Purity Aspects of Higher Alpha Olefins[1]

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ABSTRACT

The various processes which are used commercially to manufacture detergent range alpha olefins are compared in terms of the quality of the products obtained. Thermal cracking of *n*-paraffins gives the least pure olefins. Processes based on ethylene oligomerization are superior and, of these, the Shell SHOP (Shell Higher Olefins Process) process gives alpha olefins which are somewhat better in quality than those obtained from processes based on aluminum alkyl chemistry. The practical consequences of the presence of internal and vinylidene olefins, dienes and paraffins in alpha olefins are considered for the manufacture of alpha olefin sulfonates, linear alkylbenzene, epoxides, alkyl bromides, mercaptans and copolymers with ethylene (linear low density polyethylene). Low levels of impurities are desirable in most cases to minimize formation of unwanted byproducts, or to reduce the cost of bleeding of inert components, or to ensure that the quality of the final product meets the requirements of the marketplace.

INTRODUCTION

Alpha olefins in the C8-C20+ range have been manufactured for many years by thermal cracking of *n*-paraffins. Such olefins were not, by modern standards, particularly pure, but they were adequate for use as raw materials for the manufacture of surfactants. Very often these olefins were further processed by the manufacturer and did not appear as such in the marketplace. In recent years, various companies have developed new processes for the manufacture of high quality alpha olefins, and the latter have now become articles of commerce.

The chemical reactions which alpha olefins can undergo have been known for many years. Our purpose in this paper is to highlight the importance of olefin purity in practical applications, with examples taken mostly, but not exclusively, from the surfactants field. Although internal olefins are produced on a large scale by catalytic dehydrogenation or chlorination/dehydrochlorination of paraffins, they are only used captively and are not articles of commerce. We shall therefore not consider them here but restrict the discussion to alpha olefins.

ROUTES TO ALPHA OLEFINS

We shall consider only processes which have already achieved full commercial status. These fall into two types: those based on thermal cracking of larger molecules (high molecular weight *n*-paraffins) and those based on controlled polymerization (oligomerization) of ethylene.

Thermal Cracking

The first commercial application of a process of this type was the Shell wax cracker at Stanlow, which was commissioned in 1941. The feedstock used was slack wax, a byproduct of the solvent dewaxing of lubricating oils. Subsequently, further wax crackers were built at Pernis in the Netherlands and at Berre in France. In the USA, Chevron has used wax cracking as a route to alpha olefins.

In the process as currently operated by Shell, waxy distillates are extracted with urea to give the maximum *n*-paraffin content in the feedstock to the cracker. The conditions in the cracking furnace control the yield, distribution and quality of the olefins obtained. Because of secondary reactions, cracking of *n*-paraffins yields not only alpha olefins but also some conjugated and nonconjugated dienes and cyclics (1). Clearly, the olefin purity will also depend on the quality of the paraffinic feedstock. The figures (ex Chevron) in Table I indicate the levels of impurities which may be expected in cracked wax olefins.

Ethylene Oligomerization

All other commercial routes to alpha olefins employ ethylene oligomerization processes and organometallic catalysts of the Ziegler or related type. In contrast to olefins made by thermal cracking processes, olefins made by ethylene oligomerization contain only homologues with an even number of carbon atoms.

The processes operated by Gulf and by Ethyl in the USA differ in some points of detail but are both based on the catalytic influence of trialkyl aluminum (2). The processes differ in their operating conditions: the Ethyl process includes some recycling to give more control over product distribution and hence a higher yield of the most desirable C6-C14 alpha olefins than the Gulf process which is believed

TABLE I

Composition of a Typical Alpha-Olefin Product from the Cracking of a Paraffin with a Carbon Number Range of C21-C32

	(wt %)					
	C6-C7	C8-C10	C11-C12	C13-C14	C15-C18	C18-C20
Alpha olefins	83	83	88	88	89	86
Secondary olefins	12	11	5	5	3	1
Dienes	3.2	4	5	5	6	4
Paraffins	1.5	2	2	2	2	9
Aromatics	0.4	0.2	0	0	0	0

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[1] Presented at the AOCS Meeting in Toronto, May 1982.

