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INVESTIGATION OF THE AFFECT OF CATALYST ADDITIVE ON CATALYTIC CRACKING PROCESS

[1] *Gulshan Dadayeva*[0009-0002-5097-7015]
Department of "Petrochemical technology and industrial ecology"
Associate Professor, PhD in technical science, ASOIU
gulshan.dadayeva@asoiu.edu.az
[2] *Zuleykha Asgarova*
Department of "Petrochemical technology and industrial ecology"
master's student,, ASOIU
zaskerova25@gmail.com
[3]*Elchin Mammadov*
Department of "Petrochemical technology and industrial ecology"
master's student, ASOIU
elchin.mammadov000@gmail.com

Abstract:*The study of using non-traditional feedstock resources for the catalytic cracking process enables the processing of a wide range of raw materials, as well as the possibility of regulating selectivity toward various feedstocks. In this regard, the introduction of a Mo catalyst additive—prepared by mixing paramolybdate solution (PMS) with an activating ammonium sulfide solution—into the selected feedstock for the catalytic cracking process leads to the formation of molybdenum disulfide (*MoS_2*), which is a conventional hydrotreating catalyst component under cracking conditions. This compound exhibits catalytic activity in hydrogenation and hydrocracking reactions. In the presence of the additive, the optimal process conditions correspond to a temperature of 500 °C and an additive concentration of 0.05 wt%. The introduction of the catalyst additive into the feedstock increases the overall acidity of the catalyst from 23.6 to 47.2 µmol during cracking. Moreover, the acidity level of the catalyst and the ratio of acid sites of different strengths intensify the cracking of the feedstock, thereby facilitating the effective progression of reactions during the process.*

Keywords: *Pyrolysis gas, catalytic cracking, Mo catalyst additive, light gas oil fraction, regeneration, vacuum distillate.*

INTRODUCTION

To meet the current demand for engine fuels, expanding oil production volumes has nearly exhausted the available oil refining capacities. To address this issue, increasing fuel resources through deeper and chemically enhanced oil processing, improving the quality of engine fuels, and incorporating alternative fuels into refining processes have become areas of significant interest [1–3].

In the deep processing of petroleum residues, the development and implementation of flexible technological schemes, as well as high-intensity, environmentally benign thermocatalytic and hydrogenation processes, continue to maintain their relevance [4–6].

In this context, the catalytic cracking process plays a particularly important role in the deep refining of oil for the production of engine fuels. This process enables the efficient conversion of easily accessible and heavy feedstocks into high-quality motor gasoline components. At the same time, the process also yields gas components rich in propane–propylene and butane–butylene fractions, which supply the petrochemical industry. The light gas oil fraction obtained from catalytic cracking is used as a component of diesel fuel and for producing naphthalene, whereas the heavy gas oil is considered a high-quality feedstock for the production of premium "needle-like" coke [7-10].

Taking the above-mentioned factors into account, continuous research has been conducted to intensify the catalytic cracking process. Studies related to exploring new feedstocks for the catalytic cracking process and increasing product yields are considered highly relevant in the field of petrochemistry from both theoretical and practical perspectives [11,12]. In this regard, the aim of the presented scientific study is to investigate the main regularities of catalytic cracking of hydrotreated vacuum distillate in the presence of an additive prepared from a mixture of Mo catalyst precursor—paramolybdate solution (PMS)—with an activating ammonium sulfide solution, intended for the synthesis of molybdenum disulfide, as well as to study its effect on the yield of gases released during the process.

To achieve the desired result, it was necessary to solve the following tasks:

- To study the characteristics of the catalytic cracking process and the composition of the resulting products depending on the type and amount of the PMS additive;
- To determine the optimal conditions of the catalytic cracking process using the PMS additive.

EXPERIMENTAL PART

In the process, vacuum distillate obtained from mixed crude oils processed at the Baku Oil Refinery—specifically from the operating EÜDS and AVQ units—was used as the feedstock. The physicochemical properties of the selected vacuum distillate are presented in table 1.

As an additive, a Mo-containing catalyst precursor was employed, prepared by mixing a paramolybdate solution with an activating ammonium sulfide solution. For preparation, a paramolybdate solution (PMS) dissolved in 20 mL of distilled water was combined with the activating ammonium sulfide solution. The concentration of paramolybdate in the resulting mixture was 3%. The prepared additive was introduced into the vacuum distillate at a concentration of 0.01–0.05 wt% (calculated as Mo), after which the mixture was dispersed in a laboratory mixer at a rotational speed of 5000 rpm for 5 minutes. Prior to mixing, the feedstock was thermostated at 60 °C.

