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Isomerization process carried out in Petroleum Refining

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Abstract:
Isomerization is used for the conversion of n-paraffin to iso paraffin to provide good quality gasoline and to provide additional feed stock for alkylation units. Isomerization process complements catalytic reforming process (Catalytic reforming is used to convert hydrocarbons to aromatics which have high octane rating) in upgrading the octane number of refinery naphtha streams. The different isomerization technologies are briefly reviewed in this paper
Key words: *paraffins, isomerization, octane number, naphtha*

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I. Introduction

The world demand for gasoline and petrochemicals has experienced steady growth over the past few decades. Increasingly stringent regulations have been imposed by most countries thereby increasing the demand for cleaner fuels. As a result gasoline composition has been adjusted to a greater extent using the isomerization technique thereby meeting the requirement of clean fuel and premium gasoline grades.

Isomerization is used to convert n-paraffin to iso paraffin to produce good quality gasoline with high octane number.

The isomerization process is used to upgrade the octane number of light naphtha fractions. It also reduces benzene content by saturation of the benzene fraction.

II. Commercial Isomerization processes

1. Butamer process
2. Butomerate process
3. Hysomer process
4. Iso-Kel process
5. Isomate process
6. Isomerate process
7. Penex process
8. Pentafining process

2.1 Butamer process

The UOP (Universal Oil Products) ButamerTM Process isomerizes normal butane (n-C4) to isobutane (i-C4). Refineries use isobutane as a feedstock for their alkylation units to produce high octane motor fuel alkylate. The catalysts used in Butamer reactors are very sensitive to contaminants (water and sulfur) in the feed gases. n-Butane is isomerized to isobutane, which is further dehydrogenated to isobutene. The Butamer process has a fixed-bed reactor containing highly selective catalyst that promotes the conversion of n-butane to isobutane equilibrium mixture. Isobutane is then separated in deisobutanizer tower. The n-butane is recycled with make-up hydrogen. The isomerization reaction occurs at a relatively low temperature, Heart of the Butamer process is a new platinum-containing catalyst. This catalyst makes it possible to operate the reactor at relatively low temperatures, eliminates excessive n-butane recycle. Between 600° and 850° F, equilibrium concentration of isobutane in the total butane effluent ranges from 40 to 49%[1]. The process operates under hydrogen pressure. This keeps catalyst clean

2.2 Butomerate process

In a liquid phase process wherein butane is isomerized to isobutane in a reaction zone in the presence of an aluminum halide and a hydrogen halide promoter at temperatures in the range of about 50^0 to 250^0Fand wherein hydrogen halide is recovered and recycled to the reaction, the improvement which comprises removing hydrogen from the recycled hydrogen halide to the extent required to reduce the amount of hydrogen recycled to the reaction zone to less than 0.1 mol percent based on the butane entering the reaction zone[2].

2.3 Hysomer process

The Shell Hysomer process[3] uses pentane/hexane from light naphtha as the liquid feedstock. Naphtha splitters are widely used to split light naphtha, heavy naphtha and also LPG. The light naphtha (C5/C6) is combined with the recycle gas/ fresh gas mixture. The resultant combined reactor feed is routed to a feed/effluent heat exchanger, where it is heated and completely vaporised by the effluent of the reactor. The vapourised combined reactor feed is further heated to the desired reactor inlet temperature in the reactor charge heater. The hot charge enters the Hysomer reactor at the top and flows downwards through the catalyst bed, where a portion of normal and mono- branched paraffins is converted into higher branched (high octane) components. Temperature rise from the heat of reaction release is controlled by a cold quench gas injection into the reactor. Reactor effluent is cooled and subsequently separated in the product separator into two streams: a liquid product (isomerate) and a recycle gas stream returning to the reactor via the recycle gas compressor. The catalyst is a dual function catalyst consisting of platinum on a zeolite basis, highly stable and regenerable. Temperatures and pressure vary in a range of 230 - 285 ^{0}C and 13-30 bar, C5/C6 content in product relative to that in feed is 97% or better, and octane upgrading ranges between 8 and 10 points, depending on feedstock quality. The Hysomer process can be integrated with catalytic reformer, resulting in substantial equipment savings, or with iso-normal separation processes which allows for a complete conversion of pentane/hexane mixtures into isoparaffin mixtures.

2.4 Iso-Kel process

This process, developed by M. W. Kellogg Company[4], is also specifically for the isomerisation of *n* -pentanes and *n* -hexanes. It employs a precious metal, non-platinum catalyst as of 1/16th inch extrudates and operates at 700 to 850°F, 100 to 750 psig pressure.

2.5 Isomate process

Equal volumes of an n-hexane containing 5.4% of benzene (an inhibitor) and the catalyst(mesitylene:HCl:2$AlCl_3$) were mixed in a dry glass tube under nitrogen. The sample was then cooled with liquid nitrogen and sealed off by fusion with a torch under high vacuum. The sealed glass reactor was shaken continuously at 70°C for 16 hours. The sample was then cooled and opened. No HC1 or other gas was formed. The resulting phases appeared to be stable .The system was two-phase: a paraffin-rich upper phase and a catalyst-rich lower phase. Mesitylene is an active isomerization catalyst for paraffins.

The catalyst compound was made by shaking solid anhydrous aluminium chloride together with mesitylene (1,3,5-trimethyl benzene) while passing a stream of dry HCl gas through the slurry at ambient pressure and temperature. The reaction went smoothly and was complete in 3 hours[5].

$\text{Mesitylene}_{(1)}+HCl_{(g)}+Al_2Cl_6 \rightarrow \text{Mesitylene:HCl:2}AlCl_3$

2.6 Isomerate process

Isomerization processes with a straight chain of hydrocarbon molecules rearrange to form branched hydrocarbons and are one of the best processes for producing isomerate with a high octane number. Isomerization reactions are used extensively for production of both lower and higher paraffins (isoalkanes). Branched C5-C6 paraffins have high octane numbers and are good motor gasoline components. Isopentane and isobutane are valuable feed for synthetic rubber production[6]. Isobutane is also used for alkylbenzene, high-octane ethers production, methyl-tret-butyl ether (MTBE) is the most popular of those. Higher alkanes isomerization favours decreasing of diesel fuel and engine oil pour point.

2.7 Penex process

The Penex process was introduced by Universal Oil Products as a means of isomerising the unchanged n-pentane and n-hexane obtained from platformates. Pentane and hexane are separated from the latter and passed once through a bed consisting of a dual-function platinum-alumina catalyst. By isomerisation the octane number of an n-pentane feed may be raised from 62 to 93, that of n-hexane from 25 to 100. Complete isomerisation is not possible, but the high activity of the catalyst allows conversion at lower temperatures which favour the equilibrium.

2.8 Pentafining process

The Pentafining process , developed by the Atlantic Refining Company[7], employs a highly selective platinum catalyst on silica-alumina support to effect pentane and hexane isomerisation with little yield loss. A number of process combinations are possible- For eg with natural gasoline and hydrogen as starting material, the feed is depentanized and heavy material goes to a low pressure reformer. The pentane stream is split and the n-fraction is combined with recycle and make up hydrogen and charged to the reactor. Hydrogen is removed from the effluent, which is degassed and fractionated to separate n- and iso cuts.

III. Conclusion:

The different isomerization processes are briefly described here. Each process is having its own advantages and disadvantages. Depending upon the necessity and economic viability, any one of the above processes can be selected for producing the isomerate.

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