TABLE II

Analyses of Alpha-Olefins from Ziegler-type Oligomerization of Ethylene with Recycle (Data from Ethyl Corp.)

	(wt %)						
	C6	C8	C10	C12	C12-C14	C14-C16	C16-C18
Linear α-olefins	97.5	96.5	96.2	93.5	87.0	76.0	62.7
Linear olefins with internal double bonds	0.6	1.2	1.6	1.5	4.2	5.0	8.2
β-Branched α-olefins	1.9	2.3	2.2	5.0	8.8	19.0	29.1
Paraffins	0.1	0.6	0.3	0.4	0.4	0.4	0.8

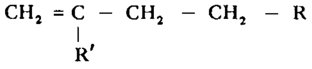
TABLE III

Composition of Alpha-Olefin Mixture from Catalytic High-Temperature Ethylene Oligomerization (wt-%) (According to Data from Gulf Oil Chemical Co.)

	(wt %)						
	C6	C8	C10	C12	C14	C16	C18
Linear α-olefins	97.0	96.0	95.0	94.0	93.0	92.0	91.0
β-Branched α-olefins[a]	1.4	2.5	3.4	4.6	5.6	6.6	7.8
Paraffins	1.4	1.4	1.4	1.4	1.4	1.4	1.4

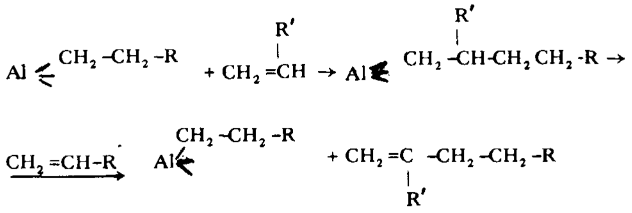
[a] Including very small amounts of olefins with internal double bonds.

not to incorporate a recycling stage. This advantage is achieved at the expense of a slight sacrifice in quality, as the Ethyl olefins tend to contain rather more branched components than olefins from the Gulf process (3). These branched components are mostly of the 2-ethyl- or vinylidene type



$$CH_2=\underset{\displaystyle R'}{\underset{|}{C}}-CH_2-CH_2-R$$

and result from further reaction of a product alpha olefins with an aluminum alkyl:



$$Al\leftarrow CH_2-CH_2-R+CH_2=\overset{\displaystyle R'}{\overset{|}{CH}}\rightarrow Al\leftarrow CH_2-\overset{\displaystyle R'}{\overset{|}{CH}}-CH_2CH_2-R\rightarrow$$

$$\xrightarrow{CH_2=CH-R} Al\leftarrow CH_2-CH_2-R+CH_2=\underset{\displaystyle R'}{\underset{|}{C}}-CH_2-CH_2-R$$

The extent of formation of these branched oligomers increases quite markedly with carbon number, as shown by the data in Table II.

The single-stage process as operated by Gulf gives lower levels of branched oligomers than the Ethyl process but somewhat more paraffin, as shown in Table III.

The newest process for making linear alpha olefins is that of Shell, known as SHOP (Shell Higher Olefins Process). The novel feature of this process is the way in which the relatively low valued lighter and heavier alpha olefins outside the detergent range can be upgraded to detergent range internal olefins by a combination of isomerization and disproportionation (4). For the purpose of this paper, however, we are concerned only with the alpha olefins as marketed and, hence, only with the first step of the SHOP process.

The catalyst employed in the SHOP process is of the transition metal-ligand type dissolved in a solvent which is largely immiscible with the alpha olefin product. The reaction is carried out at 80–120 C and 1000–2000 lb/sq in. gauge.

