EXPERIENCE IN OPERATING A REFORONING UNIT WITH COMBINED LOADING OF CATALYSTS

V. I. Gurdin and A. V. Ufimtsev

The L-35/11-1000 unit at Angarsk Refinery has been operating since 1978. KR-104A and KR-110 catalysts were used in operating it. In 1992, based on the recommendation of Lenneftekhim, combined loading of the catalysts was used for the first time. According to the reactions that take place in the different stages of the reforming unit, the catalysts were loaded: in the stage I reactor where dehydrogenation of naphthenic hydrocarbons takes place and the effect of sulfur compounds is strong: KR-110 catalyst with a medium platinum content; in stage II and III reactors, where dehydrocyclization and hydrocracking of paraffinic hydrocarbons predominate: high-rhenium catalysts RB-I and RB-II.

The experience demonstrated the existence of important reserves in increasing the efficiency of the catalysts, despite production of reformate with an octane number (ON) on the level of 82.5 – 83 with the Motor Method (MON) or 91.5 – 92 with the Research Method (RON). This primarily involved implementation of continuous chlorination of the catalyst with optimization of the water—chlorine balance and a decrease in the pressure, not given due attention previously.

In addition, due to the low loading of the reforming unit with feedstock caused by the low refinery load, the optimum space velocity was not maintained, decreasing the selectivity of the process. The space velocity was 1.05 – 1.1 h⁻¹ for a ratio of catalyst volumes by stages of 1:2:5 and a feedstock load at 60% of the rated capacity.

To partially reduce the pressure in the system, an imported Packinox heat exchanger was started up in October, 1996. Unfortunately, after a year of efficient operation, partial entrainment of the catalyst into the heat exchanger occurred during regeneration of the catalyst due to burnout of the central pipe screen in the stage III reactor. The pressure drop and temperature strain were above the acceptable values, resulting in decompression of the heat-exchanger plate stack which could not be completely remedied during repairs.

To increase the efficiency of the catalysts, the unit was converted to operation in a continuous chlorination regime in December of 1997. This allowed increasing the ON of the reformate to 84 (MON) or 95 (RON) at a temperature of 496 – 506°C in the reactors.

![Fig. 1. RON (solid curve) and MON (dashed curve) of catalyzate vs. concentration of chlorine in the catalyst for distillation of feedstock: IBP — 78-94°C, 50% — 104-115°C, EP — 157-171°C.](image)

In May, 1998, a new combination of catalysts was loaded into the unit based on the same principle as previously: KR-108U catalyst in the stage I reactor, and RB-22U catalyst in the stages II and III reactors. The ratio of their volumes by stages was varied by 1:2.5:7.5, which allowed increasing the ON of the reformate to 84.7 (MON) or 95.8 (RON) in further optimization of the water—chlorine balance of the system and temperature of 500°C in the reactors. During a brief experimental run of the unit in a harsh temperature regime (510 - 514°C), the ON of the reformate attained 85.6 (MON) or 97.1 (RON).

The overflow of feedstock into the reformate in the Packinox heat exchanger, which had increased since December 1998, does not allow obtaining a catalyzate with ON greater than 83.5 (MON) or 94.8 (RON). The quantitative estimation of the overflow with the concentration of methylcyclohexane (MCH) in feedstock and catalyzate after the heat exchanger showed that approximately 9% of the feedstock overflows into the reformate. The selection of MCH for performing this estimation is based on the almost 100% conversion into toluene in the reforming conditions. Operation of the unit with old shell-and-tube heat exchangers was used as the basis for comparison (absence of overflow). The presence of overflow in the heat exchanger causes the ON of the catalyzate to lose 2 points (MON and RON).

Because of the insufficient accuracy of existing methods of determining the concentration of chlorine in feedstock and catalyzate, we developed a method for monitoring the water—chlorine balance of the system based on the concentration of hydrogen chloride and in the hydrogen-containing reforming gas (HCG). This allowed efficiently controlling the metal and acid activity of the catalysts.

The data obtained during operation demonstrate the extremal dependence of the octane number of the catalyzate on the concentration of chlorine in the catalyzate (Fig. 1). The optimum concentration of chlorine in KR-108U and RB-22U catalysts in combined loading is 1 - 1.14 wt. %.

In selecting the working range of the moisture content of the reforming system, it is necessary to take into consideration that excessive (below 5 ppm) drying reduces the mobility of chlorine and causes its uneven distribution both in the bulk of the catalyst and in the reactors. In addition, the inertness of the reforming system to the effect of organochlorine compounds (3 - 5 days) increases significantly, which makes systematic control of the water—chlorine balance impossible. With a system moisture content above 15 - 20 ppm, it is necessary to increase feed of organochlorine compounds for dynamic equilibrium and to maintain the optimum concentration of chlorine in the catalyst. This increases the concentration of hydrogen chloride in the reforming HCG.

As experience in operating the L-35/11-1000 unit showed, the presence of more than 3 - 4 ppm of hydrogen chloride in the HCG combined with other factors of related plants using this HCG (presence of ammonia, hydrogen sulfide, oils, etc.) causes the accumulation of chlorine-containing deposits in the compressor equipment. It is difficult to solve this problem without using additional methods of removing hydrogen chloride from the HCG. From process and economic (cost of repairs) points of view, 10 - 15 ppm is the optimum moisture content range, and the inertness of the system in this case will not exceed 1 - 2 days.