

## PERP Program – New Report Alert

January 2004

Nexant's ChemSystems Process Evaluation/Research Planning program has published a new report, *Alpha Olefins (02/03-4)*.

### Background

By the end of 2002 the global demand for linear alpha olefins ( $C_4$ - $C_{20+}$ ) amounted to around 3.4 million tons. Alpha olefin markets cover polyethylene comonomers, synthetic lubricants, detergent intermediates, paper sizing agents, lubricant additives, oilfield chemicals and a myriad of small fine and performance chemical uses. The industry has been hit in recent years by the global slowdown in chemicals demand across virtually all segments of the alpha olefins market.

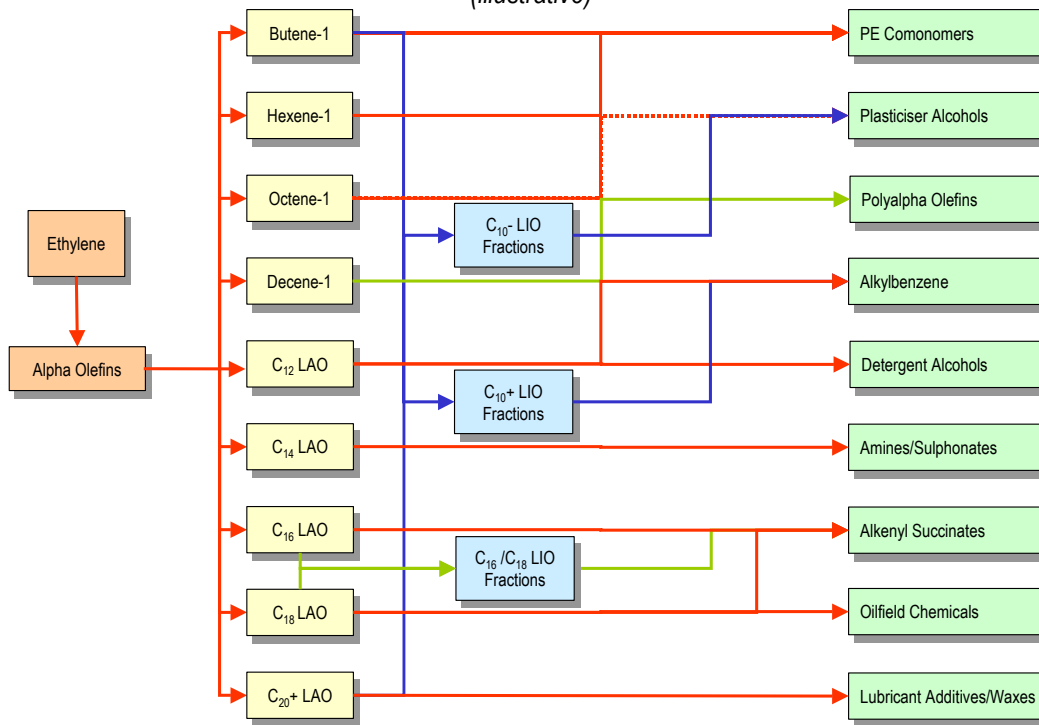
Alpha olefin producers fall into two categories; full range, i.e. those that use ethylene oligomerization to provide a  $C_4/C_6$  to  $C_{20+}$  range of products, and on-purpose, i.e. butene-1 and hexene-1 only (today). Full range producers include the majors like BP, Chevron Phillips and Shell with smaller units operated by Mitsubishi, Idemitsu and Nizhnekamsk. The other full range producer, Spolana closed in 2003. Sasol occupies a unique position in terms of alpha olefin supply in that it manufactures synthetic gasoline from coal-based synthesis gas using Fischer Tropsch processes. This stream is rich in alpha olefins which are extracted selectively. Sasol produces hexene-1 and octene-1, and it recently has begun extracting higher  $C_{11}/C_{12}$  fractions for captive detergent range alcohols production. Much of the world's butene-1 supply today comes from on purpose production from petrochemical  $C_4$  streams linked to liquids crackers. In regions with low cost ethylene, e.g. the Middle East, butene-1 is made mainly on purpose from ethylene by dimerization. Recently in Qatar the Q-Chem I project started up the first on purpose hexene-1 unit using ethylene trimerization.

