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Oligomerization of Monoolefins by Homogeneous Catalysts

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Résumé — Oligomérisation des mono-oléfines par des catalyseurs homogènes — Cet article résume les différents schémas réactionnels pour l'oligomérisation des mono-oléfines par catalyse homogène, en particulier pour l'oligomérisation de l'éthylène et des alpha-oléfines. Les principaux sujets abordés sont la production régiosélective ou non de dimères, la production d'alpha-oléfines linéaires par oligomérisation de l'éthylène ainsi que la dimérisation sélective de l'éthylène et sa trimérisation sélective. Plusieurs procédés industriels développés par l'IFP sont présentés pour illustrer ce sujet.

Abstract — Oligomerization of Monoolefins by Homogeneous Catalysts — In this article are summarized the different mechanistic pathways for the oligomerization of monoolefins by homogeneous catalysts, particularly for ethylene and alpha olefins. The major topics are: the production of non regioselective and also regioselective olefin dimers, the production of linear alpha olefins by ethylene oligomerization as well as the selective dimerization of ethylene and its selective trimerization. Several industrial developments initiated by IFP are presented to illustrate this topic.

INTRODUCTION

The two main cracking processes of the refining and petrochemical industries – Fluid Catalytic Cracking (FCC) and Steam Cracking – produce important quantities of light olefinic fractions (having two to six carbon atoms) respectively as co products of gasoline for the FCC process, and as co-products of ethylene and propylene for the Steam Cracking process. Fischer-Tropsch (F-T) processes based on coal (CTL) or gas (GTL) produce a wide range of products, in terms of carbon number and class of compounds. Among those, short chain linear olefins (C_2 - C_4 olefins, LPG and C_5 - C_9 olefins, naphtha) can be one of the major products depending on the technology (catalyst type and operating conditions).

The oligomerization of monoolefins offers an attractive way for upgrading these light olefins either to produce fuel components (gasoline and/or middle distillates) or as intermediates for the manufacture of many type of products in the petrochemical industry. A considerable number of studies have been carried out on olefin oligomerization to improve both the activity and the selectivity for the desired compounds, in order to meet the commercial demand.

The oligomerization of monoolefins is still currently achieved with acidic catalysts, sometimes as liquids but mainly as solid acids (such as solid phosphoric acid SPA), and more recent approaches have looked at using mesoporous materials and specially designed acidic zeolithes [1]. However, the use of these acidic catalytic systems remains limited to only a few specific applications, in particular for the production of fuels. Due to their cationic reactivity, the main drawbacks of acid catalysts is their high deactivation rate [2], their poor selectivity and their low activity toward linear olefins.

In contrast homogeneous organometallic catalysts offer a broader spectrum of activity and more diversified selectivities. With an appropriate choice of metal-ligand and metal activator combination, it is possible to selectively obtain oligomers instead of high molecular weight polymers [3]. The regioselectivity of homogeneous catalysts can be tuned, such as the regioselective dimerization of propene to give 2,3-dimethylbutenes, 4-methyl-1-pentene or 2-methyl-1-pentene. With a proper selection of the couples metal-ligand and metal-activators, it is possible to achieve either the selective dimerization of ethylene or its trimerization or even the tetramerization [4] associated with the trimerization of ethylene. Finally, thanks to the use of iron bis-iminopyridine complexes activated with aluminoxane, the dimerization of alpha olefins (C_3 to C_8) to linear dimers, which is known to be difficult, has been recently improved [5-7].

Today the oligomerization of ethylene is the predominant route to linear alpha olefins.

Since the first industrial oligomerization processes, called full range processes, producing a wide range of even

numbered linear alpha olefins [8] ranging from C_4 to C_{30} , significant progress has been made, in recent years, for selective oligomerization of ethylene into shorter distributions of alpha olefins or even into a main product (1-butene or 1-hexene by “on purpose” processes). Because the demand for linear alpha olefins is growing faster in the C_4 - C_{10} range than in the C_{12}^+ range (see *Tab. 1, 2*), the selective formation of light alpha olefins from ethylene has been an important topic for academic and industrial research during the last twenty years.

TABLE 1
Market survey of alpha-olefins production

| | Linear Alpha Olefin (LAO) | 1-butene | 1-hexene |
|--|---|--|---|
| Demand 2006 (Mt) | 4.3 | 1.1 | 0.650 |
| Estimated average annual growing rate (AAGR) (%) | 2006-2020 3.5 | 2006-2020 5.3 | 2006-2020 4.7 |
| Production | 90% of the production by ethylene oligomerization | 35% of the production by ethylene dimerization | less than 10% by ethylene trimerization |

The lighter alpha-olefins, 1-butene and 1-hexene, are mainly used as co-monomers for the manufacture of polyethylene (LLDPE and HDPE respectively 60% and 20% of the total demand of 1-butene and 60% and 30% of the total demand of 1-hexene).

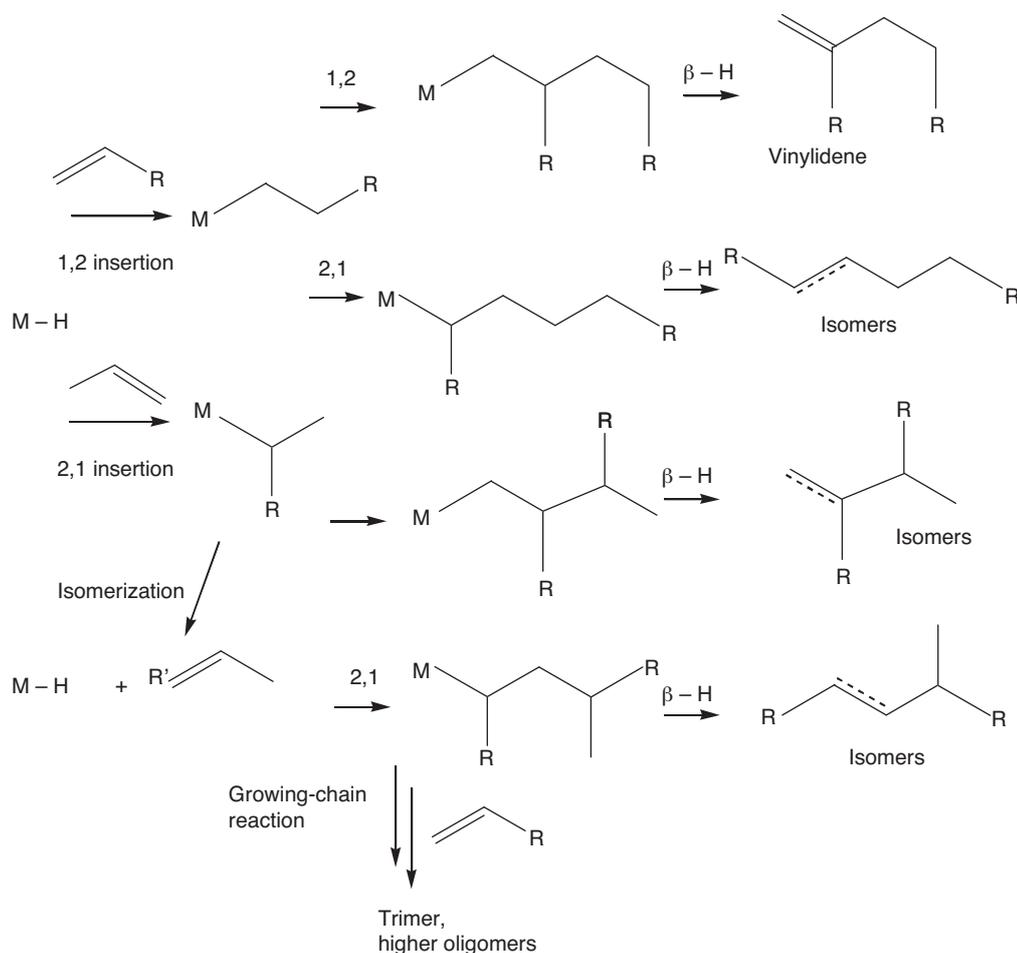
TABLE 2
Breakdown of the main uses of alpha-olefins

| Polyethylene co-monomer C_4 - C_8 | Oxo alcohols C_6 - C_{16} | Poly alpha olefins C_{10} - C_{14} | others |
|--|----------------------------------|---|--------|
| 40% | 19% | 14% | 27% |

In this article, we discuss the different mechanistic pathways for monoolefin oligomerization by homogeneous catalysts, particularly for ethylene and alpha olefins. The major topics are: the production of non regioselective and also regioselective olefin dimers, the production of linear alpha olefins by ethylene oligomerization as well as the dimerization and the trimerization of ethylene. Several industrial developments initiated by IFP will be reviewed to illustrate this topic.

1 THE DIMERIZATION OF LIGHT OLEFINS

The dimerization of light olefins by metal catalysts has been a widely studied [9-11] topic.



Scheme 1

Reaction pathways for the formation of the different dimer structures.

There are different pathways for the dimerization of alpha olefins and this reaction is generally non regioselective [12-14] (see *Scheme 1*). Most of the catalysts generate vinylidene dimers (2-alkyl-1-alkene) or dibranched dimers and are not selective for linear dimers. With these kind of catalytic systems, the challenge is to control consecutive reactions: reaction of dimers with monomers and dimer double bond isomerization. The formation of higher oligomers by these consecutive reactions can be limited by adjusting the monomer conversion. However, trimers and higher oligomers can also be formed by parallel growing chain reactions.

