PERP Program – On-Purpose Octene-1
New Report Alert

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Nexant's *ChemSystems* Process Evaluation/Research Planning program has published a new report, ***On-Purpose Octene-1 (05/06S10)***. To view the table of contents or order this report, please click on the link below:
http://65.74.131.134/reports/index.cfm?catID=2

Introduction

The alpha olefins business is complex. A full-range alpha olefins plant produces, depending on technology, a range of olefins with even numbered carbons. Alpha olefin producers serve such diverse markets as polyolefins, synthetic lubricants, detergent intermediates, oilfield chemicals, paper industry additives, etc. Each derivative market has its own characteristics in terms of demand growth, selling geography, customer base, customer fragmentation, quality requirements, off-take volumes, etc. Even a naphtha cracker with its multiplicity of products, ethylene, propylene, C_4s, aromatics, etc, does not serve markets with such different characteristics.

The business of managing an alpha olefins business is therefore a challenge of balancing the requirements of serving these diverse markets while maximizing revenue across the whole spectrum of alpha olefin fractions produced.

Owing to the fact that certain end-markets are more profitable than others, it has been a goal of industry for many years to develop technologies that can selectively target certain markets and make only one specific alpha olefin cut. Such approaches have now been developed and are termed "on-purpose" alpha olefin technologies. On-purpose butene-1, hexene-1 and octene-1 technologies are now commercial. These alpha olefins are all key components of the fast growing LLDPE business. As described in this report there are now several additional emerging routes for making octene-1 on-purpose, in addition to the one current technology.

On-Purpose Octene-1 Technologies

Octene-1 is primarily used as a comonomer in the manufacture of linear low density polyethylene. The current technology standard for the production of linear alpha olefins such as octene-1 is based on ethylene oligomerization. However, the relatively fixed nature of full-range oligomerization product distributions creates supply/demand imbalances, requiring comonomer producers to cross-subsidize the lower value products in their product sales.

Sasol's coal-based high temperature Fischer-Tropsch technology produces an Anderson-Schulz-Flory distribution of hydrocarbons with high alpha olefin content. Sasol's first commercial on-demand octene-1 plant was commissioned in Secunda, South Africa in 1998. This extraction based technology consists of a combination of acid extraction, normal and extractive distillation processing steps that extracts and purifies octene-1 from a fuel stream. Rapid growth in comonomer demand has led to the construction of a second octene-1 plant which was commissioned in 2004. This process uses an innovative azeotropic distillation process together with extensive energy integration to further improve the extraction process efficiency. Depletion of the octene-1 capacity of Sasol's Secunda complex coupled with rapid global demand for octene-1 has necessitated the search for alternative on-purpose production routes to octene-1. The Sasol F-T process is the only octene-1 on-purpose process in commercial operation. However, there exist three technologies that are currently being considered for on-purpose octene-1 production.

Sasol Ethylene Tetramerization

Phillips, prior to its merger with Chevron (to form Chevron Phillips), developed a family of chromium-based catalysts which trimerize ethylene to hexene-1 with high selectivity. This development effort successfully led to the construction and operation of an on-purpose hexene-1 plant in Qatar.

In order to achieve such high selectivity to hexene-1, a fundamentally different chemical pathway must be at work compared to full-range technologies. The key difference between this catalyst system and conventional oligomerization catalyst is the propensity of the Phillips chromium based catalyst to form 7-membered ring metallacycles.

The potential for ethylene tetramerization to afford octene-1 was thought to be highly unlikely as this would require expansion of the 7-membered ring to a 9-membered ring. 9-Membered rings are the least stable ring size and should not be a favored structure. However, researchers at Sasol have found a catalyst system and operating conditions that does indeed allow, in fact favors under certain conditions, formation of the 9-membered metallacycle in relation to the 7-membered ring. This provides a fairly selective reaction to octene-1.

The Sasol catalyst system is an aluminoxane-activated chromium/$((R^2)_2P)_2NR^1$ system. A number of diphosphino ligands with various substituents on both the N and P have been evaluated. All catalysts gave good selectivity for octene-1 and varying quantities of hexene-1, along with other cyclic C_6s such as methylcyclopentane and methylene cyclopentane. Relatively small amounts of C_{10}-C_{16}'s and polymer are also made. The use of modified methylaluminoxane (MMAO) as an activator leads to substantially higher productivities.

Sasol Heptene-1 Based Process

Sasol has been very successful in the octene-1 comonomer business. However, the capacity of Trains I and II combined is 96 thousand metric tons per year and this is bumping up against the limit of the octene-1 contained in Sasol's Secunda synfuels stream. One approach to overcome this limitation is to exploit the availability of unused heptene-1 in the Secunda synfuels stream. In order to transform heptene-1 to octene-1, five process steps are required:

- Separation of crude heptene-1

- Hydroformylation of heptene-1 to *n*-octanal
- Hydrogenation of *n*-octanal to 1-octanol
- Dehydration of 1-octanol to octene-1
- Final purification of octene-1 to comonomer grade

The chemistry of converting heptene-1 to octene-1 is shown below:

$$CH_3CH_2CH_2CH_2CH_2CH{=}CH_2 + CO/H_2 \longrightarrow CH_3CH_2CH_2CH_2CH_2CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}H$$

$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}H + H_2 \longrightarrow CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2OH$$

$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2OH \longrightarrow CH_3CH_2CH_2CH_2CH_2CH_2CH{=}CH_2 + H_2O$$

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Sasol has announced that a new octene-1 plant using all of these process steps is under construction at Sasol's Secunda complex. This plant will be the third and largest of three octene-1 trains at that location, but the first to employ a hydroformylation step. The latest train will produce 100 thousand metric tons of octene-1, and is scheduled to go into operation during the second half of 2007.