Looking ahead the alpha olefin industry is growing at around 4.9 percent per year, but there is an increasing divergence between comonomer alpha olefin demand growth and that of higher fractions. Consequently, R&D efforts have focused on reducing the carbon number make of full range units or developing new on purpose routes to comonomers.

As Figure 1 clearly demonstrates, the alpha olefins business is very complex as major producers serve a broad range of chemical industry segments from polyethylene commoners ( $C_4$ - $C_8$ ) through synthetic lubricants ( $C_{10}$ ) and detergent intermediates ( $C_{12}$ - $C_{14}$ ) to oilfield chemicals, paper sizing agents ( $C_{16}$ - $C_{18}$ ), lubricant additives ( $C_{20+}$ ), and wax rheological modifiers ( $C_{24+}$ ). In addition there are a myriad of fine and performance chemical intermediates.

The formidable challenge for the full-range alpha olefins producer is that each market segment served has very different behavior in terms of market size and growth, geography, fragmentation, need for technical service, etc.

**Figure 1** Schematic of The Alpha Olefin Business  
(illustrative)



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The challenge also comes from logistics as butene-1 is a gas and needs to be moved in dedicated refrigerated isotanks, pressurized railcars or specially designed vessels. Most alpha olefins are liquids, although higher fractions are solid and can be moved in liquid form in isotanks fitted with heating coils.

Up to dodecene-1 (C<sub>12</sub>) there is little difference in properties of the alpha olefins produced from different sources. Beyond dodecene-1, however, there arise significant variations in alpha olefin properties such as concentration of alpha olefin, internal olefin or branched species. Some applications are favored by more linear species, others benefit from modest branching. On purpose isomerization can improve suitability for specific applications.

### Commercial Full Range Processes

The global leaders in the alpha olefin business are BP, Chevron Phillips and Shell. Each operates its own process which provides a different product spectrum.

The characteristics of the various alpha olefin processes and distributions are described as follows:

Chevron Phillips employs an approach of a dilute triethylaluminum catalyst to produce a very broad alpha olefin distribution. Chevron Phillips produces C<sub>4</sub> to C<sub>30+</sub> fractions with pure C<sub>16</sub> and C<sub>18</sub> fractions. Chevron Phillips products are highly linear with high levels of alpha olefins even at high carbon number.

BP employs a more complex approach with a concentrated triethylaluminum catalyst system to peak the alpha olefin distribution in the comonomer range, with the result that higher olefin products, tetradecene-1 and above, are more branched than Chevron Phillips products of equivalent carbon numbers.

Shell operates the **Shell Higher Olefin Process (SHOP)**, combining an alpha olefin process catalyzed using a ligand modified nickel based system with a metathesis step to produce a broad product distribution of C<sub>4</sub>-C<sub>10</sub> materials, selected higher fractions, and internal olefin fractions dedicated to captive detergent intermediates production.

### **Commercial On Purpose Processes**

Although some full range units co-produce butene-1, most of the butene-1 manufactured today is made on purpose by extraction and distillation from petrochemical C<sub>4</sub> streams. In places like the Middle East where ethylene is gas-based with limited access to unsaturated C<sub>4</sub> streams, butene-1 is mainly made by ethylene dimerization.

