
1-methyl. 2-ethylbenzene	-	0.49	1.34	0.49
Isobutylbenzene	-	0.28	0.29	0.16
Deutbutylbenzene	-	0.37	0.64	0.22

Cont…

Hydrocarbons	**Catalysate of the individual stages of reactors**			
	Raw material	**After R-1**	**After R-2**	**After R-3**
1	**2**	**3**	**4**	**5**
1.2.4-trimethylbenzene	0.76	0.73	1.18	0.50
1-methyl. 3-n-propylbenzene	-	0.18	-	-
1-methyl. 4-n-propylbenzene	-	0.37	0.77	0.30
1.3-dimethyl-4-ethylbenzene	-	0.40	1.00	-
1.2-dimethyl-4-ethylbenzene	-	-	-	0.42
Unidentifiable	0.54	2.89	2.72	1.13

From Table 1, it is seen that the analyzed fractions mainly consist of normal (15-35%) and branched (23.1-25.6%) paraffins cyclopentanes (1.3-8.6%) cyclohexane (1.5-2.0%) and aromatics (10-60%) hydrocarbons. The composition obtained by reforming gasoline in separate reaction zones significantly differs from each other. In the first reactor the reforming naphthenes and paraffins under go deep dehydrogenation and dehydrocyclization reactions to form aromatic hydrocarbons. The content of heptane and methylcyclohexane in the feed is 6.12; 10.91 and 10.4, respectively and catalysate obtained after there actor R-1 and R-2 content of their reduced to 1.74; 1.94; 0.56-0.23 and 1.26-1.70% by weight. Paraffinic hydrocarbons C_8-C_9 unlike C_6-C_7 in the first two reactors and turn slightly in the third reactor is almost entirely exposed to the dehydrocyclization reaction. i.e. their content is reduced from 6-8 to 0.73-0.75% by weight. Formation of aromatic hydrocarbons in the first reactor is mainly due to the conversion of six-membered naphthenes and n-paraffins. The second-the paraffinic hydrocarbon-heptane and octane partially and R-3 by alkanes consisting of C_8 to C_9 carbon atoms and cycloslightly.

Naphthenic hydrocarbons compared with other hydrocarbons are most complete subjected to the dehydrogenation reaction and almost 85-90% converted to aromatics. Feedstock composition group hydrocarbon and obtained catalyste from various catalytic reforming reactor shown in Table 2.

From comparison of the composition of hydrocarbon feedstock and reforming products, is seen that the amount of paraffins and naphthenes after reactor R-2 and R-3 is almost three times less than the original gasoline, and aromatics concentration increases conversely. Cyclopentanes mainly subjected to isomerization, cracking and dealkylation. General physico-chemical characteristics of the feedstock and catalyzate obtained after the third reactor are presented in Table 3.

Table 2: Changes in the detailed composition of hydrocarbon types reformate after each reforming reactor

Hydrocarbons	**The composition of the reformate after each stage reactors**			
	Raw material	**After R-1**	**After R-2**	**After R-3**
1	**2**	**3**	**4**	**5**
Normal paraffins:	34.98	24.36	16.61	15.81
N-Hexane	6.12	1.74	1.94	3.71
N-heptane	10.91	4.91	0.56	0.28
N-octane	8.03	7.04	3.57	0.73
N-nonane	5.57	4.60	2.55	0.75
Isoparaffins	20.59	24.29	25.36	28.09
2-dimethylhexane	2.96	2.64	3.19	3.42
4-methylheptane	1.17	1.19	1.44	0.44
3-methylnonane	0.69	0.43	0.98	1.56
2-methylnonane	-	0.30	0.39	0.99
Naphthenic:	23.61	9.21	7.87	5.54
Methylcyclopentane	1.91	0.91	0.72	0.75
Cyclohexane + 2-methylhexane	0.62	1.49	1.74	2.70
Methylcyclohexane	10.40	1.26	1.70	0.51
Ethylcyclohexane	0.54	0.43	-	-
1.1.3-trimethylcyclohexane	1.57	0.34	-	-
Alkylcyclohexanes C10	-	0.85	0.94	0.60
Butylcyclohexane	-	0.66	0.45	0.08
Aromatic	10.28	39.32	47.44	54.41
Benzene	1.78	2.90	3.25	3.75
Toluene	1.96	13.31	9.26	22.65
Ethylbenzene	0.50	2.64	2.26	2.68
N-propylbenzene	0.15	1.38	1.99	2.41
Unidentifiable	0.54	2.89	2.72	3.13
The octane number (M.M)	54	68	79	86

