STRATCO® ALKYLATION TECHNOLOGY

Features and Developments

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The alkylation process will continue to be a favoured technology for producing clean fuels. MTBE phase out in the USA, implementation of the latest European specifications, enlargement of the EU and adoption of cleaner fuels specifications worldwide are major drivers for refiners requiring more, high octane, gasoline blending components that do not contain aromatics, benzene, olefins and sulphur. Also as the types of gasoline engine in use worldwide become more uniform, there will be a general decline in the markets for low octane gasoline requiring more components to be upgraded to high quality fuel.

STRATCO® has been extremely successful over the last decade in licensing alkylation technology as indicated in Figure 1. The diagram shows that STRATCO® technology has been selected by industry for around 90% of the capacity licensed worldwide over the last ten years.

A comparison with other olefin upgrading processes shows that alkylation provides the greatest yield and octane-volume contribution to the gasoline pool. MTBE and ETBE are components with higher absolute octane numbers, however they require the refinery to import either methanol or ethanol and they are made only from the isobutylene component. Table 1 shows the relative contribution to the gasoline pool from various C4 olefin upgrading processes.

<table>
<thead>
<tr>
<th>PROCESS</th>
<th>YIELD Volume Product/ Volume Olefin</th>
<th>RON-VOLUME/ Volume of Olefin</th>
<th>MON-VOLUME/ Volume of Olefin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butene Alkylation</td>
<td>1.7</td>
<td>163</td>
<td>158</td>
</tr>
<tr>
<td>MTBE</td>
<td>1.25</td>
<td>144</td>
<td>121</td>
</tr>
<tr>
<td>ETBE</td>
<td>1.44</td>
<td>170</td>
<td>147</td>
</tr>
<tr>
<td>Dimerisation</td>
<td>0.85</td>
<td>83</td>
<td>79</td>
</tr>
<tr>
<td>Cat Polymerisation</td>
<td>0.8</td>
<td>78</td>
<td>66</td>
</tr>
</tbody>
</table>

STRATCO® Sulphuric Acid Alkylation Technology was acquired by DuPont in January 2003. The staff of the Alkylation Division transferred to DuPont thus providing the new owners with all the experience and continuity essential to maintaining the STRATCO® position as technology of choice in the refining industry today. DuPont has provided STRATCO® with a new state of the art Technology Centre ensuring that sulphuric acid alkylation technology development will continue into the foreseeable future. This article discusses the latest features of STRATCO® Alkylation Technology.
ALKYLATION UNIT FEATURES

A typical block flow diagram of a sulphuric acid alkylation unit is shown in the following diagram.

Olefin feed and make-up isobutane are combined with recycle isobutane from the distillation and refrigeration sections and fed as one stream to the reaction section. Olefins and isobutane combine in STRATCO® Contactor™ reactors to form alkylate. Vapour is generated in the reaction section to provide refrigeration. The vapour is then compressed and condensed in the refrigeration section. Surplus propane present in the feeds is removed in this refrigeration loop.

Reactor effluent containing the alkylate product is treated to remove small quantities of intermediate reaction products in the effluent treatment section. The distillation section recovers recycle isobutane, and separates the remaining reactor effluent into the desired normal butane and alkylate products.

The blowdown section degasses the spent sulphuric acid prior to regeneration and also safely neutralises the small quantity of aqueous effluent from the product treatment.

A typical STRATCO® reaction section is depicted in Figure 3.

Inside the Contactor reactor and acid settler is a circulating emulsion of sulphuric acid and hydrocarbon. The alkylation reaction requires that the olefin be contacted with the acid catalyst concurrently with a large excess of isobutane. If these conditions are not present, polymerisation reactions will be promoted which result in a heavy, low octane product and high acid consumption.

The olefins in the feed are readily soluble in the acid phase but isobutane has a very low solubility. Intense mixing is therefore necessary to ensure that the acid phase is always saturated with isobutane to promote the alkylation reactions and to minimise undesirable side reactions. The mixing is achieved by the use of a high shear impeller that disperses the incoming feed and acid into the emulsion and also circulates the emulsion at a high rate over the tube bundle. It should be noted that the Contactor reactor design retains all the isobutane in the liquid phase to maximise availability for the reaction.
The incoming hydrocarbon and acid streams displace an equivalent volume of emulsion to the settler where acid and hydrocarbons are separated. Acid is returned to the Contactor reactor with a small quantity of acid being removed as spent. The hydrocarbons leave the settler and are then flashed through a back pressure control valve. The flashing vapourises a significant quantity of the isobutane and in turn reduces the temperature of this stream. This stream is then used to remove the heat of reaction via the tube bundle in the Contactor reactor hence the process has become know as “effluent refrigerated”. The reactor effluent then passes to a vessel where the flashed vapours are separated from the liquid and compressed, condensed and reflashed in the same vessel to form the refrigerant stream.