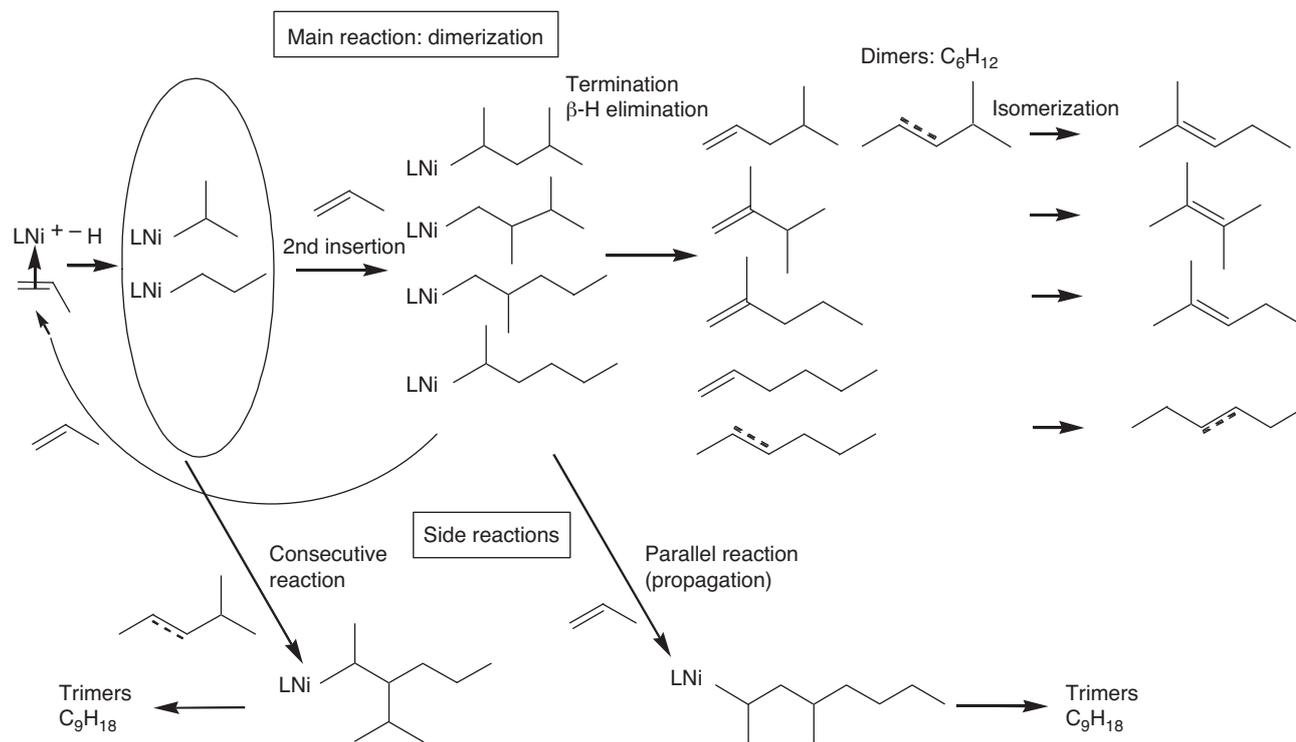
With some catalysts, particularly nickel catalysts, double bond isomerization occurs by insertion of the dimer in the metal hydride bond followed by β -H elimination. Butenes isomers (mainly 2-butenes) are produced [15] by ethylene dimerization catalyzed by bis(tri-*n*-butylphosphine)-dichloronickel activated with an alkyl aluminium halide (ethyl aluminium dichloride) but it is not possible to produce selectively 1-butene [16] by this route.

1.1 Non Regioselective Dimerization of Propene

Nickel catalysts have given rise to numerous studies and are used on an industrial scale owing to their very high activity and their relative low cost. Most of the catalytic systems described in many publications and patents generate cationic complexes by different ways and a common active cationic nickel hydride species $(\text{Ni-H})^+ \text{A}^-$ is invoked.

In the industrial Dimersol GTM process, the active catalyst is formed *in situ* by the reaction of a nickel (II) salt with an ethylaluminium chloro derivative. This catalytic system transforms propene into a mixture of dimers, trimers and tetramers of various structures. The average composition of the dimers shows little dependence on the temperature. At 50°C, the isohexenes distribution by structure is: 22% of *n*-hexenes, 72% of 2-methylpentenes and 6% of 2,3-dimethylbutenes.

Nonregioselective dimerization is widely used on an industrial scale for propene but also for *n*-butenes and also



Scheme 2

Nonregioselective dimerization of propene catalyzed by cationic nickel complexes. General scheme for the formation of oligomers.

ethylene (IFP DimersolTM Process cf. infra). The olefin reactivities decrease in the following order: ethylene > propene > n-butenes.

Olefin dimers are the major products due to the high rate of β -hydrogen abstraction but trimers and tetramers form by a parallel growing-chain reaction and also by consecutive reactions of dimers with monomer [17] (see Scheme 2 for propene dimerization). That is why, at high conversion of propene (>80%), the selectivity to dimers depends on the type of reactor used.

1.2 Regioselective Dimerizations of Propene

1.2.1 2,3-Dimethylbutenes with Ni-Catalyst

Cationic nickel complexes are generally non selective, but addition of phosphines can have a considerable effect on the regioselectivity of propene dimerization as shown by Wilke *et al.* [18] with well defined cationic η^3 -allylnickel complexes (Fig. 1). Bulky and basic phosphine ligands such as triisopropylphosphine or tricyclohexylphosphine favour the formation of 2,3-dimethylbutenes. 2,3-dimethylbutenes are especially important since they can be used as key

starting olefins for fine chemical intermediates. 2,3-dimethyl-2-butene is used for the synthesis of DanitolTM, which is a high performance pyrethroid insecticide invented by Sumitomo in 1976, and to produce other intermediates (Pinacolone). 2,3-dimethyl-1-butene is a key intermediate for the production of musk fragrances (TonalidTM).

In the Sumitomo process, very high selectivities into dimethylbutenes in the C_6 olefins (up to 85%) are obtained at 20-50°C using a sophisticated Ziegler-type catalyst comprising tricyclohexylphosphine as ligand and toluene or chlorobenzene as solvent. Due to the close boiling points of

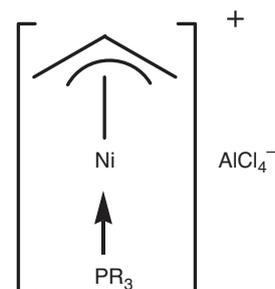
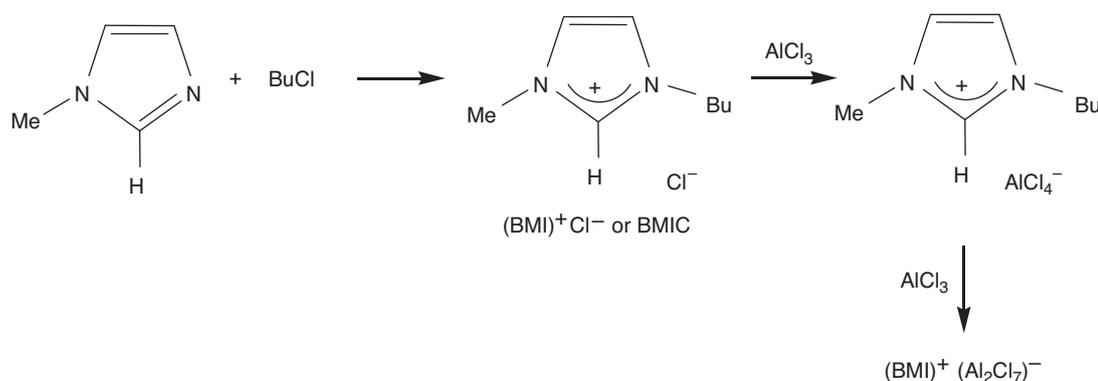


Figure 1



Scheme 3

Synthesis of acidic chloroaluminate ionic liquids.

the different isohexene isomers (Tab. 3), isomerization of 2,3-dimethyl-1-butene into 2,3-dimethyl-2-butene is achieved in the dimerization reactor and 2,3-dimethyl-2-butene can be easily extracted by distillation. The active catalyst for isomerization is a Lewis acidic component resulting from the interaction between AlEt₃ and a chlorinated phenol [19] present in the catalyst formula. When the chlorinated phenol is used at less than 1.5 moles per mole of AlEt₃, 2,3-dimethyl-1-butene can be produced without isomerization. An important increase in both the catalytic activity and the selectivity of dimers, upon addition of methanesulfonic acid or dimethyl sulfate to this catalytic system, was reported [20].

TABLE 3

Boiling points of isohexenes isomers

| | Bp (°C) |
|--------------------------|---------|
| 4-methyl-1-pentene | 53.87 |
| 2,3-dimethyl-1-butene | 55.2 |
| cis-4-methyl-2-pentene | 56.4 |
| trans-4-methyl-2-pentene | 58.61 |
| 2-methyl-1-pentene | 62.11 |
| trans-3-hexene | 66.45 |
| trans-2-hexene | 67.88 |
| 2-methyl-2-pentene | 67.31 |
| cis-2-hexene | 68.99 |
| 2,3-dimethyl-2-butene | 73.21 |

Several catalytic systems based on nickel and tricyclohexylphosphine, activated by chloroalkylaluminium compounds or methylaluminumoxane have been published [21].

Due to the high cost of the phosphine ligand, liquid-liquid biphasic catalysis can be an interesting approach to separate and recover the Ni phosphine catalytic system. The main issue is the choice of the most suitable catalyst solvent. Acidic chloroaluminate based ionic liquids proved to be the most promising [22] (Scheme 3). They act both as catalyst phase and nickel activator.