Dow Butadiene Telomerization Route

Dow has been granted a patent describing the telomerization of butadiene with methanol in the presence of a palladium catalyst to yield 1-methoxy-2,7-octadiene. The 1-methoxy-2,7-octadiene is then hydrogenated to 1-methoxyoctane. Subsequent cracking of the 1-methoxyoctane gives octene-1 and methanol for recycle. The pertinent reactions are shown below:

$$2\,CH_2{=}CH{-}CH{=}CH_2 + CH_3OH \longrightarrow CH_3O{-}CH_2CH{=}CHCH_2CH_2CH_2CH{=}CH_2$$

Butadiene Methanol 1-Methoxy-2,7-Octadiene

$$H_3CO{-}CH_2CH{=}CHCH_2CH_2CH_2CH{=}CH_2 + 2H_2 \longrightarrow CH_3O{-}CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$$

1-Methoxy-2,7-Octadiene 1-Methoxyoctane

$$CH_3O{-}CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3 \longrightarrow H_2C{=}CH{-}(CH_2)_5{-}CH_3 + CH_3OH$$

1-Methoxyoctane Octene-1 Methanol

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It is believed that Dow is not planning to separate and purify butadiene for the telomerization reaction, but instead is aiming to use the crude C_4 stream, as virtually all of the components in the C_4 stream (with the exception of the small amounts of acetylenic materials) are inert to the telomerization reaction conditions, except of course for the butadiene itself. Thus, the telomerization will serve as the means of both separating and reacting the butadiene. The remaining C_4's after the telomerization will be lightly hydrotreated to remove any unreacted butadiene leaving a C_4 cut identical to what would normally be referred to as raffinate-1.

Economic Analysis

Cost of production estimates for the following processes are presented in the report. All processes are sized such as to produce 100 KMTA of octene-1:

- INEOS/BP Full-Range Alpha Olefins (commercial)
- Sasol Recovery from Synfuels (commercial)
- Sasol Heptene-1 Based process (under construction)
- Dow Telomerization of Mixed C_4s (under construction)
- Sasol Ethylene Tetramerization (developing)

Capital costs are logically higher for those processes involving higher process step counts, less pure feed streams, and larger total capacity. Thus, the highest total plant capital is required by the BP full-range alpha olefins plant of 385 KMTA capacity (100 KMTA of which is octene-1). Close behind is the Sasol multi-step process starting with a mixed C_7 feed stream. Ranking third in terms of capital intensity is the Dow process using a mixed C_4s feed stream.

Net raw materials costs, not unexpectedly, are highest for those processes using ethylene as the major feedstock and lowest for those processes using fuel based streams.

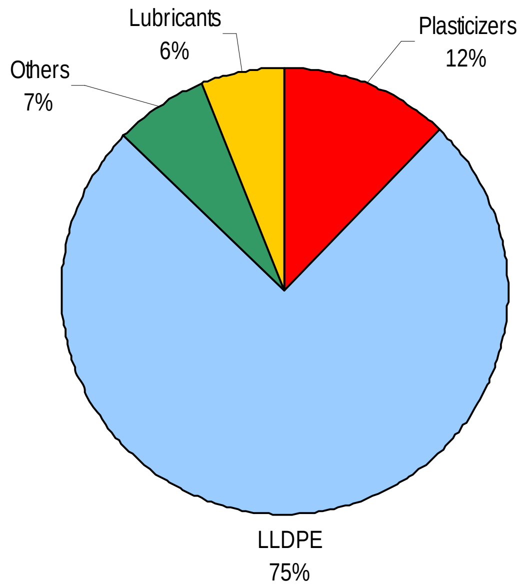
Commercial Analysis

Polyethylene/plastomers dominate octene-1 demand. Dow Chemical with its DOWLEX™ business dominates the global octene-1 market. Although other C_8-LLDPE solution polymerization technologies exist, e.g., SCLAIR®/SCLAIR II® from Nova, Dow Chemical dominates. In order to maintain its leadership position in C_8-LLDPE, the company has made tactical investments in securing competitive octene-1 supply. For example, investment in the first Sasol octene-1 line was supported by Dow Chemical. According to press reports the company is now engaged in the commercialization of its own octene-1 process at Tarragona in Spain via butadiene telomerization.

Plastomers are a niche performance product, but growth has been modest in recent years. The use of octene-1 in plasticizer production also remains a niche application where a combination of properties such as lower volatility is needed.

The chart below shows global distribution of octene-1 consumption by end use for 2006.

Global Distribution of Octene-1 Consumption by End Use, 2006



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The majority of octene-1 supply is from full-range alpha olefins complexes, and the loss of the Pasadena plant has tightened supply considerably. Octene-1, in terms of revenue generation, is very important to the full-range alpha olefin producer, irrespective of technology. The industry is moving to remarkably high operating rates for octene-1, which may prove unsustainable. This has prompted increased research and development activity in octene-1 technology as well as the commercialization of new technology based on butadiene and heptene-1 such as those described in this report.

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