**UNIQUE DESIGN FEATURES AND TECHNICAL IMPROVEMENTS OF THE CONTACTOR REACTOR**

A more detailed diagram of the Contactor reactor is shown in Figure 4.

Since the early days of alkylation, the Contactor reactor has been recognised as the superior alkylation reactor with higher product quality and lower acid consumption than competing designs. However, STRATCO® continues to modify and improve the Contactor reactor to further optimise the desirable alkylation reactions. Several of these improvements include:

1. The heat exchange bundle in the Contactor reactor has been modified to improve the flow path of the acid/hydrocarbon mixture around the tubes. Since this results in improved heat transfer, the temperature gradient across the reaction zone is less than 0.5°C.

2. The heat exchange area per Contactor reactor has been increased by more than 15% compared to older models. This has resulted in an increased capacity per Contactor reactor and also contributes to continual optimisation of the reaction conditions.

3. The design of the internal feed distributor has been modified to ensure concurrent contact of the acid catalyst and olefin/isobutane mixture at the point of injection.

4. The Contactor reactor hydraulic head has been modified to include a modern, cartridge-type mechanical seal system. This results in a reliable, easy to maintain, and long-lasting seal system. STRATCO also offers two other types of mechanical seal including a single mechanical seal with a Teflon sleeve bearing, and a double mechanical seal with ball bearings that operates with a barrier fluid. If seal replacement is required during normal operation, the Contactor reactor can be isolated, repaired, and back in service in less than 24 hours.

5. A modified single piece drive shaft and bearing system is available that provides greater reliability to the seal and bearing systems.
6. Tube Insert technology is available as an upgrade that improves the distribution of effluent coolant into the tube bundle. This improves heat transfer and has been used under conditions of high load to minimise temperature variation in the tube bundle.

All of the above features are available as upgrades for existing Contactor reactors to improve performance and increase reliability.

**STRATCO® PROCESS IMPROVEMENTS**

Several process modifications have been made to provide better alkylation reaction conditions and improve overall unit operations. Some of these modifications are:

1. Acid retention time in the acid settler has been reduced by employing coalescing media. The reduced retention time minimises the potential for undesirable polymerisation reactions in the acid settler. Two stages of coalescing are employed to separate the hydrocarbon product from the acid phase. The acid carryover rate is reduced to only 10-15 vol ppm. The use of coalescing media has enabled the settlers to be greatly reduced in size. This change gives substantial capital cost savings as well as significantly reducing the quantity of LPG and acid present in the unit.

2. Fresh H₂SO₄ is continuously added to the unit and spent H₂SO₄ is continuously withdrawn. In multiple Contactor reactor units, the H₂SO₄ flows in series between the Contactor reactors.

3. To ensure complete and intimate mixing of the olefin and isobutane feeds before contacting with the acid catalyst, these hydrocarbon feeds are pre-mixed outside the Contactor reactor and introduced as one homogeneous stream via a unique distributor nozzle. This ensures maximum availability of isobutane at the point of mixing of the hydrocarbons with the circulating emulsion. A design is available for upgrading existing Contactor reactors with two injection systems.

4. The net effluent from the reaction section will contain traces of alkyl sulphates formed by the reaction of H₂SO₄ with the olefins. Alkyl sulphates are reaction intermediates that are formed in ALL sulphuric acid alkylation units, regardless of the technology utilised. If these alkyl sulphates are not removed, they will cause corrosion and fouling problems in downstream fractionation equipment. The
alkyl sulphates are removed in a "fresh acid wash coalescer/warm alkaline water wash." Afterwards, the net effluent stream is washed with fresh process water to remove traces of caustic, and then is run through a coalescer to remove free water before being fed to the DIB tower. This system is superior to the "caustic wash/water wash" system which was implemented in older designs since caustic usage is minimised and only a very dilute alkaline effluent is produced.

STRATCO® technology offers an improved effluent treatment system by using static mixers to improve mixing, and coalescing media to improve separation and reduce vessel size, Figure 5. As a result, the capital cost of this part of the process and the LPG inventory has been reduced significantly over older designs.

5. Coriolis Meters are specified to measure and control the flow of fresh, intermediate and spent acid in the acid wash and reactor systems. This type of flow measurement has been shown to be superior to other types in acid service and gives a direct indication of mass flow. Another feature of the Coriolis flow meter is that a density indication is available and this can be correlated with acid strength giving the operator the ability to control acid usage and spending strength on a continuous basis.