Providing a right adjustment of the chloroaluminate ionic liquid composition (aluminium chloride to imidazolium chloride), the same phosphine effect than in the homogeneous system can be obtained. The cationic nickel-phosphine active species is immobilized in the ionic phase without the need of designing special ligand. The liquid isohexenes form a second phase which can be easily separated from the ionic liquid catalytic phase by decantation. However, a dramatic decrease of the dimethylbutenes selectivity is observed after a few hours of the run. This can be explained by a competition for coordination of the phosphine between the “soft” Ni complex and the “hard” AlCl₃ potentially present in the ionic liquid. This induces a decoordination of the phosphine from the nickel and a loss of the selectivity (Eq. 1).

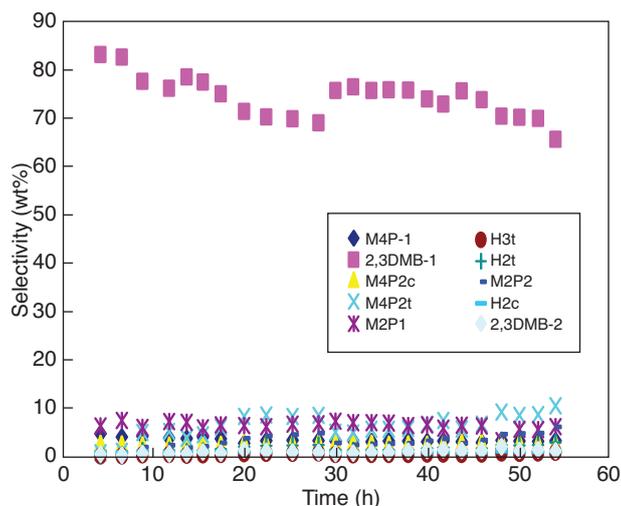


The stabilization of the selectivity towards 2,3-dimethyl-1-butene has been successively achieved by addition of small amounts of a weak organic Lewis base (noted B) such as a substituted aromatic hydrocarbon (Eq. 2).



A new biphasic continuous flow process for the selective dimerization of propene producing 2,3-dimethyl-1-butene was disclosed [23] by IFP.

The selectivity towards 2,3-dimethyl-1-butene *versus* time, for a continuous flow propene dimerization reaction in chloroaluminates, is shown in Figure 2. These results demonstrate that it is possible to produce more than 5 kg of 2,3-dimethyl-1-butene with only 15 mL of ionic liquid.



15 mL ionic liquid; atmospheric pressure of propene, production of 11 liters of liquid products; C₆ selectivity: 80-81% / total products; 2,3-DMB-1 selectivity: 70-75% / total C₆; M4P-1: 4-methyl-1-pentene; M4P2t: 4-methyl-2-pentene-trans; M4P2c: 4-methyl-2-pentene-cis; M2P1: 2-methyl-1-pentene; H3t: 3-hexene-trans; H2t: 2-hexene-trans; H2c: 2-hexene-cis; 2,3-DMB-2: 2,3-dimethyl-2-butene.

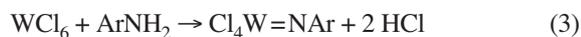
Figure 2

Continuous flow dimerization of propylene in chloroaluminate ionic liquids - Hexenes distribution.

1.2.2 2,3-Dimethylbutenes with Tungsten Catalyst

Catalysts based on tungsten hexachloride and anilines [24], activated with ethylaluminium dichloride (~10 mol. equiv.) are reported to dimerize propene with high selectivities to 2,3-dimethylbutenes.

It may be suspected that the active species precursor is the monoimido W(VI) complex such as described in Equation (3).



Isolated organoimido tungsten complexes (Cl₄W=NAr with Ar = Aryl) catalyze the dimerization of propene in the presence of ethylaluminium dichloride in a similar way as the mixture WCl₆/aniline/EtAlCl₂. With high Al to W ratio and sterically demanding arylimido groups (2,6-disubsti-

tuted phenyl groups) tail to tail coupling of two moles of propene yielding 2,3-dimethylbutenes (75-85%) is favored. These catalytic systems are also active with ethylene. Diethylaluminium chloride proved to be a better cocatalyst and a good selectivity toward formation of 1-butene was observed. The isolated complex Cl₂W=NPh(PMe₃)₃ catalyzes the ethene dimerization when activated with AlCl₃ (Al/W = 4.5). The formation of a metallacyclopentane intermediate [25] has been proposed to explain this selectivity but a strict proof remains elusive (Scheme 4). A DFT study centered on a metallacycle mechanism was recently published [26].

1.2.3 4-Methyl-1-Pentene

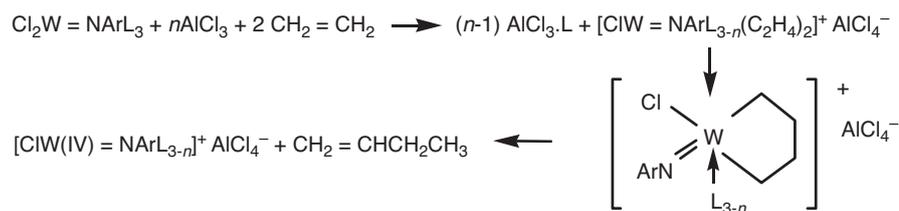
4-methyl-1-pentene is mainly used as co-monomer with linear low density polyethylene and for the production of poly-4-methyl-1-pentene (TPX), a high-quality polymer excellent in heat resistance, transparency and impact strength.

Using molecular transition metal complexes, two different mechanisms are possible for the formation of 4-methyl-1-pentene: one involving a 2,1 insertion of propene into a metal hydride bond followed by another 2,1 insertion of propene and β-hydride elimination (Scheme 5), the other involves a β-methyl elimination after a 1,2 insertion of propene into a metal methyl bond followed by a 1,2 insertion of propene (Scheme 6).

In 1990 Teuben *et al.* [27] reported that ionic group 4 complexes [Cp*₂MMe(THT)]⁺(BPh₄)⁻ (M = Zr, Hf, THT = tetrahydrothiophene) oligomerize propene and that the hafnium compound gives mainly one dimer (4-methyl-1-pentene: 72%) and one trimer (4,6-dimethyl-1-heptene: 24%). 3,3,3 Trideuteropropene was used to demonstrate that β-Me elimination is the dominant termination (Scheme 6).

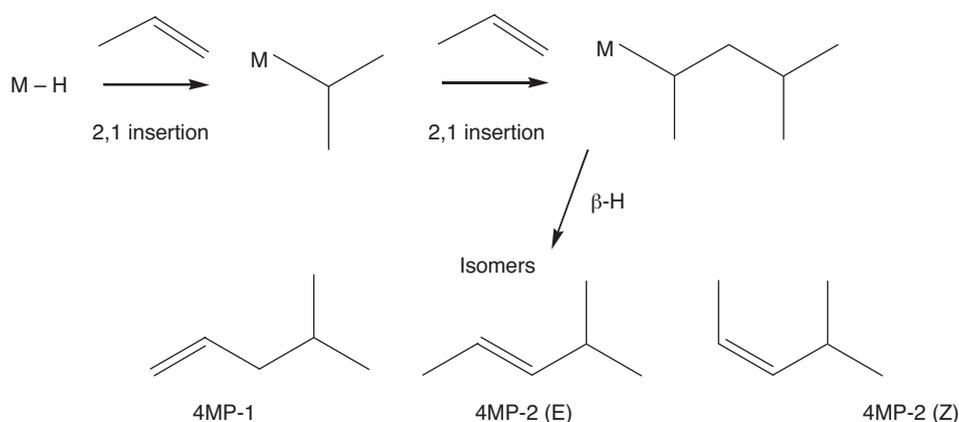
In 1991 Yamazaki *et al.* [28] reported that Cp*₂MCl₂ (M = Zr, Hf), in presence of methylaluminoxane (MAO), catalyzed the oligomerization of propene to produce mainly 4-methyl-1-pentene as well as other dimers, trimers and higher oligomers.

Recently, Okuda *et al.* [29] showed that the introduction of bulky substituents on the cyclopentadienyl ligands improve the selectivity of 4-methyl-1-pentene formation up



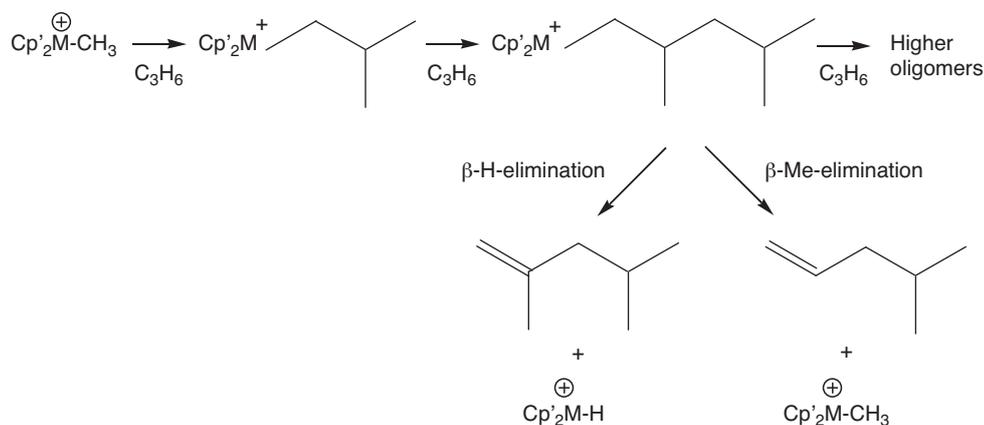
Scheme 4

Proposed reaction pathway for ethene dimerization catalyzed by Cl₂W=NArL₃ complex (L = PMe₃).



Scheme 5

Reaction pathway for the formation of 4-methyl-1-pentene (β -hydride elimination).



Scheme 6

Reaction pathway for the formation of 4-methyl-1-pentene by β -methyl elimination with $M = Zr$ or Hf .

