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# THERMOCATALYTIC CRACKING OF MAZOUT IN THE PRESENCE OF SUSPENDED CATALYST IN THE ATMOSPHERE OF $CO_2$

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Main results of thermocatalytic cracking of mazout under reduced pressure of $CO_2$ in the presence of suspended catalyst in an autoclave have been considered. X –ray study of the coked catalysts of mazout thermal cracking has been conducted. Influence of pressure (1-3 MPa) and amount of catalytic additive in the range 0-5%wt. on coke formation has been investigated

***Keywords****: thermocatalytic cracking, mazout, suspended catalyst, gasoline, coked catalyst*

The principal trend in the development of petroleum-refining industry is deepening of petroleum refining with involvement of heavy petroleum residues into refining with the purpose of an increase of motor fuels production.

The average branch depth of petroleum refining in Russian oil refineries in 2009 exceeded 71 % [1,2]. According to fore casts, for meeting a demand for petroleum products in Russia in the nearest future the depth of petroleum refining must be at the level 76-78 %. In the industrially developed countries of the world the depth of petroleum refining in average is higher than 80 %. In the USA this index is of the order 95 % [3]. Under these conditions the most efficient way is perfection of secondary processes and working-out of novel processes of heavy petroleum residues (mazouts,goudrons) refining as well as involvement of high-viscous residues of petroleum refining and petrochemistry into refining.

With deterioration petroleum residues quality traditional catalytic and hydrogenation processes require a preliminary preparation of feedstock and an increase of hydrogen pressure in the system which lead to a rise in capital and exploitation expences. Besides, due to a high rate of highly-expensive catalysts deactivation by impurities contained in the residual feedstock (resinous-asphaltene substances, metalloorganic and heteroatomic compounds) a use of traditional catalytic processes and technologies for these aims meets some difficulties. Therefore, catalysts for deep refining of heavy petroleum residues must have a sterically accessible and constantly renewable surface.

In relation to the above-said, development of a simplified technology capable to efficiently carry out a deep thermocatalytic conversion of mazout without a classic preparation under a low pressure with a use of special technological methods and processes using novel catalytic systems

is very actual and has a significant practical interest.

For solving the above-mentioned problems it is expedient to use a highly dispersed catalyst uniformly distributed in feedstock. Its advantage in comparison with traditional solid-phase catalysts in hydrogenation of heavy petroleum residues is a higher activity and practical lack of coke deposition.

The purpose of the present work is a study of thermocatalytic process of cracking of Baku crude oils mixture in the presence of highly-dispersed suspended catalyst under a low pressure of $CO_2$ for production of additional amount of light petroleum products and deepening of petroleum refining.

As a feedstock in the process of thermocatalytic cracking mazout from a mixture of Baku crude oils was studied. In table 1 averaged indices of their properties have been given.

**Table 1.** Qualitative characteristics of mazout from Baku crude oils mixture

| Indices | Values of indices |
|---|---|
| Density at 20°C, kg/m$^3$ | 939.4 |
| Fractional composition, % wt.: | |
| start of boiling, °C | 346 |
| <350 | 2 |
| 350-400 | 4 |
| 400-450 | 16 |
| 450-500 | 19 |
| >500 | 59 |
| Coking power, % wt. | 5.7 |
| Ash contents, % wt. | 0.0658 |
| Contents of metals, % | |
| V | $8.0*10^{-4}$ |
| Ni | $13.2*10^{-4}$ |
| Fe | $4.0*10^{-4}$ |
| Cu | $0.54*10^{-4}$ |
| Na | $3.2*10^{-4}$ |
| Temperature of hardening, °C | +22 |
| Kinematic viscosity at 100 °C, mm$^2$/s | 17.9 |
| Contents of asphaltenes, % wt. | 2.8 |
| Molecular weight | 475 |
| Contents of resins, % wt. | 10.28 |
| Contents of sulphur, % wt. | 0.4 |

As a catalyst of thermal cracking natural zeolite-clinopthilolite was used.

The catalyst is preliminarily made smaller down to10-50 mcm dimensions and added to the feedstock at the amount 2,5-5,0 % wt. of mazout. The catalyst possesses good adsorption properties and contributes to decomposition of asphalto resinous precursors of coke localizing the process of asphaltenes conversion to coke on the surface and taking it out of the reaction

system.

The experiments have been carried out in the autoclave of 1l volume at temperature 400-430$^0$ C and pressure 1.0-3.0 MPa.

The obtained reaction mass after filtration is subjected to distillation with isolation of gasoline ( start of boilinq - 200$^0$C ), diesel ( 200-360$^0$C ) fractions and residue >360$^0$C.

The reaction mass and isolated fractions were studied using physico-chemical methods of analysis. Physico-chemical indices of the fuel fractions were determined by methods of NMR spectrometry and chromatography.

The coked catalysts removed from the system were carefully washed with a solvent (benzene) in order to eliminate adsorbed and chemosorbed components of the feedstock and the reaction products. After dryinq these catalysts were subjected to derivatographical and X-ray analyses for determination of an amount and forms of coke deposits.