Analytical methods: – The fractional composition of the feedstock and reaction products was determined by gas chromatography using a “Kristallyuks-4000M” chromatograph equipped with a flame-ionization detector, in accordance with ASTM D2887.

– Analysis of the feedstock was performed by thermogravimetric analysis using a “TGA/DSC1 METTLER TOLEDO” instrument.

– Particle size distribution of the dispersed phase in feedstock samples prepared with Mo-containing additives was measured by laser light scattering using an “N5 Submicron Particle Size Analyzer” (Beckman Coulter).

– The composition of liquid products was analyzed using a Thermo Focus DSQ II gas chromatography–mass spectrometry (GC-MS) system.

– The molybdenum content in catalyst samples was determined by atomic absorption spectroscopy (AAS).

Table 1

Physicochemical properties of vacuum distillate

№	Density,kg/m^3	Sulfur amount, ppm	Cetane number	Fraction content, ^{0}C
1	923	2400	26,8	10% - 238 50% - 272 90% - 318

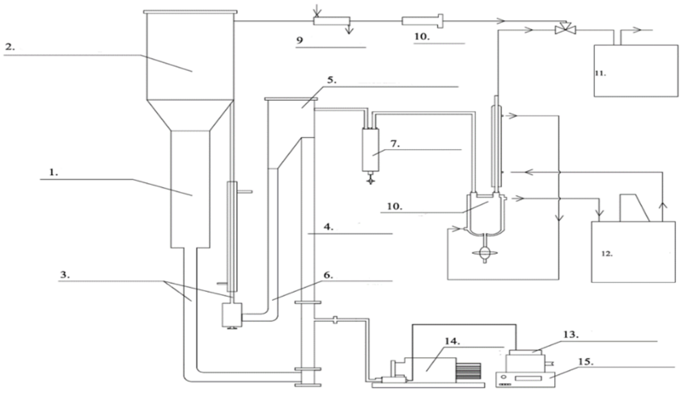

Fig 1. Laboratory equipment of catalytic cracking process: 1-regenerator; 2-separator ; 3-transportation line; 4- reactor; 5- separator; 6- desorber; 7-slime settling container; 9-cooler; 10- filter; 11- gas chromatogram ; 12- termostat; 13- vessel; 14- liquid pump; 15- electronic scale

RESULTS AND DISCUSSION

The influence of the feedstock and the molybdenum catalyst additive (PMS) on the cracking process (fig.1) was investigated in a laboratory setup within the temperature range of 480–520 °C. The concentration of the molybdenum-containing additive (PMS) was 0.05 wt%, and the feed rate was maintained at 2 h^{-1}. It was determined that both the pure vacuum distillate used as feedstock and the added PMS exert a measurable effect on the cracking performance parameters depending on temperature. Furthermore, the addition of PMS to the vacuum distillate resulted in a decrease in the average particle size of the dispersed phase compared with the initial vacuum gas oil (320 nm), yielding a particle size distribution in the range of 150–180 nm. The obtained emulsion remained stable for several hours without phase separation, indicating that PMS was uniformly distributed within the feedstock. Thus, once the prepared feed enters the reactor, molybdenum sulfide formed from the decomposition of the additive is evenly dispersed throughout the reactor volume.At process temperatures of 480 and 520 °C, the gasoline yield in cracking runs with and without PMS (fig. 2) was nearly identical; however, at 520 °C, the gasoline yield in the PMS-assisted cracking process (37%) was significantly lower than that in the process without the additive, where it reached 40.0 wt%. In both cases, the conversion of the feedstock remained nearly the same and did not change significantly within the investigated temperature interval, remaining within 90–92.7%. The yield of light gas oil increased slightly with increasing temperature, and in the PMS-modified feedstock, the light gas oil yield at certain temperatures was lower than that observed in the cracking of the pure feedstock (fig. 3).In the cracking of pure distillate, increasing the temperature from 480 to 520 °C resulted in an increase in the light gas oil yield from 16.0–16.1% to 16.7–16.8%. In the cracking of the feedstock containing PMS, the light gas oil yield under the same temperature conditions increased from 15.2% to 15.6–15.7 wt%.

The yield of gaseous products increases with rising temperature in both cases—cracking with PMS and without PMS. In the cracking of the pure feedstock, the gas yield increases from 20.6–20.8% to 26.1–26.6% as the temperature rises from 480 to 520 °C (fig. 4). It is assumed that, at elevated temperatures, the intensification of cracking reactions of unsaturated hydrocarbons leads to the increased formation of gaseous fractions.