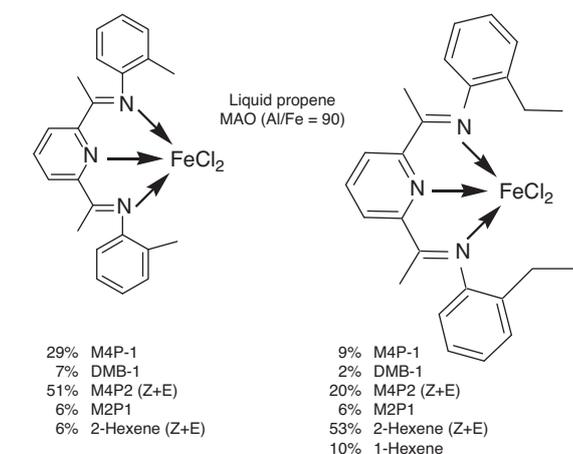
to 60% but other reaction pathways involving insertion of propene into a metal hydride bond followed by a second insertion of propene then a β -hydride elimination, a β -methyl elimination or chain growing produce considerable amounts of by products (dimers, trimers and also higher oligomers). The use of di(poly-substituted cyclopentadienyl)-allylic uranium (III) complexes, such as $Cp^*_2U(2\text{-methylallyl})$, (Cp^* = pentamethylcyclopentadienyl), to catalyze the dimerization of propene to form 4-methyl-1-pentene selectively was also described [30].

So far, all these catalytic systems have not been selective enough because the β -methyl elimination step is not sufficiently predominant on the two other competing steps: β -hydride elimination or propagation (Scheme 6).

Some interesting results were obtained using the bis-imino-pyridine iron catalytic systems [31]. The selectivity for 4-methyl-1-pentene remains low ($\sim 30\%$ of the dimers)

because it is not possible to sufficiently control the propene insertion at each stage and finally the β -hydride elimination (Z and E isomers of 4-methyl-2-pentene represents respectively $\sim 12\%$ and $\sim 39\%$ of the dimers) (Scheme 7). The substitution of the aryl groups of the imine ligand plays an essential role on directing the dimerization selectivity.

The application of the recent developments of homogeneous catalysts for the selective dimerization of alpha olefins to branched alpha olefins is limited and processes to produce 4-methyl-1-pentene are still based on propylene dimerization promoted by heterogeneous catalysts generated by dispersion of alkali metals (sodium or potassium) on potassium carbonate or other appropriate supports [32]. However it is difficult to maintain activity and selectivity at high levels for a very long period of time and some improvements of these type of heterogeneous catalyst have been disclosed [33].



M4P-1: 4-methyl-1-pentene; M4P2: 4-methyl-2-pentene; M2P1: 2-methyl-1-pentene;
DMB-1: 2,3-dimethyl-1-butene.

Scheme 7

Dimerization of propene with iron the bis-arylimino-pyridine catalysts. Effect of the aryl substitution on regioselectivity.

1.3 Dimerization Catalysts Producing Vinylidene Olefins

Among the catalysts that are selective for light olefin dimerization, most of them produce vinylidene (2-alkyl-1-alkene) dimers. Cyclopentadienyl zirconium complexes activated by an aluminoxane [34] can produce selectively 2-alkyl-1-alkene (vinylidene dimers), for example 2-methyl-1-pentene from propene with a selectivity close to 90%.

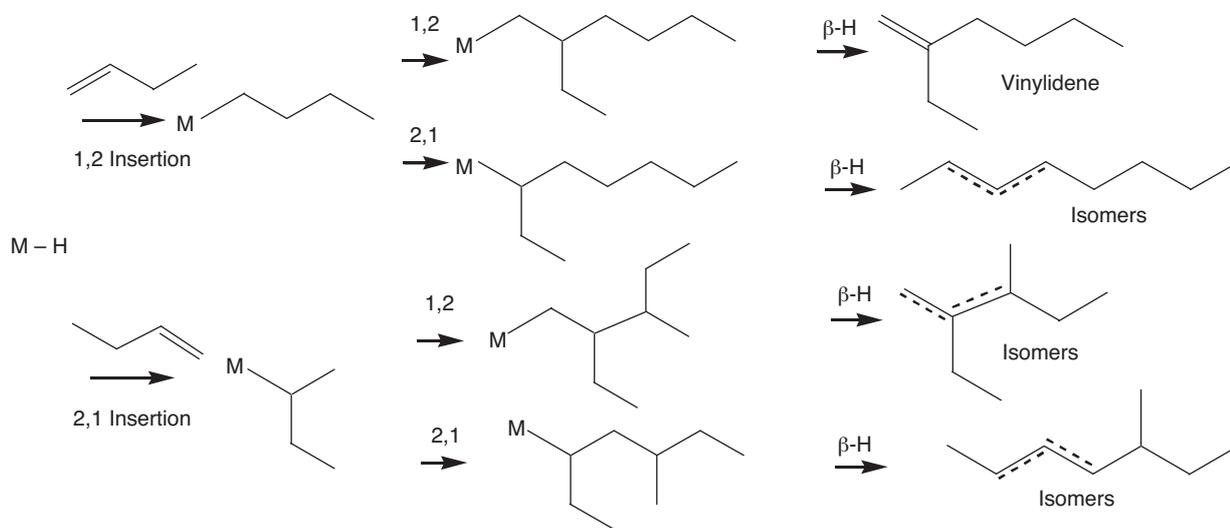
Similarly, cationic bis cyclopentadienyl zirconium complexes can form selectively vinylidene dimers. For example, 1-pentene is converted into 2-propyl-1-heptene [35] with no isomerization of the excess of 1-pentene and bis cyclopentadienyl alkyl zirconium catalysts activated with an organoborane such as $B(C_6F_5)_3$ dimerize propene into 2-methyl-1-pentene or into a mixture of 2-methyl-1-pentene [36] and 2-methyl-2-pentene.

Some catalysts have the same head to tail regioselectivity but are less selective toward dimers, and higher oligomers are also produced. The formation of a Schulz-Flory distribution of 1-butene oligomers (dimers to heptamers) was reported for the catalytic system [37] ethylenebis (tetrahydroindenyl) zirconium dichloride/MAO.

1.4 Catalysts with Improved Selectivity for Linear Dimers

The formation of linear olefin dimers is the result of head-to-head coupling of alpha olefins. Starting from a metal hydride active species, the first step is a (1,2) insertion of an alpha olefin to generate a primary alkyl species. It is followed by a (2,1) insertion of the olefin in the metal alkyl bond then linear dimers isomers are formed by chain transfer (β -H elimination to metal or β -H transfer to monomer).

There is no catalyst known to produce only linear dimers from alpha olefins. For the best catalytic systems, the selectivity into linear dimers in the dimer fraction was generally less than 80% and these systems [38] based on non ionic nickel complexes containing chelating ligands like acetylacetonate generally exhibit low activity.



Scheme 8

Reaction pathway for 1-butene dimerization.

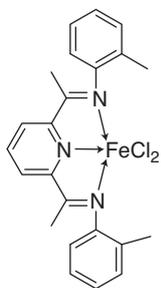


Figure 3

Bis-imino-pyridine iron complex used for 1-butene dimerization.

The transformation of 1-butene into a mixture of octenes with good activities and a high selectivity for linear octenes [5] using bis(imino)pyridine iron complexes (Fig. 3) activated with methylaluminoxane (MAO) or modified methylaluminoxane (MMAO) was recently disclosed (Scheme 8: 57% conversion of 1-butene, 85% dimers, 68% of which are linear octenes). For the dimerization of propene and 1-butene catalyzed by cobalt bis(imino)pyridine complexes, significant improvements in terms of activity and selectivity were reported using fluorinated iminopyridine ligands [39] (propene dimers: 72% with 1-hexene: 90%, 2-hexenes: 9%).

The acidity of the ligand is essential for a catalytic activity and best results are obtained with hexafluoro (or trifluoro) acetylacetonone. The combination of high ligand cost and low activity has prevented industrial development.

2 ETHYLENE OLIGOMERIZATION

Ethylene is a readily available feedstock, and its oligomerization represents the main source for alpha-olefins in industry. The oligomers possess exclusively an even number of carbon

TABLE 4
Industrial commercial processes for ethylene oligomerization to alpha-olefins ("full range processes")

| Industrial | Process name | Catalytic system | Product Characteristics | Technology characteristics |
|--------------------------------------|--------------|--|---|--|
| <i>Chevron Phillips</i> | Gulfene | Al Ziegler catalyst | Schulz-Flory distribution C_4-C_{30+} $K = 0.5-0.75$ little isomerization, broad distribution limited flexibility | – single stage process – low catalyst concentration – no catalyst recovery (Al destroyed by alkali hydrolysis) |
| <i>Shell</i> | SHOP | Ni molecular complex (Fig. 4) | Schulz-Flory distribution $K = 0.75-0.8$ C_6-C_{30+} | – biphasic oligomerization (1,4-butanediol as the solvent) – isomerization – metathesis |
| <i>Ineos</i> | Ethyl | Al Ziegler | Poisson distribution branched products | – 2 separate steps: • growth chain ($AlEt_3$) low T° (100-120°C) • displacement (high T° and pressure) – large quantity of catalyst – recycling of low olefins (C_4-C_8) |
| <i>Idemitsu</i> | | Zr Ziegler-Natta Zr + $Et_3Al_2Cl_6$ + $AlEt_3$ thiophene ligand | Schulz-Flory distribution K non disclosed | – homogeneous system cyclohexane as solvent [48a] |
| <i>Emerging commercial processes</i> | | | | |
| <i>IFP-Axens</i> | Alphaselect | Zr Ziegler-Natta Zr + ligand + Al alkyl | max C_4-C_{10} several distributions possible K factor can be adjusted (for a given set of conditions, a given Zr/Al combination directs the oligomerization to a given distribution) | – homogeneous catalysis aromatic solvent [48b] |
| <i>UOP</i> | Linear-1 | Ni complex Ni + phosphine | C_4-C_{10} $K: 0.55-0.67$ | – homogeneous system [49] |
| <i>Sabir</i> | Alpha-Sablin | Zr Ziegler-Natta Zr + Al alkyl | C_4-C_{10} and C_4-C_{18} K non disclosed | – homogeneous system [48c] |

