PERP Program
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Developments in Alpha Olefin Production Technology (97/98S14)

The conventional route to linear alpha-olefins (LAO) is via oligomerization of ethylene. The three largest producers of LAOs via ethylene oligomerization are Shell, Amoco, and Chevron. The technologies employed yield a relatively fixed range of products having a distribution that does not match the pattern of market demand. Demand is growing fastest in the C_6-C_{10} range. Therefore, a major challenge for producers has been to control the oligomerization process and/or incorporate other processes in order to best tailor output to market demands.

Sasol has now become the fourth major producer of LAOs (currently C_5s and C_6s) via recovery from coal based hydrocarbon streams. By the nature of its technology, Sasol can select individual products and capacity within the limits set by the raw gasoline feedstock composition and production rate. The Sasol process was assessed in PERP Report 93-6.

An assessment of a Phillips route to hexene-1 employing a chromium based ethylene trimerization catalyst was made in PERP report 94/95S12. Butene-1 is also produced by ethylene oligomerization (dimerization), but the more important commercial sources are as byproducts of refining and petrochemical steam cracking operations.

This new report reviews processes to LAOs being offered for license by UOP and IFP and examines an interesting approach to LAOs patented by BP Chemical. Speculative economics for comparison with the existing oligomerization routes to LAO are presented.

UOP's Linear-1™ process employs a homogeneous Ni catalyst. The structure of the particular ligand used in the catalyst has a strong influence on the results. Although one catalyst may produce mainly C_4 to C_{12} alpha-olefins, other catalysts will yield higher or lower molecular weight distributions depending mainly on the size of their ligand cone angles. Although twenty-four different ligands were studied, it appears that 2-diphenyl-phosphino-1-naphthalene sulfonic acid is used in the Linear-1™ process.

UOP claims that the Linear-1™ process is flexible and can be operated between the Schulz-Flory constants of 0.55 and 0.67 by making simple adjustments to the operating parameters. This results in varying the C_4 to C_{10} products from 59 to 80 weight percent.

IFP's AlphaSelect™ is an oligomerization process that operates in the liquid phase using a proprietary soluble catalyst system. The catalyst system is composed of a catalyst and a cocatalyst. The ratio of the catalyst and cocatalyst can easily be varied and tightly controlled to permit different product distributions.

IFP claims that the catalyst system is nontoxic and there are no heavy metals or group VIII metals employed. The spent catalyst is oxidized to eliminate residual hydrocarbons. The resulting solid oxide material is nontoxic and easy to handle. The catalyst employs a solvent that enables the isolation of all the various alpha-olefins constituents even those above C_{12} if desired, although the technology is oriented toward producing alpha-olefins for polyethylene comonomers (C_4-C_8), plasticizer alcohols (C_6-C_{10}), and polyalpha-olefins (C_8-C_{12}).

BP Chemical has been awarded a patent that can be used to produce lower alpha olefins from ethylene. Although BP has not announced plans to commercialize this technology, Chem Systems has evaluated the BP approach based on a speculative process design. The essence of BP's approach is to allow ethylene to undergo oligomerization using relatively low cost, low activity oligomerization catalysts, but to then break down any higher molecular weight internal olefin oligomers (which have lower commercial value) by way of metathesis of these materials with additional ethylene to yield commercially valuable lower alpha-olefins.

This method is reminiscent of Shell's SHOP process. However, the unique aspect of the BP approach is the matching of reaction conditions of both the oligomerization and metathesis steps so as to allow the use of a single reactor with two catalyst beds.