



## CATALYSTS FOR CATALYTIC CRACKING OF HEAVY REFINERY RESIDUES

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### Abstract

The purpose of this work is to develop the oil refining and petrochemical industry of the republic by increasing the depth of processing of heavy oil residue - fuel oil, obtained in the process of refining oils at the atmospheric distillation unit of the oil refinery.

At present, the oil refining industry of Uzbekistan faces the task of complex processing of hydrocarbon raw materials, increasing the depth of processing and the yield of light oil products. In this regard, it is important to solve the problem of shortage of raw materials for oil refineries of the Republic of Uzbekistan.

The problems of the possibility of modernizing catalytic cracking process units by including the process of hydrodesulfurization of raw materials were considered, as a result of which the quality and yield of light products are increased when using fuel oil and secondary semi-finished products containing a large volume of various sulfur compounds.

**Keywords:** catalytic cracking, fuel oil, gasoline, light and heavy gas oil, reactor, octane number, heavy metals, pilot run and catalysts.

### Introduction

Due to the increase in oil production, the growing demand for motor fuels is increasing. To solve this urgent problem, it is necessary to develop new areas of oil refining and motor fuel consumption : - deepening and chemicalization of oil refining; - optimizing the quality of motor fuel with the expansion of resources and reducing their actual consumption; - using alternative fuel [1]. The first area is the main line of modern oil refining. It is associated with the development and implementation of new process flow charts and advanced high-intensity, environmentally friendly, thermocatalytic and hydrogenation processes for deep processing of oil residues [2].





Catalytic cracking of heavy oil residues is one of the promising areas of oil refining development in the processing industry. The capacity of heavy residue catalytic cracking units at CIS oil refineries is about 2 million tons per year and specializes in processing heavy oil and secondary residues in order to increase the range of raw materials. Vacuum gas oils and fuel oil were subjected to catalytic cracking. The number of installations that use heavy oil residues with a boiling point in the range of 540-580 °C as raw materials is increasing: fuel oils, deasphalted oils and their mixtures with vacuum distillates [3].

High metal content in the feedstock and high coking ability of the feedstock directly affect the activity of the catalyst [4]. At high temperatures, porphyrin compounds of nickel and vanadium decompose on the surface of the zeolite, resulting in the poisoning of the catalyst. For this reason, it is considered relevant to create new or modify catalysts for catalytic cracking [5]. The granulated cracking catalyst of the Adamant series [6] consists of REHY zeolite, with a micro- and mesoporous structure and a selected chemical composition. It is thermally stable and has a high resistance to catalytic poisons. When using such a catalyst, the yield of coke and gas decreases and the yield of gasoline increases. As a result of catalytic cracking of heavy and residual feedstock, the yield of coke increases, which reduces the yield of the target product - gasoline. Special catalysts with improved selectivity for the yield of coke have been developed for cracking heavy feedstock. Such catalysts with a mesopore diameter of 500 Å or more prevent the condensation of hydrocarbons in the pores and their clogging [7]. Zeolite-containing catalysts are characterized by relatively low rates of hydrogen transfer reactions, which prevent the formation of polynuclear coke compounds.

The materials used were heavy oil residues from Zhanazhol, Kumkol Republic of Kazakhstan and oils from Kashkadarya region of the Republic of Uzbekistan. A catalytic method was used for oil refining. Splitting reactions occur on the surface of the catalyst [8]. As a result, coke deposits are formed. Coke burning is an important process and this process is called catalyst regeneration.

The need to develop and create more active and selective catalysts increases the intensification of the process of obtaining high-octane environmentally friendly components of gasoline and diesel fuel, increasing their yield during catalytic cracking of heavy types of raw materials.