Coke contents and character of coke deposition on the catalysts of thermal cracking were studied by method of differential-thermal analysis (DTA) on the derivatograph " MOM" OD-102 where platinum crucibles were used, $\alpha$-$Al_2O_3$ being a reference. The samples were heated in the air medium with the rate 10$^0$ / min in the range 20-1000$^0$C.

Analysis of the obtained results showed that the yield of light petroleum products in thermocatalytic cracking of mazout in the atmosphere of $CO_2$ significantly depends on the process temperature and makes 73-75% vol. ( Table 2 ).

Thus, the yield of light petroleum products rises from 49 up to 75 % vol. with an increase of temperature from 400 up to 430$^0$ C (pressure 1.0 MPa, amount of the additive 2.5 % wt.). An increase of pressure and contents of the catalytic additive insignificantly influences the yield of light petroleum products.

**Table 2.** Material balance of mazout thermocatalytic cracking in the presence of suspended catalyst in $CO_2$ atmosphere in autoclave

| Indices | P$_{CO_2}$ =1.0MPa T=400 °C catal. – 2.5%wt. | P$_{CO_2}$ =1.0MPa T=430 °C catal. – 2.5%wt. | P$_{CO_2}$ =2.0MPa T=430 °C catal. – 2.5 %wt. | P$_{CO_2}$ =2.0MPa T=430 °C catal. – 5.0 %wt. |
|---|---|---|---|---|
| Yield of products, % wt.: gas $C_1$-$C_4$ | 3 | 6 | 7 | 8 |
| gasoline start of boiling - 200°C | 11 | 26 | 27.4 | 26.37 |
| fraction 200-360°C | 29 | 37 | 36.2 | 36.33 |
| Σ fraction < 360°C, % wt: | 40 | 63 | 63.6 | 62.7 |
| % vol. | 49 | 75 | 76 | 73 |
| residue >360°C, % wt: | 57 | 31 | 29.4 | 29.3 |

Analysis of quality of the gasoline and diesel fractions (Table 3) obtained by thermocatalytic cracking of mazout in $CO_2$ atmosphere in autoclave shows that due to increased contents of the actual resins they may be recommended as a trade fuel after refining.

**Table 3.** Qualitative characteristics of products of thermocatalytic cracking of mazout in $CO_2$ atmosphere

| Indices | P $co_2$ =1.0 MPa T=400 °C catal. -2.5 % wt. | P $co_2$ =1.0 MPa T=430 °C catal. – 2.5 % wt. | P $co_2$ =2.0 MPa T=430 °C catal.– 2.5 % wt. | P $co_2$ =2.0MPa T=430 °C catal. 5.0 % wt. |
|---|---|---|---|---|
| Gasoline fraction | | | | |
| Density at 20 °C, kg/m$^3$ | 740 | 742 | 723 | 725 |
| Contents of sulphur, % wt. | 0.05 | 0.06 | 0.05 | 0.05 |
| Sulphurizability , % vol. | 16 | 17 | 16 | 17 |
| Iodine number, g $J_2$/100g | 30 | 29 | 28 | 27 |
| Contents of resins, mg/100 ml | 45 | 40 | 35 | 25 |
| Hydrocarbon composition, % wt.: aromatic unsaturated paraffinic-naphthenic | 8.1 12.0 79.9 | 7.9 11.1 81 | 9 10.0 81 | 8.8 10.6 86 |
| Octane number, according to motor method. | 71 | 71 | 72 | 73 |
| Diesel fraction | | | | |
| Density at 20°C, kg/m$^3$ | 849 | 856 | 852 | 850 |
| Sulphurizability, %vol. | 24 | 34 | 32 | 31 |
| Iodine number, g$J_2$/100g | 34 | 30 | 27 | 30 |
| Contents of resins, mg/100 ml | 200 | 180 | 120 | 100 |
| Cetane number | 48 | 46 | 46.5 | 46.5 |
| Coke, % | | | | 1.5 |
| Contents of sulphur, % wt. | 0.08 | 0.08 | 0.07 | 0.09 |

The results of the studies of structural characteristics of gasoline and diesel fractions of thermocatalytic cracking of mazout with various contents (0-5.0 % wt.) of microcatalytic additive (clinopthilolite) by NMR method on the impulse spectrometer of "Bruker" firm at room temperature have been presented in tables 4 and 5.

The data of the gasoline fractions analysis (Table 4) show that with an increase of the catalyst amount a decrease of unsaturated hydrocarbons contents and a rise of the contents of hydrocarbons of aromatic and saturated structures as well as of terminal methyl groups are observed [4].

For diesel fraction (Table 5) with an increase of the catalyst amount up to 2.5% wt. a number of hydrogen atoms in saturated and olefinic structures rises and a degree of aromaticity falls down. Then, with an increase of the catalyst quantity up to 5 % wt. a degree of aromaticity rises.

