SULFURIC ACID ALKYLATION OF ISOBUTANE BY OLEFINS.
EXPERIENCE IN OPERATION OF A JET MIXING REACTOR

S. Sh. Gershuni, M. I. Belkin, A. A. Nikitin, A. A. Romanov,
S. B. Yukhtin, S. V. Rumyantsev, and E. A. Esipko

Experience in operating a sulfuric-acid alkylation jet reactor of new design – with no mixers and heat-exchange bank and a process scheme that includes this reactor, a hydrocyclone, three-phase separator, and circulating centrifugal pumps are described. An additional quantity of feedstock is added to the jet reactor operating in tandem with a cascade reactor without addition of circulating isobutane. The concentration of high-octane components in the products of the reaction, i.e., the alkylation production volume, increases. The results of operating the jet reactor in incorporation of propylene feedstock from the cascade reactor to “butylene” alkylation are reported. The additional volume of “propylene” alkylation is up to 1/3 of the total output of the unit, distillation is improved, and the Motor Octane Number decreases insignificantly – by a maximum of 0.5 points.

World trends in the evolution of automobile manufacture and motor fuel production are increasingly defined by environmental requirements. It is possible to predict an increase in production of alkylate – an environmentally clean, high-octane component of automotive fuels. World experience in alkylation production shows that in the very near future, this increase will be due to an increase in the capacities for sulfuric-acid alkylation (SAA) of isobutane by olefins. In this respect, the results of implementing new process solutions on the 25/7 SAA unit at Slavneft’-Yaroslavlnefteorgsintez OJSC are of interest.

The efficiency of operation of any SAA unit is a function of the reactor (contactor) design – one of the most complicated units in the oil refining industry – to a significant degree. The complexity of its design is due to the necessity of creating and maintaining a finely disperse emulsion of heavy and viscous sulfuric acid in a light and low-viscosity liquefied gas and the necessity of removing the heat from the exothermic alkylation reaction.

The SAA process is very sensitive to the local ratio of concentrations of the reacting components – isobutane and olefins in the reaction zone and to the local temperature in this zone. Additional complications are created by the corrosiveness of the many sulfur-containing compounds formed on contact of sulfuric acid with the unsaturated hydrocarbons in the feedstock.

The classic SAA reactor designs with mixers developed several decades ago are complicated to operate due to the long shafts, gaskets, and bearings. Vibration and corrosion of the tubes in reactors with built-in heat-exchange banks create even greater complications than the mixer drives. For this reason, attempts have been made to create a reliably operating SAA reactor with no mixers and tube bank.

VNIInefte Mash OJSC and Slavneft’-Yaroslavlnefteorgsintez OJSC created an adiabatic reactor that operates under pressure above 0.45 MPa in which the emulsion is formed and circulated with a jet mixer. However, it was necessary to change the process scheme to introduce it.

A pilot run conducted in 1991 with a provisional process scheme showed that at total capacity of the unit, the reactor produced high-quality alkylate. However, it was not possible to create a permanent operating scheme due to organizational and financial difficulties.

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At the end of the 90s, the 25/7 unit was redesigned at Slavneft'–Yaroslavnefteorgsintez OJSC with an increase in alkylate output to 90,000 tons per year and simultaneous improvement in its quality and reduced acid consumption [1]. Tekhno-Alko OJSC, established in 1998, resumed operation on a jet reactor. The jet reactor was included in the plant scheme in 2000.

Bashkir State University together with Novo-Ufa Oil Refinery parallelly worked to create an isothermal continuous-flow reactor with jet blending of the components [2]. As in the cascade reactor, the reaction heat in this reactor is removed as a result of evaporation of isobutane and the streams are turbulized by internal ring packing. The required contact time (approximately 30 sec) is one order of magnitude less than in SAA reactors of traditional designs, ensured by the high linear flow rates.

A semi-industrial continuous-flow isothermal reactor 104 mm in diameter was tested with feedstock throughput of 0.16–0.6 m³/h, pressure of 0.05 MPa, flow rates in the reactor of up to 0.4 m/sec, and contact time of less than 30 sec [2]. Conversion of olefin feedstock attained 80% and the Motor Octane Number (MON) of the alkylate obtained with an isobutane:olefin ratio equal to 13:1 was 91.8.

Unsatisfactory operating indexes for a reactor of this type – low degree of conversion, noncompetitive alkylate (high iodine number) – were previously predicted before development of the jet reactor for Slavneft'–Yaroslavnefteorgsintez OJSC. For this reason, the goal was initially to create a reactor that was better than the existing industrial units with respect to the level of flow turbulence and organization of reaction of the reacting components. By combining the forces of specialists at Slavneft'–Yaroslavnefteorgsintez OJSC, VNIIneftemash OJSC, and Tekhno-Alko OJSC, this problem was successfully solved.

The adiabatic jet reactor is a vertical unit 5 m high with a reaction volume of approximately 1.5 m³. As in reactors of existing designs (Stratko contactor and cascade rector), it is based on a circuit consisting of an internal circulating pipe and a ring-shaped gap between this pipe and the body. The reactor design provides for several independent feedstock inputs to different zones.

A jet pump is used for circulating the emulsion in the circuit instead of a propeller (axial) pump. The pressure at the outlet in the circulating centrifugal pumps for sulfuric acid and products of the reaction is 0.75–0.8 MPa. An external circuit through the reactor, hydrocyclone, and three-phase separator was created with these pumps to supplement the internal circuit.

In the hydrocyclone, the emulsion is separated into acid and hydrocarbon phases. The flows coming from it are constricted and go to the three-phase separator for separation of liberated vapors which then go into the compressor. As a result of constricted, the acid and hydrocarbons are cooled to a temperature determined by the pressure in the separator and go in separate streams from the three-phase separator to the jet reactor and the alkylate treatment and separation systems.

In installing the jet reactor, the problem of positioning the additional equipment on the operating 25/7 unit did not arise due to the small size and vertical execution of this reactor and hydrocyclone and use of the existing separator for separating vapors from the products of the reaction in the jet and cascade reactors.

Reaction products from the cascade reactor enter the jet reactor circuit. Olefin feedstock – (–1:1) butane-butylene cut (BBC) mixture – together with part of the circulating isobutane also goes into the cascade reactor. The circulating isobutane goes to the same place. The reaction products from the cascade reactor go into the jet reactor circuit and an additional quantity of olefin feedstock is added.

In designing the scheme, feed of circulating isobutane into the jet reactor as well was provided for. However, the efficiency of the process in the jet reactor is so much greater than in the cascade reactor that

![Graph](image-url)

**Fig. 1.** Motor Octane Number of alkylate vs. proportion of propylene in jet reactor feedstock.