When selecting a catalyst, it is necessary to pay attention to the fact that it is responsible for the yield and quality of the target products. In cracking, a special place is occupied by zeolite-containing catalysts, which consist of: - a matrix consisting of amorphous aluminosilicate; - zeolite types X, Y and ZSM-5; - additives that increase



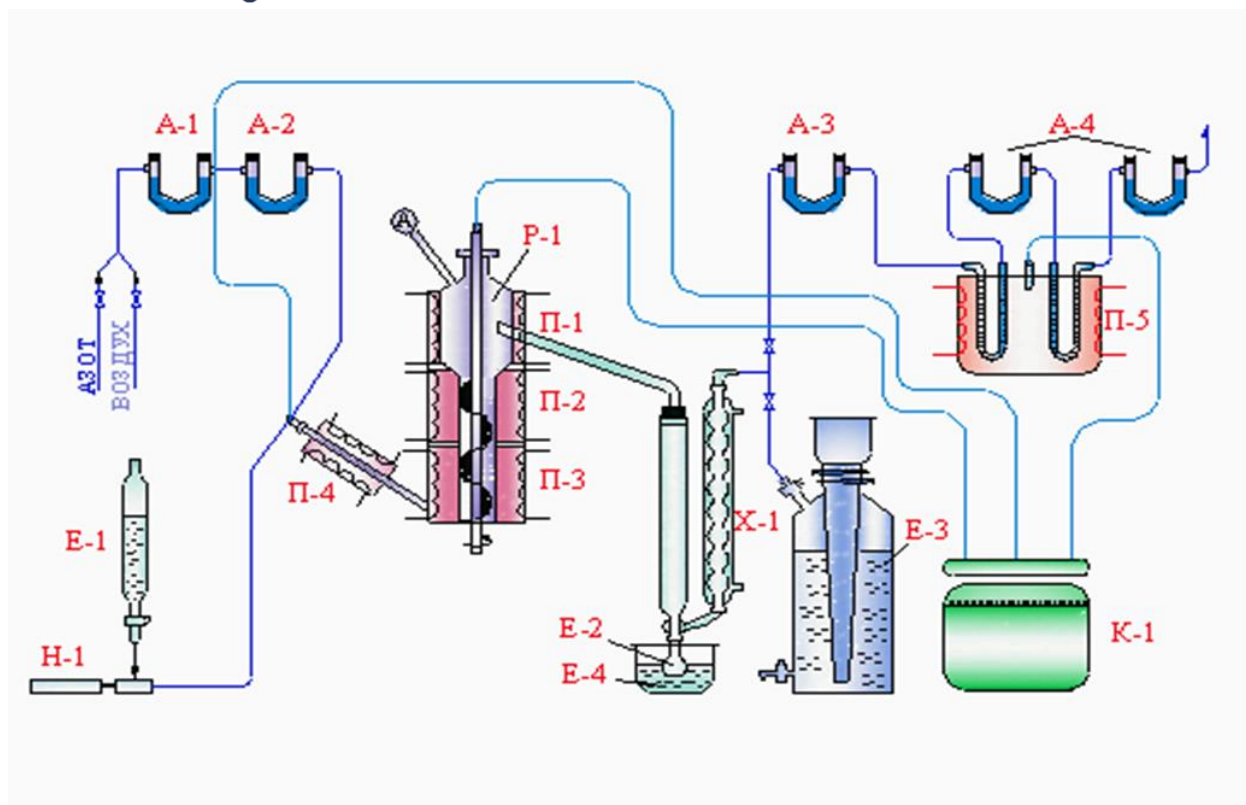


the activity of the catalyst. During catalytic cracking of heavy and residual raw materials, increased coke formation occurs, resulting in a decrease in the yield and quality of gasoline. In this paper, a study was conducted of the effect of the composition of zeolite-containing catalysts on the yield and quality of catalytic cracking products of heavy oil of the Republic of Kazakhstan and oils of the Republic of Uzbekistan.. Laboratory flow-type installations in reactors with a stationary and fluidized catalyst bed were developed. The effect of the composition of zeolite-containing catalysts ( coarse-granulated Tseokar-2 and micro spherical Super- D ) on the catalytic performance was studied cracking. The ratio of catalyst to feedstock (K :C ) is 3:1, with a mass feed rate of  $2 \text{ h}^{-1}$  and  $4 \text{ h}^{-1}$  in a fluidized bed reactor and at a feed volumetric feed rate of  $0.8 \text{ h}^{-1}$  and  $1.0 \text{ h}^{-1}$  in a reactor with a fixed catalyst bed, the process temperature is  $510 \text{ }^\circ\text{C}$ . A basic process flow diagram of a laboratory catalytic cracking unit with a fluidized catalyst bed was developed (Fig. 1). Raw materials were fed into the lower part of the reactor with mechanical mixing of the catalyst bed with a screw mixer, thus creating a fluidized catalyst bed [9].

The raw material for cracking from the heated burette ( E - I ) and with the help of the pump H-1, then evaporating in the heater P-4, enters the cracking reactor P - I . In the heater P-4, the raw material moves along a narrow annular gap between the thermocouple pocket and the heating element of the furnace at high speed, in order to prevent thermal decomposition of the raw material at temperatures of  $450\text{-}550^\circ\text{C}$ .

