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A REVIEW PAPER ON PRODUCTION OF LINEAR ALPHA-OLEFINS BY UNDERGOING OLIGOMERIZATION OF ETHYLEN

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Abstract - The following paper gives an overview to the production of linear alpha-olefins. It also focuses on the various processes which are being used by the companies, their yield pattern and the applications of linear alpha-olefins according to the chain length of the product molecule. The monomer used as raw material is ethylene and the process focused is oligomerization. Oligomerization gives the products which are short chained (C₄-C₂₀₊). This process differs from polymerization by the degree of polymerization which is very low in case of oligomerization and is very high in case of polymerization.

I. INTRODUCTION

Alpha-olefins are straight-chain hydrocarbons characterized by the double bond in the terminal or alpha position. Production of linear alpha-olefins (LAOs) based on ethylene oligomerization yields an entire range of even-numbered carbon chain-length LAOs rather than a single product. Chain lengths vary from four carbons (butene-1) to more than thirty carbons (expressed as C₃₀₊). Since 1994, Sasol Chemical Industries has recovered C₅ and C₆ alpha-olefins contained in product streams for its coal-based synthetic fuel plant in Secunda, South Africa. It is the only producer of pentene-1 (C₅) in commercial quantities and has the potential to recover other LAOs.

The physical properties, and, therefore, commercial applications, vary depending on the chain length. Butene- 1 is a gas at room temperature and C₆-C₁₈ LAOs are clear, colourless liquids, whereas C₂₀₊ LAOs are waxy solids. The utility of LAOs is usually because of the reactivity of the double bond. The most common commercial reactions involving LAOs include oxo reactions (hydroformylations), oligomerization/polymerization, simple addition reactions, alkylation reactions, sulfations/sulfonations and oxidations. Even-numbered alpha-olefins below C₂₀ are available

individually or in narrow carbon ranges. C₂₀₊ alpha-olefins are generally consumed in a broad range of chain lengths and some of these products contain high levels of other impurities. The below is a table given which summarizes major applications for linear alpha-olefins by carbon chain length:

Linear alpha-olefins applications by chain length	
C ₄ -C ₈	Polymer and polyethylene comonomer
C ₆ -C ₈	Low-molecular-weight fatty acids and mercaptans
C ₆ -C ₁₀	Plasticizer alcohols
C ₁₀ -C ₁₂	Polyalphaolefins and other additives for lubricants, amine oxides and amines
C ₁₀ -C ₁₆	Detergent alcohols, non-ionics and oil field chemicals
C ₁₆ -C ₁₈	Oil field chemical, lube oil additives and surfactants
C ₂₀ -C ₃₀₊	Oil field chemicals and wax replacement

Most linear alpha-olefins are currently commercially produced by ethylene oligomerization. The products of the oligomerization consist of even-numbered carbon chains ranging from C₄ to C₃₀₊. There also exist other alpha-olefin synthesis routes which include Sasol's Purification Process, Paraffin Wax Cracking, Dehydration of Alcohols and Isomerization of Internal Olefins. But the commercial production of linear alpha olefins is by ethylene oligomerization this is because they have relatively small amounts of branched and internal olefin isomers and paraffin impurities.



II. LITERATURE SURVEY

The first commercial production of linear alpha-olefins by ethylene oligomerization is in 1966. All but one LAO producer worldwide currently uses an oligomerization process, and the catalyzed chain growth chemistry is similar in all of the methods. However, modifications by some producers at different stages of the reaction sequence lead to different product and chain-length distributions.

There are three main processes currently in use—Chevron Phillips Chemicals (CPChem), Ethyl and Shell. The CPChem route uses a single stage for chain growth and displacement reactions, but is the least flexible of these processes in product distribution. The Ethyl process, which uses two separate steps for chain growth and displacement, gives greater flexibility in product distribution at the expense of increased process complexity and increased branching of heavier fractions. Shell's process is the most complex process of these three routes. It feeds selected alpha-olefins to an isomerization-disproportionation unit that can produce internal olefins for subsequent internal consumption or merchant sale at generally higher market values than the feed materials. The SHOP (Shell Higher Olefins Process) process is the most flexible with regard to product distribution. The isomerization-disproportionation part of the SHOP process converts alpha-olefins to internal olefins. The chemical composition and quality of the alpha-olefin products vary somewhat from process to process. The CPChem and Shell processes result in a higher alpha-olefin content in C₁₂₊ cuts compared with the Ethyl process. Higher linearity in alpha-olefins is desired in some end-use applications, while the higher branching in C₁₄-C₁₈ olefins produced by the Ethyl process is preferred in some other applications.

The different processes also yield different chain-length distributions. The following table presents the typical product distribution for each of these processes, although each has some flexibility in chain-length distribution.