Table 3: Physical and chemical properties of raw materials and reforming catalysate

Indicators	Raw materials	Catalysate
Density at 20°C. g/cm^3	0.742	0.784
Fractional compositionatthe following temperature (°C)		
Initialboiling	82	34
Boils at 10%	93	59
Boils at 50%	115	101
Boils at 90%	149	152
Finalboiling	175	187
Total sulfur content. wt.%	0.003	absence
Octane number	54	86
Grouphydrocarbon composition. wt.%		
Paraffinic	59.9	37.70
n-paraffins	34.3	15.8
Iso-alkanes	25.6	21.9
Naphthenic	28.7	4.8
aromatic	11.4	57.50

If, the feedstock contains only aromatic hydrocarbons 10.28% by weight, after each stage of reforming content increases continuously. Wherein in the reactor R-1 concentration of aromatic hydrocarbons is increased from 10.28 to 39.32% i.e. 4 times in the reactor and P-2, P-3, 47.44 and 54.41 wt.%, i.e. 5,4 and 4.7 times above as compared with the feedstock.

Significant increase in octane after the final catalytic reforming reactor - P-3, probably occurs due to an increase in the amount of isoparaffins and aromatics in the final product.

The chemism of catalytic reforming process

In terms of catalytic reforming reactors in various stages occur sequentially and in parallel the following main reactions leading to the production of aromatic and isoparaffin hydrocarbons that contribute to higher octane catalysate:

(1) Dehydrogenation of six-membered cycloalkanes

$$C_6H_{12} \longrightarrow C_6H_6 + 4\ H_2$$

n-Hexane Benzene

$$C_6H_{11} - CH_3 \longrightarrow C_6H_5 - CH_3 + 3\ H_2$$

n-Heptane Methylbenzene

(2) Dehydroisomerization five-membered cycloalkanes. From methylcyclohexane to obtain cyclohexane and then benzene

$$C_5H_{11}CH_3 \longrightarrow C_6H_{14} \longrightarrow C_6H_6 + 3\ H_2$$

Methylcyclopentane Cyclohexane Benzene

(3) The dehydrocyclization of alkanes. Due to the dehydrocyclization n-paraffin hydrocarbons, aromatic hydrocarbons are formed.

$$C_7H_{16} \rightarrow C_6H_5CH_3 + 4H_2 \text{ or } C_7H_{16} \rightarrow C_7H_{14} + H_2 \rightarrow C_7H_{14} \rightarrow C_6H_5CH_3 + 3H_2$$

Heptane Toluene Heptanes Heptene n-Heptane Toluene

(4) Dehydrogenation of alkanes cycle

$$C_7H_{14} \longrightarrow C_7H_{14} \longrightarrow C_6H_5CH_3 + 3\ H_2$$

Heptene n-Heptane Toluene

Along with the reactions leading to the accumulation of arenas in the reformate, and other processes occur: the cracking of alkanes, followed by hydrogenation of the fragments; isomerization of alkanes; isomerization side chains scene.

The important amount for improving the octane number of the isomerization reaction are n-paraffins, in particular for the isomerization n-hexane produced 2,3 dimethylbutane:

$$CH_3CH_2CH_2CH_2CH_2CH_3 \longrightarrow (CH_3)_2CH\text{-}CH(CH_3)_2$$

n-Hexane 2,3 Dimethylbutane

CONCLUSION

It is shown that the study of individual and group hydrocarbon composition of raw materials and fuel reforming after each stage of the reactor allows you to set some patterns of chemical conversion rate of individual hydrocarbons occurring in a catalytic reforming process. It is established that as a result of isomerization, dehydrocyclization of n-paraffins and cycloalkanes dehydrogenation intensively formed in the isoparaffinic composition reformate, and aromatic hydrocarbons, which leads to an increase in the octane number of the gasoline reformate.

It was revealed that a catalytic reforming process in reactors also occurs hydrocracking paraffinic hydrocarbons, wherein large molecules are formed from lower molecular weight hydrocarbons with subsequent hydrogenation.

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