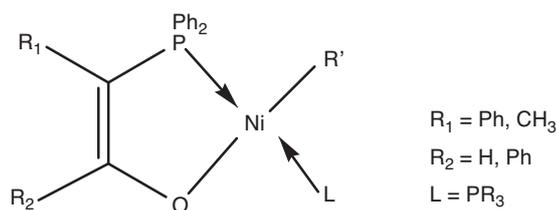


Figure 4

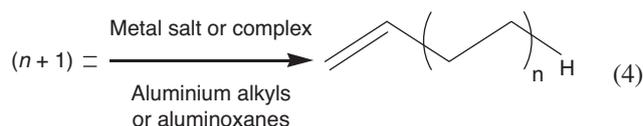
Molecular active Ni catalyst (SHOP process).

atoms and represent commercially valuable products [10, 11, 8]. The production of alpha-olefins was initially realized by the “stoichiometric” Alfen process [40, 41], whereby the chain-growth reaction on aluminum was followed by the liberation of the product in a separate reactor at higher temperatures. A one step catalytic process was developed by *Gulf* (now *Chevron Phillips*), where both reactions occur simultaneously in the same reactor. The Ethyl process (now *INEOS*) is a combination of stoichiometric and catalytic chain-growth reactions [8, 41] (*Tab. 4*).

A remarkable catalytic system for the oligomerization of ethylene with selective formation of linear alpha-olefins is the Shell Higher Olefin Process (SHOP). Keim and coworkers [42] used the $\text{Ni}(\text{P}_2\text{O})(\text{PR}_3)_2\text{R}'$ system, shown in Figure 4, for ethylene oligomerization.

Recent developments for the oligomerization of ethylene with nickel complexes containing chelating ligands were reviewed recently [43].

In contrast to the SHOP process, which is based on a molecular organometallic nickel complex, other systems for ethylene oligomerization or polymerization require Ziegler-Natta type systems *e.g.* a transition metal associated with an alkylaluminum cocatalysts [10, 44, 45, 46, 47] (*Eq. 4*).



These catalytic systems generally afford a geometric Schulz-Flory distribution of olefins mainly by a metal-hydride type mechanism (*Scheme 9*).

The repartition of the alpha olefins is determined by two competing reactions, chain growth (rate constant k_g) versus chain termination (rate constant k_t) and characterised by a K value ($K = k_g/(k_g + k_t)$).

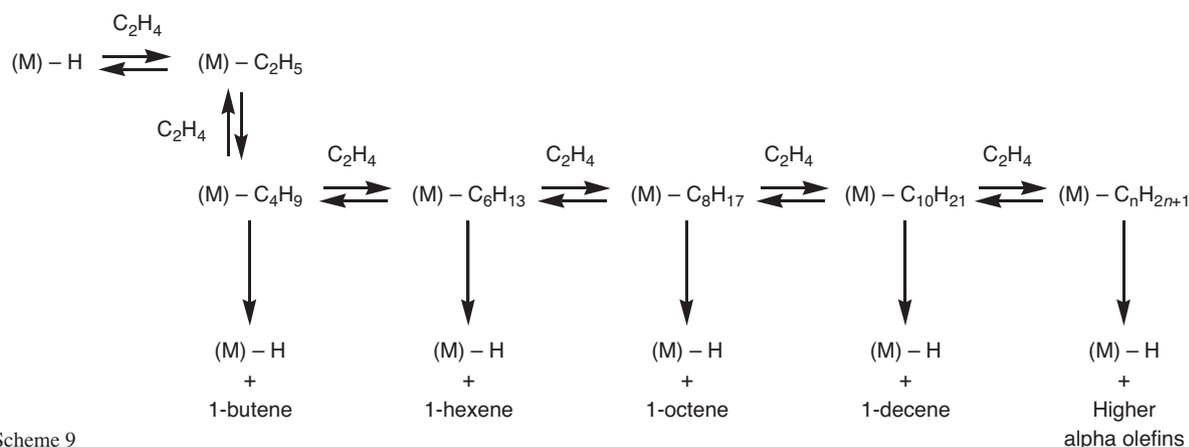
Due to consecutive reactions of the alpha olefins with ethylene, increasing amount of branched olefins are obtained with increasing chain length.

Short chain linear alpha-olefins (1-butene, 1-hexene, 1-octene) are of particular interest because of their use for example as comonomers in the synthesis of linear low density polyethylene.

In the last twenty years, new processes operating with zirconium [48] or nickel [49] catalysts were developed, most of them trying to produce mainly C_4 to C_{12} olefins in order to maximize the amount of alpha-olefins in the comonomer range.

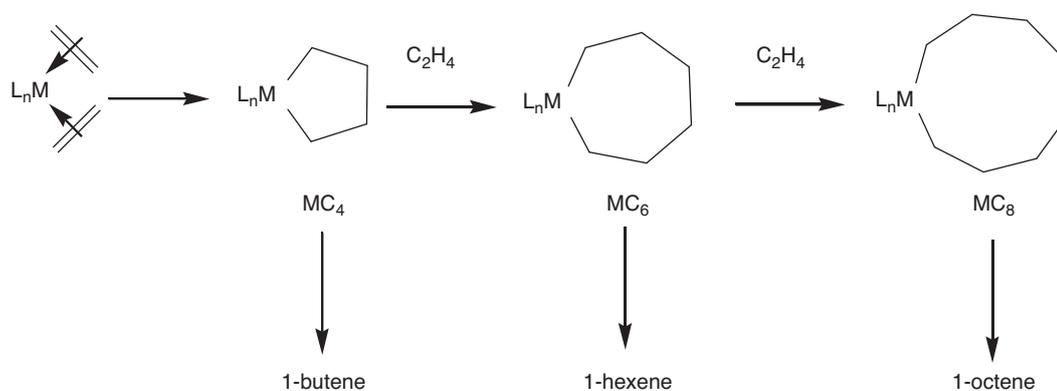
Development of Selective Oligomerization Catalytic Systems

The development of efficient catalysts systems for the selective production of these olefins has triggered intensive research in both academia and industry. For this purpose, titanium [50] and chromium-based catalysts have attracted much attention [4]. Homogeneous chromium catalysts play a major role in ethylene trimerization [51] and tetramerization reactions [4b, 52].



Scheme 9

Geometric distribution of alpha olefins by a metal-hydride mechanism.

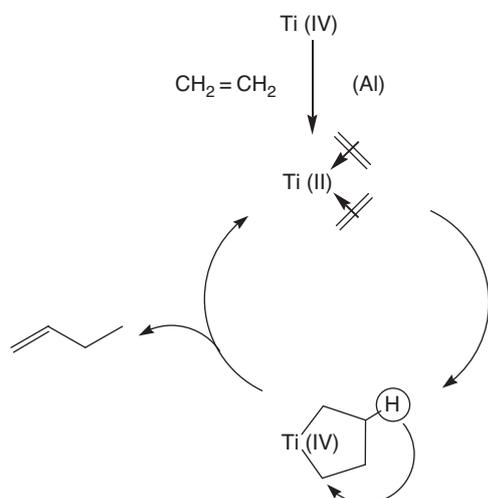


Scheme 10

Metallacyclic mechanism for selective ethylene oligomerization.

For titanium catalysts, selective dimerization of ethylene to 1-butene is well known [12] and occurs via a metallacyclic mechanism (see *Schemes 10 and 11*).

The observed selectivity in ethylene dimerization, trimerization or tetramerization reactions is a consequence of the metallacyclic mechanism in operation (*Scheme 10*). This non-Schulz-Flory-type of oligomerization process involves a two-electron redox couple (Ti(II)/Ti(IV) and probably Cr(I)/Cr(III)). Since polymerization generally accompanies, to variable extents, selective trimerization or tetramerization catalyzed by chromium complexes, the metal oxidation state responsible for each of these mechanistically distinct processes is an important topic of investigation [53].



Scheme 11

1-Butene formation mechanism with the Alkylbutyl Catalyst.

The key to the selectivity of these systems appears to be the energetically preferred tendency of MC_4 , MC_6 and MC_8 metallacycles to undergo a product releasing β -hydrogen shift rather than further ethylene insertion. Bercaw and co-workers [54] demonstrated this metallacyclic mechanism, for a chromium catalyst, with a trimerization experiment involving a mixture of ethylene and deuterated ethylene, which leads to a 1-hexene isotopomer distribution of only C_6H_{12} , $C_6H_8D_4$, $C_6H_4D_8$, and C_6D_{12} . The absence of H/D scrambling strongly indicates a metallacycle mechanism and is inconsistent with a Cossee-Arlman linear chain growth mechanism (non-redox polymerization-type mechanism).

In *Scheme 10*, we have limited the metallacyclic growth at the MC_8 stage but the possibility of growth to large ring metallacycles leading to a distribution of higher olefins has been recently [55] reported and demonstrated by deuterium-labelling studies.