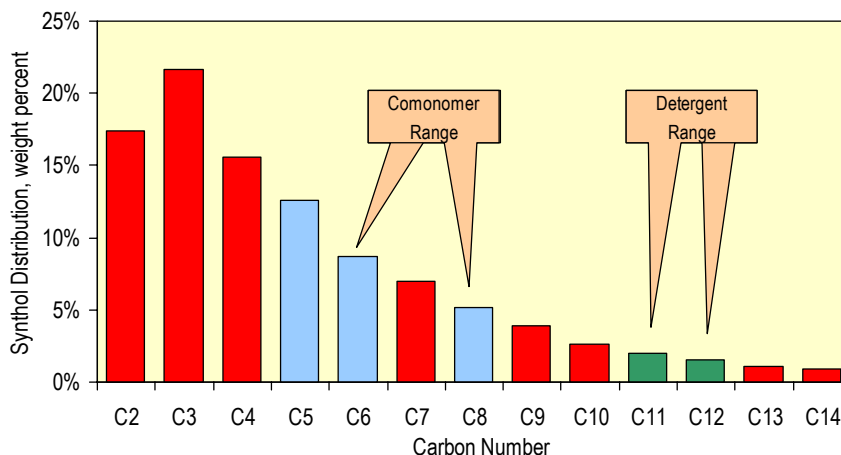
During 2002/2003 as part of the Q-Chem I project in Qatar, Chevron Phillips brought on stream the first ethylene trimerization unit for on purpose hexene-1 production.

Nexant ChemSystems classifies Sasol technology as on purpose alpha olefin production. As Figure 2 illustrates, the Sasol SYNTHOL® process at Secunda, South Africa, provides a distribution of odd and even numbered carbon numbers. In the early 1990s Sasol began extracting hexene-1 (and even pentene-1) for the comonomer market. Since then Sasol has continued to expand hexene-1 capacity and in 1998 added octene-1 production at Secunda. More recently Sasol has begun extracting a C<sub>11</sub>/C<sub>12</sub> cut (mainly alpha olefin) for captive detergent alcohols production.

### **New Full Range Processes**

In the main, the drive behind new developments in full range alpha olefin technology has been to narrow down the carbon number distribution to the C<sub>4</sub>-C<sub>10</sub> range. The catalysts employed by Axens (ALPHASELECT®) and Sabic/Linde (ALPHA-SABLIN®) are based on zirconium/aluminum systems and provide narrow carbon number distributions but with branched higher fractions. The UOP/Dow process (LINEAR-1®) provides a broader distribution.

**Figure 2 Sasol Alpha Olefin Distribution**  
(weight percent)



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## New On Purpose Processes

While there is still considerable research activity into ethylene trimerization, olefin metathesis has become the focus of attention in that ABB Lummus has developed a process to convert butylenes contained in petrochemical C<sub>4</sub> streams into hexene-1 with ethylene and propylene co-products. The process involves a complex number of steps, especially if crude C<sub>4</sub>s are the starting point. Crude C<sub>4</sub>s can be hydrogenated selectively to provide a butylenes-rich C<sub>4</sub> stream. Isobutylene can be removed via two-stage MTBE or a de-isobutenizer column. A Nexant ChemSystems interpretation of the process is provided in the report. The process scheme proposed includes BUTENEX® (from Krupp Uhde) and super-base catalyzed olefin isomerization to increase process flexibility in terms of the C<sub>4</sub> streams that can be accommodated.

Technology to convert butadiene into octene-1 has been developed and available for commercialization. However, the employment of this technology can only be made on a tactical basis. It is possible, though to combine butadiene to octene-1 conversion with a broader C<sub>4</sub> processing scheme with butene-1 and hexene-1 production. A possible configuration of such a complex is presented in the report.

## Economics

This report provides economic analyses for both commercial (4 full range and 5 on purpose) and new (3 full range and 4 on purpose) processes.

Summary tabular and bar-chart comparisons are supported by individual cost of production estimates.

## Supply/Demand

The report details end-use applications as well as global alpha olefin demand by end use for 2002 and by 6 regions with projections to 2015. Consumption of individual products is also provided by end use and by region, again with projections to 2015. Sources of alpha olefin supply are likewise presented.

## Strategic Issues

The report also discusses two key strategic issues:

- The development of chemicals production based on gas-to-liquids technology
- The need for increased investment in on purpose comonomer production

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