H_2SO_4 Technology Comparison

The most important variables which affect product quality in a sulfuric acid alkylation unit are temperature, mixing, space velocity, acid strength, and concentration of isobutane in the reactor(s). It is possible to trade one operating variable for another, so there is often more than one way to design a new plant to meet octane requirements with a given olefin feed.

Going beyond the customary alkylation process variables, DuPont™ STRATCO® has developed unique expertise in separate processing of different olefin feeds. This technology can improve product quality, compared to alkylation of the same olefins mixed together.

The two major H_2SO_4 alkylation processes are the STRATCO® Effluent Refrigerated process and the auto-refrigerated process. By design, these two processes take different approaches to achieve product quality requirements. These design differences, and their impacts on operability and reliability, are discussed below:

A. Cooling and Temperature Control

The DuPont™ STRATCO® Effluent Refrigerated process utilizes a liquid-full reactor/acid settler system. The heat of reaction is removed by an internal tube bundle. In the auto-refrigerated process, the heat of reaction is removed by operating the reactor at a pressure where the acid/hydrocarbon mixture boils. The auto-refrigerated reactor and acid settler therefore contain a vapor phase above the two mixed liquid phases. Both systems can be operated in the same temperature range. However, the STRATCO® system is much easier to operate.

Temperature control in the STRATCO® Effluent Refrigerated process is simpler than the auto-refrigerated process. The pressure of the refrigerant flash drum is used to control the operating temperature of all the STRATCO® Contactor reactors in the reaction zone. The auto-refrigerated process requires two or more pressure zones per reactor, to control temperature and to maintain liquid flow between the reactor zones.

Good control of the acid-to-hydrocarbon ratio in a sulfuric acid alkylation reactor is critical to reactor performance. This is the area where the

STRATCO® system has its largest operability advantage. Since the STRATCO® reactor system operates liquid-full, gravity flow is used between the Contactor reactor and acid settler.The Contactor reactor/settler system is hydraulically designed to maintain the optimum acid-to-hydrocarbon ratio in the reactor as long as the acid level in the acid settler is controlled in the correct range. The acid-to-hydrocarbon ratio in the STRATCO® Contactor reactor can be easily verified by direct measurement. In contrast, the auto-refrigerated process requires manipulation of an external acid recycle stream in order to control the acid-to-hydrocarbon ratio in the reactor. As a result, the acid-to-hydrocarbon ratio in the different mixing zones varies, and cannot be readily measured.

The STRATCO® Contactor reactor/settler system is also designed to minimize acid inventory in the acid settler. Minimizing the unmixed acid inventory suppresses undesirable side reactions, which degrade product quality and increase acid consumption. Quick, clean separation of the acid and hydrocarbon phases is much more difficult in the boiling auto-refrigerated process.

When operated at the same temperature, the effluent refrigerated system requires somewhat more refrigeration compressor horsepower than the auto-refrigerated process, because of resistance to heat transfer across the tube bundle.

B. Mixing

The topic of mixing in a sulfuric acid alkylation unit encompasses 1) mixing of the isobutane and olefin feeds outside the reactor, 2) the method of feed injection, and 3) mixing intensity inside the reactor. The best quality alkylate is produced with the lowest acid consumption when the "local" isobutane-to-olefin ratio in the mixing zone is maximized by premixing the olefin and isobutane feeds, the feed is rapidly dispersed into the acid/hydrocarbon emulsion, and intense mixing gives the emulsion a high interfacial area.

In the DuPont™ STRATCO® Effluent Refrigerated process, all of the isobutane sent to the reactors is premixed with olefin feed, maximizing the "local" isobutane concentration at the feed point. The feed mixture is rapidly dispersed into the acid catalyst via a special injection nozzle. Mixing occurs as the acid/hydrocarbon emulsion passes through the hydraulic head

impeller, and as it circulates through the tube bundle. The tube bundle in the STRATCO® Contactor reactor is an integral part of the mixing system. The superior mixing in the Contactor reactor produces an emulsion with a high interfacial area, even heat dissipation, and uniform distribution of the hydrocarbons in the acid. Intense mixing reduces the temperature gradient within the STRATCO Contactor reactors 43.5 m3 (11,500 gallon) volume to less than 0.6C (1F). The result is suppression of olefin polymerization reactions in favor of the alkylation reaction. Good mixing is particularly important when the olefin feed contains propylene.

In the auto-refrigerated process, only a portion of the isobutane is premixed with the olefin feed. The "local" concentration of isobutane is therefore lower when the feeds first make contact with acid catalyst. The less intensive mixing in the auto-refrigerated process can result in non-uniform distribution of the hydrocarbons in the acid. The desired finely dispersed hydrocarbon in acid emulsion cannot be easily controlled throughout the different reaction zones. As a consequence, the auto-refrigerated alkylation process must be operated at a very low space velocity and temperature, to make up for its disadvantage in mixing.

C. Acid Strength

The acid cascade system employed by DuPont™ STRATCO® provides a higher average acid strength in the reaction zone than can usually be accomplished with large auto-refrigerated reactors. The higher average acid strength results in higher alkylate octane, with reduced acid consumption. STRATCO® has recently completed pilot plant studies, which enable us to optimize the acid cascade system for different plant capacities. Large auto-refrigerated reactors must be designed for lower space velocity and/or lower operating temperature, to compensate for this difference.