The production of 1-hexene with titanium catalysts was recently realized by the development of a modified cyclopentadienyl system [56] (*Fig. 5*). The authors showed

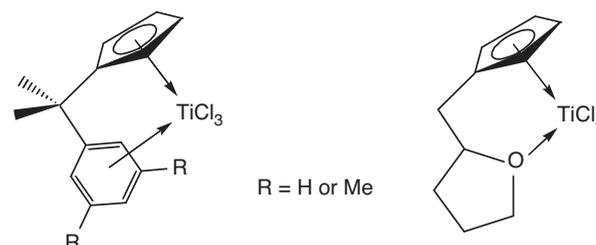


Figure 5

Modified Titanium catalyst precursors used for the selective ethylene trimerization.

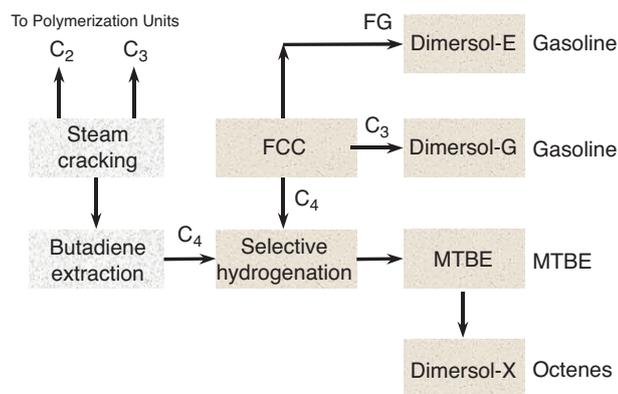


Figure 6

Upgrading Light Olefins fractions by oligomerization Dimersol processes.

that the addition of an aromatic side arm to a Cp ligand dramatically changes the selectivity of the known ethylene polymerization system [CpTiCl₃]-MAO. The main drawback of this catalyst is the requirement of a very high MAO/Ti ratio.

3 EXAMPLES OF INDUSTRIAL PROCESSES

3.1 The Dimersol Processes

In 1965, dimerization and oligomerization of light olefins became the subject of intensive R&D activity in IFP. In 1977, the first Dimersol plant was put on-stream in the

United States by Total Petroleum in Michigan (producing 50 000 t/y of gasoline by dimerization and oligomerization of propylene from an FCC C₃ cut). The Dimersol technology is now used in three different processes, Dimersol-ETM, Dimersol-GTM and Dimersol-XTM, depending on feedstock and desired product quality. Till now, 35 Dimersol units have been licensed corresponding to an overall processing capacity exceeding 4.5 million tons of feed per year.

Despite a planned restriction of olefin levels in gasoline in the U.S. and an increasing demand of propylene from FCC for petrochemistry, some Dimersol GTM are still in operation to produce octane booster additives for gasoline.

The Dimersol processes are offering an attractive alternative to upgrade olefinic light ends produced by Fluid Cracking or Steam Cracking processes and still satisfy the market requirements of motor-fuels or petrochemicals. The typical placement of Dimersol processes in refineries and petrochemical plants is shown in Figure 6.

The C₂ cut extracted from high severity FCC fuel-gas appears as an excellent feed for a Dimersol E unit. Conversion of ethylene from Fischer-Tropsch unit is also an option to optimize the synthetic gasoline pool.

Despite an increasing demand for propylene extraction, C₃ cut from FCC remains the preferred feed for a DimersolG unit producing and excellent high octane sulfur free gasoline base.

After selective hydrogenation of Steam Cracking C₄ raffinate downstream of a butadiene extraction or FCC C₄ cuts, the resulting C₄ stream can be sent to an MTBE unit which separates isobutylene. The raffinate-2, sometimes after deisobutanization, may be upgraded in a Dimersol-XTM unit where the residual butenes are converted to high value octenes and dodecenes. The C₈ olefins are used as precursors for oxoalcohols (Isononyl Alcohols) which are transformed

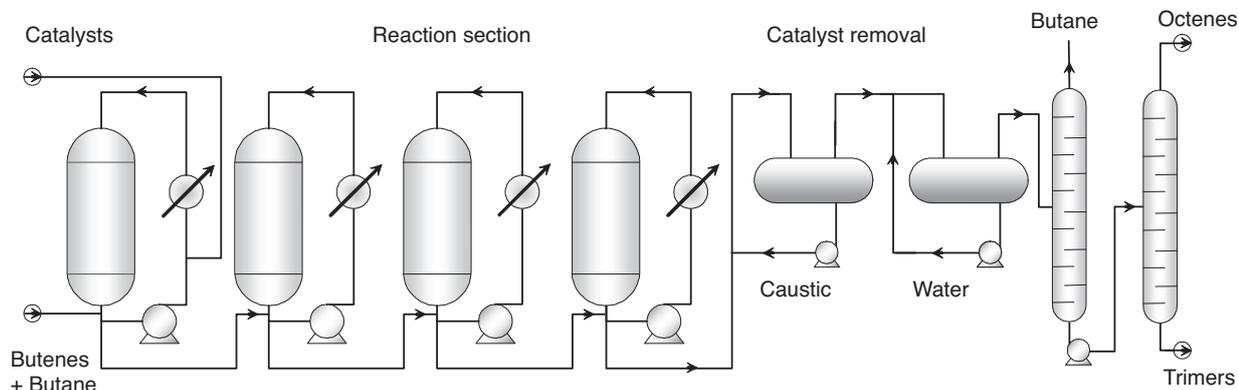


Figure 7

Dimersol Process Scheme.

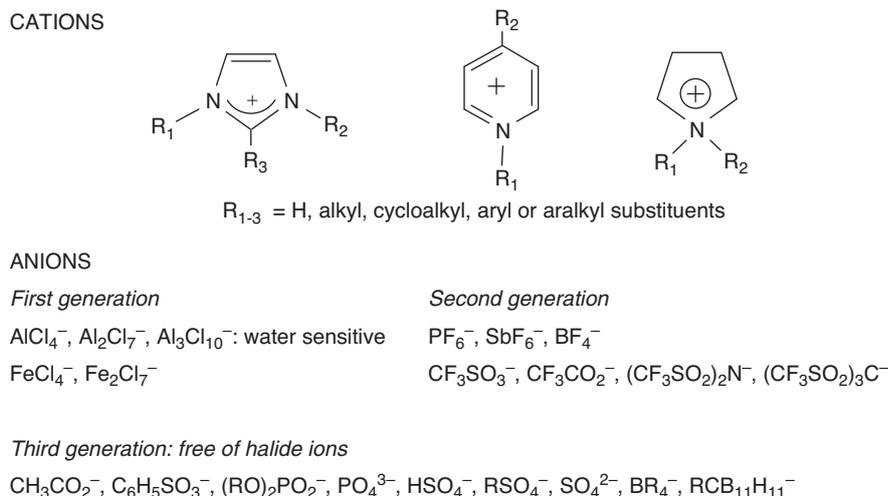


Figure 8

Selected examples of mostly used ionic liquids.

into diisononylphthalates (DINP) which are high value PVC plasticizers.

Dimersol- X^{TM} can also process a mixture of C_3 and C_4 olefins to make dimers and co-dimers.

3.1.1 The Dimersol Technology

Despite the diversity of the feeds, all Dimersol processes are based on the same processing steps. The reaction section comprises one or more cascaded reactors. Feed is injected continuously into the first reactor, Figure 7. The process takes place in the liquid phase using a soluble catalytic system at low pressure and mild temperature.

The catalyst system results from the reaction, in dilute medium, of two components: a catalyst precursor mixture containing a nickel organic salt and an aluminum-based co-catalyst. The two components produce the working Ziegler nickel hydride catalyst. The proprietary hydrocarbon-diluted nickel catalyst and aluminum-based co-catalyst are injected separately into the reaction loop under precise flow control. An external heat exchanger system enables accurate temperature control. To ensure complete separation of catalyst from the organic medium, the reactor effluent is chemically neutralized and the catalyst residue is removed from the hydrocarbon phase by aqueous washing in the neutralization section. A distillation column separates non-reactive hydrocarbons and unconverted olefins from oligomers.

The Dimersol- X^{TM} process produces octenes by butenes dimerization. These octenes are mainly used as starting material for isononanol manufacture, which are then converted into dialkylphthalate plasticizers.

The Dimersol- X^{TM} process scheme requires the same equipment with additional distillation enabling the separation of pure octenes and dodecenes.

The low degree of branching of these octenes has many advantages over the propylene or diisobutylene routes. Low-branched octenes are the preferred feedstocks for producing nonanols by the oxonation reaction because, compared with the propylene route, the feed costs less and the plasticizers are of higher quality. Compared with nonanols produced using the diisobutylene route, the Dimersol- X^{TM} allows a higher oxonation yield and produces better quality plasticizers.

3.1.2 The New Difasol Liquid-Liquid Biphasic Technology in Ionic Liquid

In the mid-1990s, research was initiated in one of the most promising recent areas in liquid phase catalysis: non-conventional, non-aqueous ionic liquids for biphasic catalysis. This technique employs a homogeneous catalyst dissolved in a liquid phase practically immiscible with the product, which enables easy separation of catalyst and organic products by simple phase decantation [57].

As a non-conventional class of solvent, non-aqueous ionic liquids are gaining importance in homogeneous catalysis. Previously, these media had been used extensively for electrochemical applications. Ionic liquids are only composed of ions. Although other cations have been extensively described in the literature, the most popular ones remain the dialkylimidazolium cations and particularly the 1-butyl-3-methylimidazolium or BMI^+ (Fig. 8).