Typical Chain-length Distribution of Linear alpha-Olefins by Process (percent by weight)			
	CPChem	Ethyl	Shell
C ₄	14	0	7-14
C ₆ -C ₁₀	41	70-77	25-41
C ₁₂ -C ₁₄	19	21-28	15-18

C ₁₆ -C ₁₈	12	0	11-15
C ₂₀₊	14	2	14-42

The processes used by INEOS and CPChem are based on Ziegler chemistry using ethylene and a triethyl-aluminum catalyst to promote chain growth of even-carbon-number alpha-olefin molecules. In both of these methods, the chain-length distribution of the linear alpha-olefin product can be changed to a limited extent by altering operating conditions. Shell's SHOP ethylene oligomerization route to alpha-olefins differs from the others in that it uses a proprietary nickel complex catalyst in the initial chain-growth step and it can convert alpha-olefins to internal olefins of a desired carbon number by isomerization and disproportionation.

Chevron Phillips' process uses a technology developed by Gulf Oil Chemicals Company, which Chevron Acquired in 1985. This one-step conventional Ziegler process combines high-temperature addition of ethylene and displacement of the generated aluminum alkyls to produce linear alpha-olefins. Ethylene reacts with the triethylaluminum growth products to yield even-numbered carbon olefins by displacement. Typical reaction conditions are 175- 290°C at pressures of 2,000-4,000 psi. The resulting carbon number range for this process is C₄-C₃₀₊. The catalyst used by Chevron Phillips company is Cr/pyrrole. This catalyst gives a productivity of 100,000 g/gCrh (at 54 bar). Catalyst selectivity is 94.5@ 68% conversion. Purity of 1-hexene is 99.6%. The curve typically is a geometric distribution with ranges as follows:

	Percent by weight
C ₄	14
C ₆ -C ₁₀	41
C ₁₂ -C ₁₄	19
C ₁₆ -C ₁₈	12
C ₂₀₊	14

The process used by INEOS Company consists of three main steps. In the first step, ethylene is oligomerized by trialkylaluminum growth promotion in a process similar to the one-step process. Typical reaction conditions are temperatures of 116-132°C and pressures of 2,700-3,000 psi. The second step is called the



displacement step in which the trialkylaluminum compounds formed in the first stage are displaced with ethylene to yield linear alpha-olefins in the C₄-C₁₈ range and to regenerate the triethylaluminum for recycle. Reaction conditions range from temperatures of 260-316°C and pressures of 230-250 psi. The third step is called the product separation step in which the unconverted ethylene from the growth and displacement reactor stage is processed for recycle and separates the individual C₄-C₁₈ olefins. The typical product distribution by chain-length range exhibits a Poisson distribution, as follows:

	Percent by weight
C ₄	12
C ₆ -C ₁₀	54-60
C ₁₂ -C ₁₄	20-25
C ₁₆ -C ₁₈	5-7
C ₂₀₊	2

Unlike the Ethyl and CPChem processes, which use a triethylaluminum catalyst, the ethylene oligomerization step in SHOP is based on a non-Ziegler catalyst system. SHOP's initial products are even-numbered carbon linear alpha-olefins from C₄ to C₂₀₊. Shell distills selected individual carbon-number products in the C₄-C₂₀ range and also supplies blends. The alpha-olefins not separated for sale are converted to C₈-C₁₈₊ internal olefins via a series of isomerization and disproportionation steps. The internal olefins are subsequently converted via a modified oxo process to detergent-range primary alcohols or sold. This process selectively yields high-purity linear alpha-olefins and detergent-range internal olefins. The SHOP process is very flexible and alpha-olefins can be withdrawn for sale or converted into internal olefins as desired. The chain-length distribution of alpha-olefins from the oligomerization step can be varied over the following range:

	Percent by weight
C ₄	7-14
C ₆	8-15
C ₈	9-14

C ₁₀	8-12
C ₁₂	8-10
C ₁₄	7-8
C ₁₆	6-7
C ₁₈	5-8
C ₂₀₊	14-42

There are other processes which are used commercially for the production of linear alpha olefins like Idemitsu's Ethylene Oligomerization Process, Vista's Alfene process, Exxon's Ethylene Oligomerization Process, Dupont's Versipol Process and Sabic/Linde Alpha-Sablin Process.

The Idemitsu's process also based on ethylene oligomerization, utilizes a proprietary zirconium-based catalyst system. The reported advantage of this process is that it produces fewer branched and internal olefins and fewer waxes are formed. Recommended reaction conditions are 100-150°C at pressures of more than 355 psi. Product distribution can be controlled within the constraints of the geometric pattern by appropriately selecting the reaction conditions and catalyst concentration and composition.

Exxon Research and Engineering Company has a low-pressure, low-temperature variation of the ethylene oligomerization process that uses a soluble catalyst derived from alkyl aluminum halides and transition metal compounds. Products are high-purity (greater than 98%) linear alpha-olefins with an even number of carbon atoms. Product distribution, which follows a geometric pattern, can be controlled by altering the process conditions. This process has not been commercialized.

DuPont has developed a one-step ethylene oligomerization process using its Versipol™ family of catalysts (such as a mixture of an iron tridentate catalyst and an alkyl aluminum cocatalyst) in the production of LAOs with low capital and operating costs and high product purity (98%). This system offers greater flexibility in the selection of the LAO product distribution.

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