D. Isobutane Concentration and Residence

Time in the reactor: Since the DuPont™ STRATCO® Contactor reactor is operated liquid-full, all of the isobutane fed to the reactor is available for reaction. In the auto-refrigerated process, a portion of the isobutane fed to the reactor is vaporized, to provide the necessary refrigeration. The isobutane is also diluted by reaction products as it cascades through the

reactor. In order to match the liquid phase isobutane concentration in the STRATCO® process, the deisobutanizer (DIB) recycle rate and/or purity in the auto-refrigerated process must be increased, to compensate for the dilution and isobutane flashed. The DIB operating costs will therefore be higher for the auto-refrigerated process unless other variables, such as space velocity or temperature, are used to compensate for a lower isobutane concentration.

Research studies have shown that trimethylpentanes, the alkylate components which have the highest octane, are degraded by extended contact with acid. It is therefore desirable to remove alkylate product from the reactor as soon as it is produced. STRATCO Contactor reactors operating in parallel approach this ideal more closely than the series operation of reaction zones in auto-refrigerated reactors.

E. Reliability One

of the primary factors affecting the reliability of an alkylation unit is the number and type of mechanical seals required in the reaction zone.

Each DuPont™ STRATCO® Contactor reactor has one mechanical seal. STRATCO® offers two types of mechanical seals, a single mechanical seal with a Teflon sleeve bearing, and a double mechanical seal with ball bearings, that operates with a barrier fluid. The single seal is less expensive, and has a life of approximately 18-24 months. The double seal costs more, but has about twice the expected life. The STRATCO® Contactor reactors can be taken off line individually if any maintenance is required. If seal replacement is required during normal operation, the Contactor reactor can be isolated, repaired, and back in service in less than 24 hours.

The number of mechanical seals required for auto-refrigerated reactor systems is higher. An agitator for every reactor compartment, and redundant acid recycle pumps are required. The dry running seals often used on auto-refrigerated reactor agitators have a shorter expected life than the STRATCO® double mechanical seal. While special agitators are available which allow mechanical seals to be replaced without shutting down the reactor, many refiners' safety procedures require the auto-refrigerated reactor to be shut down for this type of maintenance. It is common practice to shut down the agitator and stop feed to a reactor chamber in the event of

agitator seal or shaft problems. Product quality will then be degraded until the reactor can be shut down for repairs.

F. Separate Processing Of Different

Olefin feed composition is not normally an independent variable in an alkylation unit. DuPont™ STRATCO® has recently developed a unique design of alkylation units which keep different olefin feeds separate and alkylate them in separate reactors. By employing this technology, each olefin can be alkylated at its optimum conditions, while avoiding "negative synergy" which occurs when certain olefins are alkylated together. This know-how provides an advantage with mixtures of propylene, butylene and amylene, and also with mixtures of iso and normal olefins. As a result, alkylate product quality requirements can be met at more economical reaction conditions.

G. Experience and Technical Services

There are 75 STRATCO® Effluent Refrigerated alkylation units currently operating worldwide. STRATCO® maintains an active relationship with many of these refineries. This broad experience has enabled STRATCO® to refine its process design, instrumentation, and operating procedures. Refinery alkylation technology is primary business of STRATCO®. Unlike some other alkylation process licensers, STRATCO® does not have any refining operations which might place us in competition with our customers. We have a staff of 20 engineers and technicians devoted full-time to serving our alkylation customers. We supply a full range of process design, mechanical, training, consulting, and field services. We provide engineering services to refiners who operate auto-refrigerated alkylation units and are unable to get the quality technical support they need elsewhere.

STRATCO® provides consultation via telephone, facsimile, and E-mail, and if necessary, can dispatch personnel to provide field service on short notice.

H. Summary

Trends in the alkylation industry in recent years provide evidence that

DuPont™ STRATCO® Effluent Refrigerated process is the predominant H_2SO_4 alkylation technology. In the last ten years, in excess of 85% of the H_2SO_4 alkylation capacity added worldwide has utilized STRATCO® technology. Revamp and expansion activity in H_2SO_4 alkylation also are testimony to the popularity of the STRATCO® Effluent Refrigerated process. The first replacement of an auto-refrigerated unit with a STRATCO® Effluent Refrigerated unit took place over 30 years ago. In the last few years, three major U.S. refiners have expanded or replaced their existing auto-refrigerated alkylation units with a STRATCO® design.

STRATCO® has numerous technological and competitive advantages over EMRE when it comes to licensing of H_2SO_4 alkylation technology. From a competitive standpoint, we feel our advantages are best summarized as follows:

OVERALL COMPARISON STRATCO vs EMRE

	STRATCO	**EMRE**
YEARS IN ALKYLATION	61	<10
PEOPLE DEDICATED TO TECHNOLOGY	40	2*
BARRELS OF INSTALLED CAPACITY	605,000	92,000**
ON-GOING ALKYLATION R&D	YES	NO
IN-HOUSE TECHNICAL SERVICE EXPERTISE	YES	NO
IN-HOUSE ENGINEERING EXPERTISE	YES	NO

* Estimated