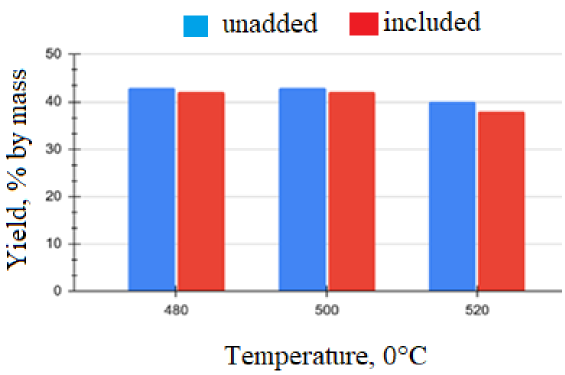

Fig.2. Temperature dependence of gasoline yield

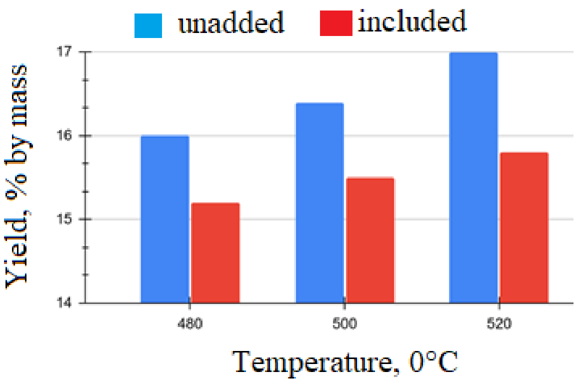

Fig. 3. Temperature dependence of light gas oil yield

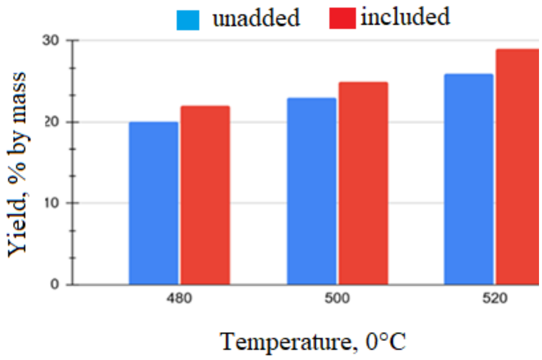

Fig.4. Temperature dependence of cracking gaz yield

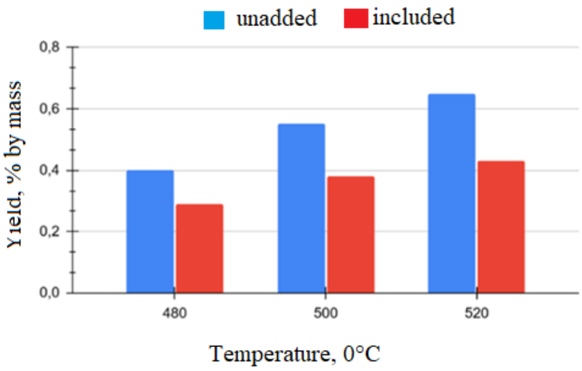

Fig. 5. Temperature dependence of hydrogen yield

A decrease in the hydrogen yield within the gaseous products was observed when PMM was introduced into the process (fig. 5). This indicates an intensification of hydrogenation reactions, which proceed with hydrogen consumption. At the same time, during the cracking of the feedstock in the presence of PMS, hydrogen loss varies depending on temperature. At 480 °C, hydrogen loss is 26%, at 500 °C it increases to 38%, and at 520 °C it reaches 42%. Based on these results, the optimal technological parameters for the catalytic cracking of vacuum distillate with PMS were determined to be a temperature of 500 °C and a PMS concentration of 0.05 wt% in the feedstock.

CONCLUSION

- The effect of introducing an additive (PMS)—prepared by mixing a paramolybdate solution with an activating ammonium sulfide solution—into the catalytic cracking feedstock (vacuum distillate) in liquid form was investigated.
- The influence of molybdenum-containing additives on product yield, the hydrocarbon composition of the products, and the acidic properties of the catalyst was examined. It was established that the introduction of PMS into hydrotreated vacuum distillate intensifies hydrogenation reactions of hydrocarbons. This is attributed to an increase in the acidity of the active sites of the molybdenum

catalyst from 23.6 to 47.2 μmol, thereby promoting a more intensive progression of the reactions.

- It is assumed that the preliminary mixing of PMS with vacuum distillate at a concentration of 0.05 wt% leads to a decrease in the amount of H_2 in the gaseous products at 500 °C. It is believed that a portion of the hydrogen is consumed through the enhancement of hydrogenation reactions during the process.

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