The mixture of 1-Butyl-3-Methyl Imidazolium Chloride (BMIC) and aluminum chloride affords a liquid well below

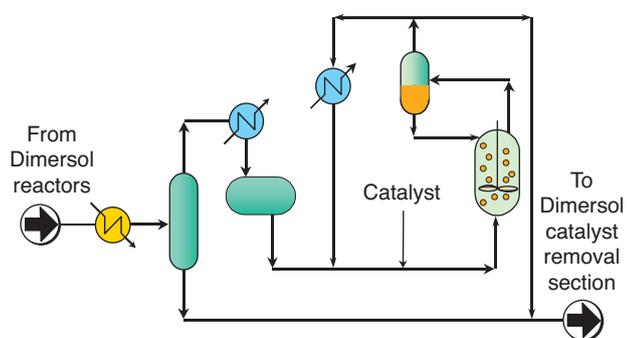


Figure 9

Biphasic Difasol section used as finishing step after a homogeneous Dimersol section.

room temperature and over a large range of compositions. These liquids proved to be good solvents for Ni catalyst for a variety of reasons:

- they are non-protic solvents and therefore compatible with the metal-carbon or metal-hydride bond active species;
- they are poorly miscible with hexenes, octenes and longer olefins (which, actually, is the first prerequisite to form a biphasic system) while propene and butenes solubility in ionic liquid is sufficient enough to stabilize the nickel active species and ensure high catalytic activity;
- chloroaluminates can easily be prepared from commercially available *N*-alkylimidazole, alkylchloride and aluminium chloride;
- the chloroaluminate anions proved to be weakly coordinating toward nickel complex. Moreover, nickel active species is efficiently stabilized in the ionic medium, without the need of further modification;
- chloroaluminate ionic liquids could be extended to chloroalkylaluminium derivatives, the ionic liquids play both the role of solvent and co-catalyst;
- chloroaluminate ionic liquids can be turned acidic by adjusting the aluminium chloride amount.

Compared to the corresponding single-phase homogeneous process, the new biphasic process leads to a more economical utilization of the catalyst. New and existing Dimersol units can be fitted with Difasol enabling lower dimer production costs.

Difasol Process: Dimersol Finishing Technology

Dimersol-XTM, in its present commercial form, can achieve up to 80% of *n*-butenes conversion with 85% octenes selectivity. Unfortunately the butenes conversion level is dependent on their initial concentration in the Dimersol-XTM feedstock, limiting industrial applications to C₄ cuts with a minimum butenes content of about 60%.

This was a potential limitation to Dimersol-XTM yield until the Difasol technology became available. This new

biphasic process promotes *n*-butenes dimerization even in poorly concentrated C₄ cuts and is thus ideally suited as a Dimersol-XTM finishing step (Fig. 9).

Effluent from the last Dimersol reactor is partly vaporized to separate unconverted C₄'s from octenes, heavy products and catalyst which are sent to the neutralization section. The vapor phase is totally condensed and sent to the Difasol reactor where the reaction occurs in liquid phase using the same nickel-based catalytic system as for the Dimersol process. The Difasol section consists of a stirred reactor that provides efficient mixing of the two liquid phases. The reactor outlet is sent to a settler where solvent and organic phases are separated. The solvent phase is returned to the reactor and a portion of the organic phase is recycled to the reactor through a cooler designed to remove the heat of reaction while the other part is sent to the neutralization section along with the effluent from the Dimersol reactors.

Difasol Process Features

Compared to conventional homogeneous Dimersol-XTM process, the biphasic system ensures more efficient catalyst utilization and reduces both residue production and operating cost. The dimer selectivity is higher, in the range of 90-95% compared to 85% in standard Dimersol X process. This is ascribed to the difference between the solubility of monomers and dimers in the ionic phase (Fig. 10). Improved butenes conversion (in the range of 70 to 80%) are easily achieved in a single step even with diluted feedstocks.

Difasol is ideally suited for use as the finishing reaction section for a conventional Dimersol unit. This arrangement is applicable either for grassroots units or for revamping of existing Dimersol-XTM plants.

The use of Difasol technology also extends the field of application of the Dimersol processes to less reactive feeds

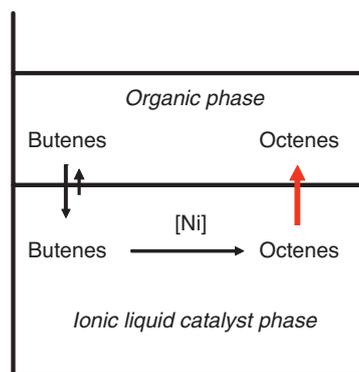


Figure 10

Schematic representation of biphasic catalysis in ionic liquids: improved selectivity for the dimers by a coupling of reaction and primary product separation.

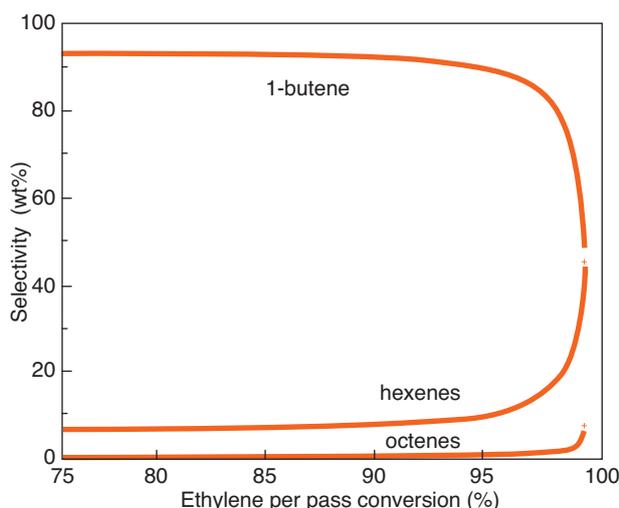
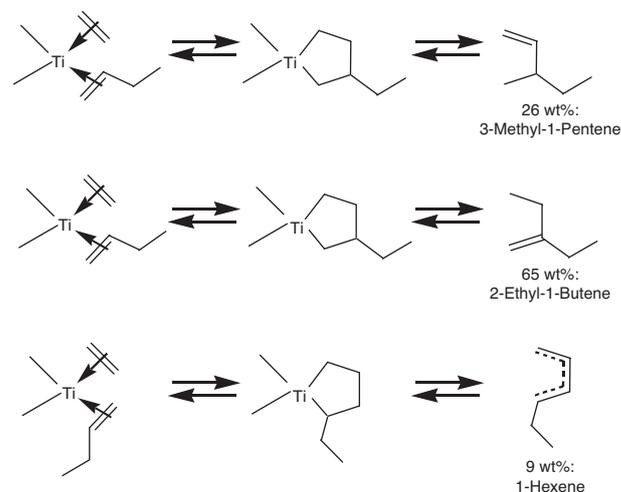


Figure 11

Impact of ethylene conversion on 1-butene selectivity.



Scheme 12

Consecutive side reactions responsible for the ethylene trimers in the Alphabutol process.

such as C_5 olefins, allowing for the production of nonenes and decenes through co-dimerization of C_4 and C_5 olefins.

3.2 The Alphabutol™ Process

In 1981, a challenging project was launched: the production of 1-butene by selective dimerization of ethylene. An efficient soluble titanium-triethylaluminum complex was identified and rapidly tested in a pilot plant. In 1985, the commercial viability of the catalyst was proved and definitively established. The first Alphabutol unit was started up in 1986 in Thailand (TPIC, 3 000 t/y), immediately followed by a much bigger plant for *Sabir* in Saudi Arabia (Petrokemya, 50 000 t/y). Today, 24 Alphabutol units have been licensed, for a cumulated 1-butene production capacity of 500 000 t/y. Nearly 25% of the world's 1-butene consumption as co-monomer in PE units is currently produced by Alphabutol technology.

The Alphabutol catalyst results from the reaction in the reaction medium of two components: a catalyst precursor mixture containing a titanium-based active metal and a co-catalyst diluted in 1-butene. Both components are separately injected into the reaction loop and react in situ to produce the catalyst. The principle catalytic step involves the coupling of two molecules of ethylene on the active titanium center to form a titanium (IV) heterocycle which then decomposes to 1-butene by an intra-molecular β hydrogen transfer as shown in Scheme 11. This chemical mechanism explains the high dimer selectivity. The absence of hydride species ensures low isomerization from 1 to 2-butenes, and less than 100 ppm of internal butenes is achieved.

A very minor amount of disproportionation produces *n*-butane (< 1500 ppm) and butadiene (<10 ppm), the latter being immediately converted to hexadienes. The production of higher molecular weight oligomers is minimized by adjusting the per pass conversion. In industrial plants the per-pass conversion is generally limited to about 80 to 85%. When conditions are optimized, 1-butene selectivity can attain 93%, Figure 11.

In this process, 1-butene is not highly reactive by itself, but it can react with ethylene, giving hexene isomers (Scheme 12). This is typically a consecutive-type reaction which depends on the level of ethylene conversion. The rate constant of the main reaction is much higher than the one of the trimerization. Therefore it is possible to minimize oligomer production by adjusting the ethylene conversion (Fig. 11).

The Alphabutol process, Figure 12, was developed in cooperation with Sabir to produce high purity 1-butene by ethylene dimerization. Directly derived from the Dimersol E technology, (bubble point reactor operated under temperature and pressure controls) the process operates in the liquid phase using a soluble catalyst system.

Polymer grade ethylene is dissolved into the reaction medium. The metal-based catalyst and the co-catalyst, both diluted in 1-butene, are continuously injected in the reaction loop. The unit is designed to ensure uniform distribution of the catalyst components without local over-concentration.

Ethylene concentration in the reaction loop is simply monitored by pressure control (flash reactor operated at its bubble point).