**Table 4.** Structural characteristics of the gasoline fraction of mazout thermocatalytic cracking determined by NMR method

| Indices | P $CO_2$ =2.0MPa T=430°C without catalyst | P $CO_2$ =3.0MPa T=400 °C catal. -2.5 % wt. | P $CO_2$ =2.0MPa T=430°C catal.- 5.0 % wt. |
|---|---|---|---|
| $H_{ar}$ | 2.2 | 1.9 | 2.7 |
| $H_{ol}$ | 3.9 | 2.0 | 1.5 |
| $H_{\alpha}$ | 7.0 | 7.6 | 6.3 |
| $H_{naph}$ | 14.7 | 14.9 | 14.5 |
| $H_{par}$ | 33.6 | 34.6 | 35.0 |
| $H_{\gamma}$ | 38.6 | 39.0 | 40.0 |
| $CH_2/CH_3$ ratio | 1.31 | 1.33 | 1.31 |
| Hydrocarbons composition. % wt. | | | |
| aromatic | 8.0 | 8.1 | 8.8 |
| unsaturated | 23.0 | 12.6 | 9.5 |
| saturated | 69.0 | 79.3 | 81.7 |
| Octane number (according to motor method.) | 70.0 | 71.0 | 72.0 |

**Table 5.** Stuctural characteristics of diesel fractions of mazout thermocatalytic cracking

| Indices | P $CO_2$ =2.0MPa T=430 °C without catalyst | P $CO_2$ =3.0MPa T=400 °C catalyst -2.5% wt. | P $CO_2$ =2.0MPa T=430 °C catalyst -5.0% wt. |
|---|---|---|---|
| $H_{ar}$ | 5.3 | 3.8 | 6.1 |
| $H_{ol}$ | 0.4 | 0.7 | 0.4 |
| $H_{\alpha}$ | 10.0 | 8.0 | 11.8 |
| $H_{naph}$ | 14.5 | 14.6 | 14.2 |
| $H_{par}$ | 44.9 | 45.1 | 42.8 |
| $H_{\gamma}$ | 24.9 | 27.8 | 24.8 |
| $CH_2/CH_3$ ratio | 3.58 | 3.22 | 3.44 |
| Degree of aromaticity | 23.5 | 18.0 | 25.5 |
| Cetane number | 50.8 | 51.8 | 47.1 |

X-ray study of the coked catalysts (clinopthilolite) of mazout thermocatalytic cracking has been carried out. An influence of pressure (1-3 MPa) and catalyst (clinopthilolite) amount (0-5 % wt.) on coke formation in the process of mazout thermocatalytic cracking has been investigated.

The analyses were conducted on X- ray diffractometer DRON-3M under following conditions: irradiation $\gamma CuK_{\alpha}$, U=30 kV; I = 20 mA; range of measurements $2 \cdot 10^3$ imp/sec, $\tau$ (time constant) = 2.5 sec; velocity of detector rotation $\omega$=2 degree/min; velocity of the tape movement $\upsilon$=720 mm/hour.

Influence of conditions of mazout thermocatalytic cracking on coke formation may be considered according to changes of the peak corresponding to the coke and located in the range of angles $22\text{-}28^0$. By preliminary phase analysis presence of calcite ,clinoptilolite and α –quartz in the composition of the fresh catalyst was established. A study of the coked catalysts showed formation of significant amount of the graphitized coke when carrying out the process in any atmosphere ($CO_2$ and $N_2$) without entering a highly-dispersed catalyst in to the system in the pure thermal regime. In all cases an addition of only 2,5 % wt. catalyst leads to a sharp decrease of the coke amont whereas an increase of the catalyst amount up to 5% wt.brings about a further lowering of the coke quantity.

Thus, it may be concluded that coke formation in mazout thermocatalytic cracking mainly depends on pressure and catalyst amount, i.e. an increase of pressure and catalyst amount sharply lowers extent of coke formation [5].

There fore, the process of mazout thermocatalytic cracking in the presence of highly-dispersed suspended catalyst in an autoclave in $CO_2$ atmosphere, worked out by us, allows to obtain 73-75 % vol. light petroleum products per run.

## REFERENCES

1. *Ryabov V.A.* Problems of development of petroleum-refining and petrochemical industry // Mir Nefteproduktov (World of Petroleum Products), 2009, №1, pp. 5-7 (in Russian).
2. *Galliyev R.G, Khavkin V.A.* Applied science of development of Russia petroleum refining complex // Mir Nefteproduktov (World of Petroleum Products), 2008, №8, pp.5-8 (in Russian).
3. *Galliyev R.G., Khavkin V.A., Danilov A.M.* On goals of Russian petroleum refining // Mir Nefteproduktov (World of Petroleum Products), 2009, 2. pp.3-7 (in Russian).
4. *Abad-zade H.I., Mukhtarova G.S., Aliyev B.M., et al.* Study of structural characteristics of mazout thermocracking products by NMR method /Materials of V Republic Conference on Chemistry,Georgia, 2004, pp.78-80 (in Russian)
5. *Rustamov M.I., Abad-zade H.I., Mukhtarova G.S., et al.* Thermocatalytic cracking of mazout in $CO_2$ atmosphere / Materials of VII Baku International Mamedaliyev Conference on Petrochemistry devoted to 80 years Jubilee of Institute of Petrochemical Processes of National Academy of Sciences of Azerbaijan. Baku, 2009, pp.42-43 (in Russian).

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