Reactor P-1 functions as a gravity settler. The fittings for the vapor outlet from P - I also help separate the catalyst dust. Reactor P - I is equipped with a removable threaded cover and gland devices for free rotation of the stirrer. The cracking products formed in P - I enter the refrigerator-condenser X-1. Liquid products are condensed in the catalyst receiver E-2, and the gas enters the gas meter E-3. The coke deposited on the catalyst is burned off in a stream of dried air in P - I . Regeneration gases enter the carbon monoxide afterburning furnace through drying tubes , then are discharged into the fume hood.





**Figure 1 – Flow chart of a laboratory catalytic cracking unit with a pseudo -fluidized catalyst bed**

E-1-raw material burette, H-1-raw material pump, R-1-reactor, P-1,2,3- heaters, P-4-heater, P-5-furnace afterburner CO, X-1 – refrigerator-condenser , E-2 - catalyst receiver, E-3 gasometer, E-4 - water bath, A-1,2,3 - dryers, A -4 ascari tubes , K-1 self-recording potentiometer

The principle of operation is that before the experiment, the catalyst is loaded into the reactor. In furnaces P-1,2,3 in P - I and in P-4. 2-1, a given temperature is set. The feed tubes are filled with raw material. Before the experiment, the P - I reactor is purged with nitrogen for 5 minutes at a rate of 0.3 l / min. The required amount of raw material is pumped into the reactor using pump H - I , and P - I is again purged with nitrogen, purging is carried out in E-3. After the end of the purging, the temperature in the reactor is raised to the specified regeneration temperature and regeneration of the catalyst is carried out in a stream of dried air at a rate of 0.5 l / min. After cooling the ascarite tubes, regeneration is completed. The yield of cracking gas was determined by its volume and density. The catalyzate from E-2 is distilled into fractions: n.k. – 200 0 C (gasoline), 200-350 °C (light catalytic gas oil) and the



remainder because  $> 350\text{ }^{\circ}\text{C}$  (heavy catalytic gas oil). The coke yield was determined by the weight gain of the ascarite tubes, using the formula:  $K = A \cdot 1.06 \cdot 12 \cdot 100 / 44 \cdot G$

where:  $A$  – total weight gain of ascarite tubes, g

$G$  – amount of raw material passed through, g

12 – molecular weight of carbon

44 – molecular mass of carbon dioxide

In catalytic cracking of heavy petroleum residues, the Super- D catalyst, compared to Tseokar-2, increases the yield of the gasoline fraction [10].

The results of the influence of the composition of zeolite-containing catalysts (microspherical Super-D and coarse-granulated Zeokar-2) on the yield of products of catalytic cracking of heavy oil residues are given in Table 1.