The mechanism of the oligomerization is not quite the same as that involved in the case of the Ziegler systems, hence the product distribution is different. The secondary reactions leading to impurities are characteristic of an oligomerization reaction and lead to the same types of impurities found in the Ziegler systems, viz. branched and internal olefins, with traces of dienes, paraffins and aromatics also being found. A high partial pressure of ethylene and a high degree of ethylene saturation in the catalyst solution ensure maximum product linearity and also a high reaction rate. Table IV shows the typical quality of alpha olefins obtained from the SHOP process.

To allow an overall comparison, the data from Tables I–IV have been averaged and are presented in Table V.

It is clear from Table V that olefins made by thermal cracking are inferior in quality to those made by oligomerization of ethylene. In view of the severity of the processes involved in thermal cracking, this conclusion comes as no surprise.

It is also clear that, of the oligomerization processes, SHOP gives the most desirable product in terms of highest alpha olefins and lowest paraffin content.

APPLICATIONS OF ALPHA OLEFINS

The major markets for alpha olefins are currently: plasticizer alcohols (hydroformylation), polymers (linear low density polyethylene), alpha olefin sulfonates (AOS), and synthetic lubricants (oligomerization).

TABLE IV

Typical Quality of Alpha Olefins from SHOP Process

	Composition (wt %)						
Hydrocarbon type	C6	C8	C10	C12	C14	C16	C18
n-Alpha olefins	97.0	96.5	97.5	96.5	96.0	96.0	96.0
Branched olefins	1.0	1.0	1.0	2.0	2.5	3.0	3.0
β internal olefins	2.2	2.4	1.0	1.5	1.5	1.5	1.5
Paraffins	<0.1	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05
Conjugated dienes	<0.1	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05
Aromatics	<0.1	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05
Total monoolefins	99.9	99.9	99.9	99.9	99.9	99.9	99.9

TABLE V

Overall Comparison of Typical Qualities of C6-C18 Alpha Olefins from Various Processes

		Ethylene oligomerization		
	Thermal cracking	Ziegler single-pass	Ziegler with recycle	SHOP
Alpha olefins	83–89	91–97	63–97.5	96–97.5
Branched olefins	3–12	1.6–7.8	1.9–29.1	1.0–3.0
Internal olefins			0.6–8.2	1.0–2.4
Paraffins	1.5–2	1.4	0.1–0.8	<0.1
Dienes	3.2–6	n/d	n/d	<0.1
Aromatics	0–0.4	n/d	n/d	<0.1
Total monoolefins	(92–95)	98.6	(<99)	99.9

n/d = No data available.
Data in brackets are our own estimates.

Significant quantities are also used for the manufacturing of: amines (amine oxides and quaternaries), mercaptans, synthetic acids, metal alkyls, epoxides, and luboil additives.

In the remainder of this paper, we shall discuss the practical significance of olefin purity as it affects some of the uses of alpha olefins as chemical feedstock. The discussion is primarily based on the various uses of alpha olefins in the detergent industry, although some other applications are also mentioned.

SULFONATION TO ALPHA OLEFIN SULFONATES (AOS)

Color Aspects

AOS in the range C12-C18 has been known for many years to have interesting properties as a surfactant. Only in the last decade or so, however, has it been used commercially to any significant extent and it now finds increasing use in household detergents, particularly in Japan (5), as well as in cosmetics and toiletries (6). To gain acceptance in such outlets, product quality, especially color, is vitally important.

Until a few years ago it was not possible to make AOS of acceptable color on a commercial scale. One reason for this is that it required a special sulfonation technology to be developed by Lion Corp. to handle the highly exothermic reaction of an alpha olefin with sulfur trioxide (5). It also required high quality olefin feedstock essentially free from color precursors such as dienes. Hence, it is not possible to make AOS of acceptable quality from an alpha olefin resulting from a thermal cracking process, although various claims have been made for techniques for purifying either the starting olefin or the sulfonate (7-9).