6. The fractionation system can be designed to accommodate makeup isobutane of any purity, eliminating the need for upstream fractionation of the makeup isobutane. A deisobutaniser column is a minimum requirement, and many units today also include a debutaniser column to simultaneously control alkylate RVP and n-butane product quality (which may be fed to an isomerisation unit to provide more isobutane). In cases where the refinery installs an n-butane isomerisation unit, this can easily be integrated with the deisobutaniser in the alkylation unit for separation of the isomerisation unit reactor product.

7. STRATCO® technology employs a cascading caustic system in order to minimise the volume and strength of the waste caustic (NaOH) stream from the alkylation unit. In this system, fresh caustic is added to the blowdown vapour scrubber, from which it is cascaded to the depropaniser feed caustic wash and then to the alkaline water wash. The only waste stream from the alkylation unit containing caustic is the spent alkaline water stream. The spent alkaline water stream has a very low concentration of NaOH (<0.05 wt%) and is completely neutralised in the alkylation unit neutralisation system before being released to the refinery wastewater treatment facility. Since the cascading system maintains a continuous caustic makeup flow, it has the additional advantages of reduced monitoring requirements and reduced chance of poor treating due to inadequate caustic strength. Also dehydration of the circulating caustic in the blowdown scrubber system is avoided, a problem which historically has caused blockages.

ALKYLATE PROPERTIES AND ACID USAGE
Table 2 provides typical yield, alkylate properties and catalyst information for the common alkylation unit feeds. Catalyst usage quoted does not account for contaminants that may be present in the feeds.

<table>
<thead>
<tr>
<th>Feed Type</th>
<th>( C_3^+ )</th>
<th>( C_4^+ )</th>
<th>( C_5^+ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield, vol/vol Olefin</td>
<td>1.70 - 2.00</td>
<td>1.75 - 1.8</td>
<td>1.76 - 2.04</td>
</tr>
<tr>
<td>IC4 Required, vol/vol Olefin</td>
<td>1.23 - 1.72</td>
<td>1.13 - 1.18</td>
<td>1.07 - 1.39</td>
</tr>
</tbody>
</table>

**Whole Alkylate Properties**

<table>
<thead>
<tr>
<th>Property</th>
<th>( C_3^+ )</th>
<th>( C_4^+ )</th>
<th>( C_5^+ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>RON</td>
<td>89-92</td>
<td>94-98</td>
<td>89-92</td>
</tr>
<tr>
<td>MON</td>
<td>88-90</td>
<td>92-95</td>
<td>88-90</td>
</tr>
<tr>
<td>ASTM D86 T50 °C</td>
<td>93</td>
<td>111</td>
<td>124</td>
</tr>
<tr>
<td>T90 °C</td>
<td>127</td>
<td>125</td>
<td>153</td>
</tr>
<tr>
<td>End Point °C</td>
<td>189</td>
<td>202</td>
<td>224</td>
</tr>
<tr>
<td>Acid Usage, kg/m³ alkylate</td>
<td>72-96</td>
<td>36-60</td>
<td>36-72</td>
</tr>
</tbody>
</table>

**MULTIPLE FEEDSTOCKS**

Olefin feed composition is not normally an independent variable in an alkylation unit. STRATCO® has unique expertise in the design of alkylation units which keep different olefin feeds separate and alkylates 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 in optimising the design of the alkylation unit. As a result, alkylate product quality requirements can be met at more economical reaction conditions and with reduced acid consumption.

**INVESTMENT ECONOMICS**

Alkylation economics vary from region to region and from season to season. Currently the high demand for gasoline in the USA and the Far East is maintaining high gasoline prices even in Western Europe, which is known to be long in gasoline and short in diesel. Studies based on generic refinery modelling show that a 100,000 BPSD (15,900 m³/day or 4.4 million tonnes/year) FCC based refinery could increase Euro-grade gasoline production by up to 1000 m³/day with a simple \( C_4^+ \) alkylation investment. Economic studies show that such an investment could produce a simple payback of around 2 years including an on site acid regeneration unit. Alternatives such as coupling the alkylation unit with MTBE, ETBE or Dimerisation and Amylene (pentene) alkylation are more difficult to evaluate on a generic basis since the benefits depend more on local factors such as the demand for higher octane grades and isobutane availability. Political issues such as the acceptability of MTBE and Ethanol subsidies also have a major impact.

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**Pam Pryor** is the Manager of Licensing & Marketing for DuPont’s STRATCO® Alkylation Technology based in Leawood, Kansas in the USA. Ms. Pryor has a Bachelor of Science degree in Petroleum Engineering from the University of Kansas. She joined STRATCO® in January 1986 and has held various technical and managerial positions since that time. Currently, she is responsible for STRATCO® licensing and marketing activities in The Americas and the Far East.