Table 1 The influence of the composition of zeolite-containing catalysts microspherical Super- D and coarse-granulated Zeokar-2 on the yield of catalytic cracking products

Indicators	Heavy oil residue			
	Zhanazhol oil		Kumkol oil	
Types of industrial catalysts	Super- D	Tseokar-2	Super- D	Tseokar-2
Reactor type	Pseudo-liquid layer	Stationary layer	Pseudo-liquid layer	Stationary layer
Material balance, % mass				
Taken from:	100,0	100,0	100,0	100,0
Received:				
gas $C_3 - C_4$	16, 2	15, 8	17, 0	14, 5
Gasoline, fr.n.k.-195 °C	44, 0	35, 0	46, 0	38, 5
Light gas oil, fr. 195-270 °C	15, 0	16, 4	13, 0	15, 8
Heavy gas oil, fr.270-420 °C	10, 6	13, 3	10, 0	13, 0
Fr. $> 420\text{ }^{\circ}\text{C}$	9, 2	11, 8	8, 5	10, 2
Coke burnt	5, 0	7, 7	5, 5	8, 0
Conversion depth, % by weight	65, 2	58, 5	68, 5	61, 0
Selectivity, % mass	67, 4	59, 8	67, 1	63, 1

Based on the work carried out, it can be concluded that Super- D can be used for cracking heavy vacuum gas oil. When using vacuum gas oil at a mass feed rate (MFR) of  $2\text{ h}^{-1}$  and a temperature of  $510\text{ }^{\circ}\text{C}$ , the yield of gasoline and  $C_3 - C_4$  olefins increases significantly (by 0.4% by weight). As a result, the composition of the cracking gas improves, the ratio of "olefins : paraffins" in the  $C_3 - C_4$  fraction increases by 1.1-1.2 times. The selectivity of the process increases by 1.17-1.23 times. As a result, the



operation of the compression and gas separation unit of catalytic cracking units improves [11].

Table 2 Physicochemical characteristics of zeolite-containing cracking catalysts

Indicators	Catalyst brand		
	Tseokar 2	KMCR	SUPER D
Bulk density	690	750	945
Activity index	-	46	-
Stable activity, % mass.	49.6	-	49
Structural characteristics:			
Specific pore volume, $\text{cm}_3/\text{g}$	0.50	0.45	0.16
Specific surface area, $\text{m}^2/\text{g}$	220	170	150
Avg. por radius, $\mu\text{m}$	3.8	3.6	3.9
Chemical composition, % mass Including: $\text{Al}_2\text{O}_3$	10.0	10.1	29.6
$\text{Fe}_2\text{O}_3$	0.20	0.3	0.7
$\text{Na}_2\text{O}$	0.31	0.34	0.70
Rare earth element oxides	-	3.4	2.9
Fractions with the remainder % mass Fraction $10^6$	-		
More than 315	-	0.2	-
315-160	-	2.8	0.3
160-10	-	11.0	1.9
100-50	-	40.0	53.0
50-20	-	45.0	41.0
less	-	1.0	3.8

During cracking of heavy vacuum gas oil under the accepted conditions, the physicochemical properties of the products changed insignificantly. The octane number of gasoline decreased, which corresponds to the literature data. When adding 14.7% vol. of residual fractions to the feedstock, the octane number of gasoline is preserved. Compared with conventional gas oil, the content of residual fractions in heavy vacuum gas oil is 8.3% by weight [12].



## Conclusion

Thus, as a result of the conducted studies, it can be concluded that the use of zeolite-containing catalysts - microspherical Super - D and coarse-granulated Zeokar-2 for catalytic cracking of low-sulfur vacuum gas oils (with an increased boiling point) allows to deepen oil refining and increase the production of catalytic cracking gasoline and propane-propylene and butane - butylene ( $C_3 - C_4$ ) fractions.

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