Powder Production

The final step in the manufacture of a household detergent powder is often a spray drying operation in which water is removed from a slurry of the detergent by contact with a stream of hot air. It is desirable that the level of volatile organic materials (such as nonsulfonated matter) in the feed to the spray drier be as low as possible to minimize fire and explosion hazards and effluent problems, as well as for economic reasons. Any paraffins in the olefin fed to the sulfonation unit will persist unchanged through to the sulfonated product and will largely be lost by evaporation in the spray drier. Hence, a low level of paraffin in the olefin feedstock is desirable for easy and safe operation of the spray drying tower, although it is not possible to set a limit on this.

It should also be mentioned that the presence of appreciable amounts of disulfonates, or sulfonates of branched or internal olefins, may reduce the flowability of the finished powder and thereby increase the tendency to "caking" (Lion Corp., private communication).

Olefin Structure and Product Performance

Some of the alpha olefin fractions made by Ziegler chemistry contain appreciable amounts of branched olefins, mostly of the vinylidene type. It is known that such vinlidene olefins are readily sulfonated (10) but the detergency and wetting performance of the derived sulfonates are inferior to those of sulfonates based on the corresponding linear alpha olefins (11). Similar reservations apply to sulfonates of internal olefins.

ALKYLBENZENES (Detergent Alkylate)

Detergent alkylate (linear alkylbenzene) is in volume terms the most important detergent intermediate. It is manufactured by a Friedel-Crafts catalyzed alkylation of benzene with either alkyl chlorides or olefins. In the latter case, it is more usual to start with internal olefins, which are obtained by dehydrogenation of *n*-paraffins, either directly (catalytically) or indirectly via chlorination/dehydrochlorination. Alpha olefins can, of course, be used as feedstock but, because of the possibilities of isomerization of the olefin and/or the alkylated benzene by the catalyst in the course of the process, generally offer no advantage over internal olefins.

It should perhaps be mentioned that dienes in cracked wax olefins and dichlorinated compounds in chloroparaffins are believed to be the source of alkyltetralins and alkylindanes (at a level of a few per cent) in linear alkylbenzene (12). Dienes can also give rise to diphenylalkanes and heavy ends (13). It is therefore to be expected that the use of high quality alpha olefins would give a linear alkylbenzene containing lower levels of these undesirable byproducts. This expectation has been borne out in practice (Shell, unpublished observations). Internal olefins produced by dehydrogenation also yield low levels of these byproducts, as expected.

EPOXIDATION

Reaction of an alpha olefin with a peracid is a well established route to olefin epoxides, which in turn are useful intermediates for the synthesis of a wide range of difunctional derivatives, of interest in the detergent industry and elsewhere (14). It is known that the rate of epoxidation of an alpha olefin is hardly affected by chain length (15). Internal olefins are considerably more reactive towards peracids than alpha olefins (2), and 1,1-disubstituted ethylenes (i.e., vinylidene olefins) and dienes should be even more reactive. Hence, in any attempt to epoxidize an impure alpha olefin, the internal and vinylidene olefin and diene impurities will react preferentially with the peracid. Paraffins, of course, will not react at all and will remain as an impurity in the derived epoxide.

However, epoxides of internal olefins are much less reactive than epoxides of alpha olefins (14), which may lead to some problems in subsequent chemical processing. It follows, therefore, that for the most successful results in converting alpha olefins into derivatives via the epoxide, the alpha olefins should be as pure as possible.

ADDITION OF HYDROGEN BROMIDE

As is well known, this reaction can lead to the 1-bromo or to the 2-bromo derivative depending on the reaction conditions. In the detergent industry, the 1-bromo derivatives are of more interest as they provide a route to dialkylamines and hence to amine oxides and quaternary amines.

$$R - CH = CH_2 + HBr\,(O_2) \rightarrow R - CH_2 - CH_2\,Br \xrightarrow{(CH_3)_2\,NH} R - CH_2 - CH_2 - N(CH_3)_2$$

Process details of the HBr addition are rather scanty but it is reported that any internal olefins present (which in principle are more reactive than alpha olefins) will react to form internal bromides (15). Similarly, vinylidene olefins would rapidly add HBr. Hence, an impure alpha olefin would lead ultimately to a tertiary amine containing a wide range of impurities. This fact probably explains why one company is reported to have abandoned this route to quaternized amines (16).