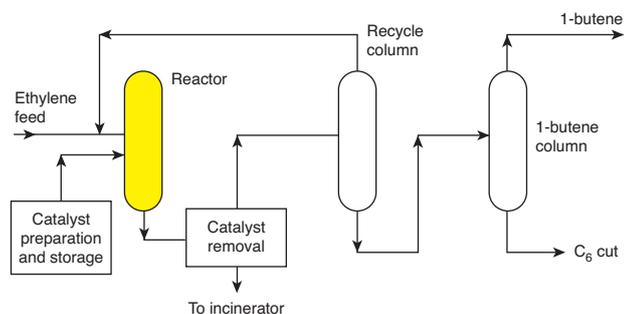


Figure 12
The Alphabutol Process.

Dimerization takes place in the liquid phase at mild conditions (typically 50-55°C) and under controlled catalyst and ethylene concentrations. The exothermic heat of reaction is removed by external cooling. No specific solvent is required since the reaction takes place directly in the reactant-products mixture. The reactor effluent leaves the reaction loop for a spent catalyst separation system. The spent catalyst is removed and transformed into a non-toxic material before disposal. The hydrocarbon portion is vaporized and sent to the distillation section. The first distillation column separates unconverted ethylene, which is recycled to the reaction section. The second column recovers high purity 1-butene and a C₆+ gasoline cut.

The Alphabutol process exhibits a major advantage if compared with any other industrial sources of 1-butene available on the open market: its steady high quality of 1-butene, Table 5. This enables to minimize the ethylene purge in downstream polyethylene unit.

TABLE 5
Alphabutol 1-butene characteristics

| | |
|------------------------|------------|
| 1-butene | 99.5% min |
| butane | < 1500 ppm |
| 2-butenes | < 200 ppm |
| C ₆ olefins | < 100 ppm |

Advantages of Alphabutol Over Competing Routes to 1-Butene Production

1-Butene is available in the C₄ fractions from naphtha crackers, but its recovery at a high purity level involves a sophisticated scheme. Among the various possible schemes, the most commonly used is the first to either extract or selectively hydrogenate butadiene, then to completely remove isobutene through MTBE synthesis at high conversion, followed by the separation of 1-butene from the other C₄'s either by super fractionation or by molecular sieves.

This processing scheme has the important drawback of being expensive in investment and operating cost compared to the Alphabutol route. To be economically viable, this scheme needs a local outlet for butadiene and MTBE. This favourable situation may hold for highly industrialized countries, mainly the USA, Japan and Europe, but it is not often the case in other countries. For a petrochemical company, the MTBE co-production can be problematic due to the recent MTBE ban in several locations.

A difficult market for these associated products or the lack of C₄ cut in case of ethane crackers, lead LLDPE manufacturers to envisage ethylene dimerization by Alphabutol for 1-butene production.

3.3 The AlphaSelect™ Process

The AlphaSelect process, developed in IFP's facilities in the beginning of the 90's, is oriented toward the production of high purity, linear alpha-olefins (C₄ to C₁₀) that can be used as ethylene co-monomers for LLDPE production. These olefins can also be used as precursors for plasticizer alcohols, organic acids or higher molecular weight poly-alpha-olefins.

This new technology, very similar to the industrially proven Alphabutol process, operates in the liquid phase using a proprietary soluble catalytic system. Polymer grade ethylene is dissolved in the reaction medium. The oligomerization reaction takes place in the presence of a solvent system, at moderate operating temperature and pressure (70-90 bar, 130-150°C). The solvent maintains the higher molecular weight co-products soluble and enhances the catalyst activity. The catalyst and co-catalyst are diluted in the same solvent and are continuously injected in the reaction loop. The oligomerization takes place under controlled catalyst/co-catalyst ratio, ethylene/solvent ratio and of course ethylene concentration. The catalyst/co-catalyst ratio is a key parameter that enables the modification of the molecular weight distribution of the linear alpha-olefins.

The reaction mechanism is different from that found with the Alphabutol catalyst. AlphaSelect employs a different active center and a metal hydride complex, represented by [M]-H, is probably the actual *in situ* catalyst (Scheme 9). Alpha-olefin oligomers follow a geometric Schulz-Flory distribution which is affected by the aluminum-to-metal ratio. Alpha-olefins from AlphaSelect are also of very high quality (see Tab. 6); however, in this process, since multiple additions of ethylene are required, purity does decrease with increasing molecular weight. The impurities which make up the remaining balance of the AlphaSelect streams are composed of slightly branched and linear internal olefins.

AlphaSelect is highly selective, up to 93 wt%, toward C₄-C₁₀ alpha-olefins. The product slate that is available with this process is one of its attractive features. The alpha-olefin distribution can be adjusted to obtain distributions that may vary with market demand, Table 7.

TABLE 6
Characteristics of the α -olefins produced

| AlphaSelect olefins | α -olefin purity (wt%) |
|---------------------|-------------------------------|
| 1-butene | 99 |
| 1-hexene | 98 |
| 1-octene | 96 |
| 1-decene | 92 |

TABLE 7
AlphaSelect C₄-C₁₀ olefin production flexibility

| AlphaSelect olefins | Distribution (wt%) |
|---------------------|--------------------|
| 1-butene | 35-40 |
| 1-hexene | 29-30 |
| 1-octene | 19-21 |
| 1-decene | 11-14 |

As with the Alphabutol process, the catalyst results from the reaction of two components diluted in the reaction medium. The catalyst precursor is freshly prepared in a preparation vessel near the reactor to ensure maximum activity. The precursor has a stability of a few weeks once freshly prepared.

The reactor effluent leaves the reaction loop for a spent catalyst separation system, Figure 13. The spent catalyst is removed and oxidized to a non-toxic form and is stored for disposal. The hydrocarbon portion is vaporized and sent to the distillation section. The first distillation column separates the unconverted ethylene which is directly recycled to the reactor. A following distillation section enables the separation of pure 1-butene, 1-hexene, 1-octene and 1-decene product streams. The solvent is purified in the separation

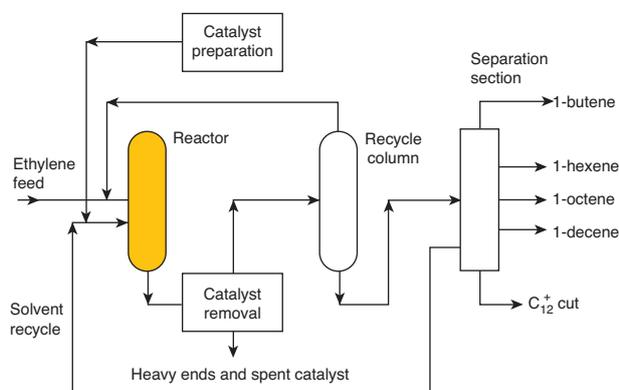


Figure 13
The AlphaSelect process

section and recycled to the reactor. The C₁₂+ oligomers are withdrawn from the fractionation bottom and from which valuable higher olefins can also be recovered.

Common Key Process Features

Both Alphabutol and AlphaSelect are characterized by their process simplicity. They employ carbon steel equipment and exhibit high turndown operations. Both processes are easy to operate and can produce high quality ethylene comonomers nearby polyethylene production units. The comparative economics of these processes are indicated in Table 8, below.

The Alphabutol process ensures a reliable, local source of steady, high purity 1-butene nearby the polyethylene unit.

AlphaSelect provides a flexible yield of C₄ to C₁₀ alpha-olefins and allows in-situ comonomers production for modern multi grade LLDPE units.

TABLE 8
Comparative Alphabutol and AlphaSelect economics

| | Alphabutol (30000 t/y 1-butene) | AlphaSelect (100000 t/y C ₄ -C ₁₀ alpha-olefins) |
|--|---|--|
| Battery limits erected cost ⁽¹⁾ , 10 ⁶ U.S.\$ | 14 | 80 |
| Raw material ⁽²⁾ - Ethylene, tons | 1.1 | 1.22 |
| By-products ⁽²⁾ , tons | C ₆ ⁺ cut: 0.08 Fuel gas: 0.02 | C ₁₂ ⁺ olefins: 0.14 Fuel gas: 0.04 Heavy ends: 0.04 |
| Utilities Cost ⁽³⁾ , \$/t of product | 27 | 173 |
| Catalyst & Chemical Cost ⁽³⁾ , \$/t of product | 27 | 30 |

(1) 2007 Gulf Coast Basis, excluding licensor fees and detailed engineering.

(2) Expressed in tons per ton of 1-butene (Alphabutol) or C₄-C₁₀ α -olefins (AlphaSelect).

(3) Expressed in U.S.\$ per ton of 1-butene (Alphabutol) or C₄-C₁₀ α -olefins (AlphaSelect).

Recently IFP has completed the development of a new process able to produce selectively pure 1-hexene from ethylene. This new process is based on a proprietary chromium catalyst. Twenty years' experience of Alphabutol industrial applications has been integrated in this new technology to provide polymer grade purity 1-hexene close to a polyethylene unit.

CONCLUSION

During the last twenty years, the development of new ligands has been essential for the improvement of olefin oligomerization catalysts. Homogeneous catalysts allow good flexibility in the processes. Their high activity at low

concentration level (ppm) enables to limit costs resulting from catalyst consumption and spent catalyst disposal. Progress have been made by finding more active and more selective catalysts and also by the development of two-phase catalytic processes.

The lighter linear alpha-olefins such as 1-butene, 1-hexene and 1-octene are predominantly produced by metal-catalyzed oligomerization of ethylene, which usually leads to a distribution of alpha-olefins with different chain lengths that frequently does not match the market demand. Now, 1-butene, 1-hexene can be produced by selective dimerization or trimerization of ethylene.

The production of these high purity olefins with these new on purpose processes has several advantages over other sources of supply: better and more steady product quality, a small amount of by-products, and a feedstock normally available at a polyethylene plant site.

According to recent progress, the extension of selective oligomerization route to the production of 1-octene and perhaps 1-decene seems possible.

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