ADDITION OF HYDROGEN SULFIDE

This reaction is also carried out under peroxide conditions to yield the 1-thiol. Little information is available about process conditions but care is necessary to minimize formation of unwanted alkyl sulfides:

$$R - CH = CH_2 + H_2S \rightarrow R - CH_2 - CH_2 - SH$$

$$R - CH_2 - CH_2 - SH + R\text{-}CH = CH_2 \rightarrow$$

$$R - CH_2 - CH_2 - S - CH_2 - CH_2 - R$$

The considerations about the complicating effects of the presence of internal and vinylidene olefins as applied to HBr addition clearly apply again here.

COPOLYMERIZATION OF ETHYLENE WITH ALPHA OLEFINS

Although not related to the detergent industry directly, this relatively new development in polymer technology known as linear low density polyethylene (LLDPE) is of importance in the context of detergents because it seems likely to consume large quantities of lower alpha olefins (C4 to C8); the availability of these lower olefins impinges directly on that of the higher olefins, as both come from one of the same total olefin package (2).

LLDPE is a modification of high density polyethylene (as made with a Ziegler or related type of catalyst) by including a higher alpha olefin (butene-1, hexene-1 or octene-1) as a comonomer at levels up to ca. 10%. The resulting copolymers have improved mechanical properties and offer economic advantages in some circumstances over conventional polyethylene (17).

In any catalytic polymerization process, purity of the monomer(s) is of key importance and the plant would normally include facilities for removal of adventitious impurities such as traces of water, oxygen, etc., which would otherwise deactivate the catalyst.

However, in the copolymerization of ethylene with higher alpha olefins, the effects of olefinic and paraffinic impurities in the alpha olefin comonomer have to be taken into account.

In general, in a Ziegler-type polymerization, higher alpha olefins are less reactive than ethylene and the rate of polymerization decreases as the molecular weight of the alpha olefin comonomer increases; vinylidene type olefins are reluctant to undergo Ziegler-type polymerization (18). Thus, in order to incorporate eight per cent of butene-1 into a copolymer with ethylene, it is necessary to operate with some twenty percent of butene-1 in the polymerization feed, which leads to a rather low rate of reaction (17). Corresponding figures for higher olefins such as octene-1 are not available but it would not be unreasonable to suppose that the polymerization feedstock would need to contain approximately equal amounts of ethylene and octene-1.

Because of heat transfer limitations, it is necessary to operate polymerization systems of this type at a low conversion per pass (e.g., 2% per pass in the Unipol process) (17). Now impurities in the octene-1 such as vinylidene olefins, internal olefins or paraffins, will either interfere with the polymerization process in some way, or will tend to build up in the recycle feed to the polymerization reactor. To overcome this, it will be necessary to maintain a bleed on the recycle feedstream. It follows that the operating costs of such a copolymerization process will increase with the level of impurities in the monomers. Our contacts with the industry confirm that this is a factor of real practical importance.

The most significant impurities in higher alpha olefins, irrespective of the manufacturing process employed, are internal and vinylidene olefins, dienes and paraffins. From our survey of a representative selection of the reactions of alpha olefins, two main types of effect may be distinguished. In the first, characteristic of reactions involving electrophilic or free radical addition, the non-alpha olefins are *more* reactive than the alpha olefin (e.g., peroxidation, HBr addition under anti-Markownikoff conditions) and will therefore lead to isomeric products in the reaction mixture. In the second category, typified by Ziegler-type copolymerizations, the non-alpha olefins are much *less* reactive than the alpha olefin and will persist unchanged in the final reaction product.

In all cases, the presence of dienes is not very desirable as they will certainly react to form byproducts which may (as in the case of AOS) make the desired product unacceptable in terms of quality.

In any system operating on a continuous basis with recycle, a build-up of inert impurities has to be prevented by a bleed system which (as, for example, in the Ziegler-type copolymerization of ethylene with a higher alpha olefin) can have a serious effect on the economics of the process.

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