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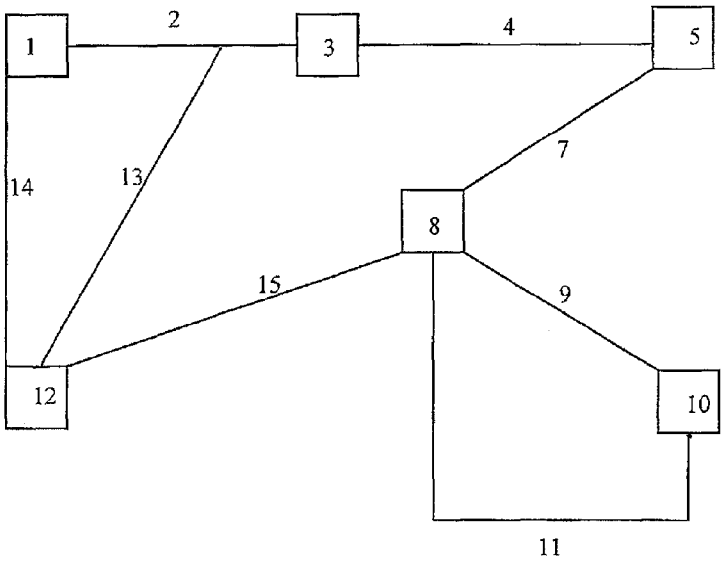
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(54) Title: INTEGRATED CHEMICALS COMPLEX CONTAINING OLEFINS

Figure 1



(57) Abstract: The present invention provides an integrated chemical complex comprising one or more unit operations selected from the group consisting of a steam cracker comprising a C_2 splitter, a linear alpha olefin plant and a solution or slurry polyethylene plant the improvement comprising integrating into the complex a reactor for the trimerization or tetramerization of ethylene in the presence of a catalyst system comprising: (iv) a source of chromium; (v) a defined P-N-P ligand; and (vi) an activator and a distillation column to separate one or more of ethylene, 1-hexene, 1-octene which olefins containing less than 1.5 weight % of internal olefins. The integration provides savings in terms of capital costs, operating costs or both.

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INTEGRATED CHEMICALS COMPLEX CONTAINING OLEFINS

TECHNICAL FIELD

The present invention relates to an integrated chemical complex containing an integrated olefins oligomerization plant and at least one common distillation column. It is known to oligomerize olefins and particularly ethylene to produce higher alpha olefins. Oligomerizations based on aluminum alkyls tend to produce a number of C_{2n} olefins where n is a whole number generally between about 2 and about 10, and isomers (e.g. 1-olefins and internal olefins). The separation of these various olefins requires an extensive and expensive separation train. New technology is being developed where on demand fairly clean oligomers can be prepared (e.g. 1-hexene and 1-octene). Under these conditions it is possible to separate the oligomers in a column which is common with at least one other unit operations such as at the back end of a slurry or solution polyethylene plant.

BACKGROUND ART

Two drivers for changes in chemical complexes are the cost of energy and the reduction of emissions. As the cost of energy rises it becomes more important to, where possible, use common equipment among various unit operations to reduce capital and operating costs and to reduce emissions.

One approach has been to try to eliminate or significantly down size the back end of a cracker. In some circumstances it is possible to reduce the equipment on the cold side of a cracker by eliminating or down sizing the C_2 splitter. The result is the production of "dilute ethylene" which may be fed directly to some unit operations such as polymerization, alkylation or even a linear alpha olefins (LAO) unit and to recycle unconsumed ethane from the dilute stream back to the cracker. Some examples of this approach include U.S. patent 5,981,818 issued Nov 9, 1999 to Purvis et al. assigned to Stone & Webster; U.S. 6,111,156 issued Aug. 29, 2000 to Oballa et al. assigned to NOVA Chemicals International S.A.; and WO2007/016993 published Feb 15, 2007 in the name of Fritz et al. assigned to Saudi Basic Industries Corporation and Linde AG.

There are a number of patents in the name of BP Chemicals Limited that teach oligomerization of ethylene using P-N-P ligands. One example of such a patent is U.S. 6,800,702 issued Oct. 5, 2004 in the name of Wass. While the patent suggests combining the trimerization reaction with a separation step such as reactive distillation

the patent does not clearly teach combining common separation steps of the oligomerization reaction with a similar separation of another unit operation such as polymerization.

United States patent application 2007/0129583 published June 7, 2007 in the name of De Boer et al., teaches a process for the concurrent trimerization and tetramerization of ethylene. While the patent describes the separation of hexene and octene it does not appear to contemplate the integration of the separation process with other unit operations such as polymerization.

United States patent applications 2010/0081777 and 2010/0081842 both in the name of Gao et al., assigned to NOVA Chemicals both published April 1, 2010 disclose phosphorous–nitrogen–phosphorous (P-N-P) catalysts and processes for the tetramerization and trimerization of ethylene to 1-octene and 1-hexene respectively.

The present invention seeks to provide an improved integrated chemical complex comprising an oligomerization operation, preferably for trimers and tetramers of ethylene with low amounts of internal olefins (e.g. less than 1.5 %) and other unit operations including solution phase polymerization of ethylene and octene with a common separation unit for the oligomerization process and the down stream separation for example of the polyethylene plant.

DISCLOSURE OF THE INVENTION

In one embodiment the present invention provides in a chemical complex comprising one or more unit operations selected from the group consisting of a steam cracker, either ethane or naphtha, comprising a C_2 splitter, a linear alpha olefin plant and a solution or slurry polyethylene plant the improvement comprising integrating into the complex a reactor for the trimerization or tetramerization ethylene in the presence of a catalyst system comprising:

(i) a source of chromium;

(ii) a defined P-N-P ligand; and

(iii) an activator

and a distillation column to separate one or more of ethylene, 1-hexene, 1-octene which olefins containing less than 1.5 weight % of internal olefins.

In a further embodiment the complex comprises two or more unit operations.

In a further embodiment the distillation column is an integrated common distillation column shared by the reactor for the trimerization or tetramerization of ethylene and at least one other unit operation.

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In a further embodiment the unit operations are integrated with the reactor for the trimerization or tetramerization of ethylene to reduce capital or operating costs or both in the complex by:

(i) using common distillation columns for the separation C_{6-8} olefins; or

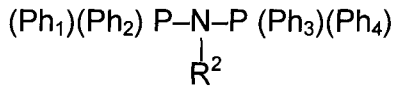
(ii) passing at least a portion of the feed to the C_2 splitter of the steam cracker to the tetramerization or trimerization reactor(s) or both and recycling unconsumed ethane to the cracker; or

(iii) both (i) and (ii).

In a further embodiment the reactor for trimerization or tetramerization of ethylene produces a liquid product stream which contains linear octenes and linear hexenes. Preferably the linear octenes and hexenes are alpha olefins containing less than 1.5, preferably less than 1 weight % of internal olefins.

In a further embodiment the P-N-P ligand in the trimerization or tetramerization reactor is selected from the group consisting of

(a) P-N-P ligands having the formula:



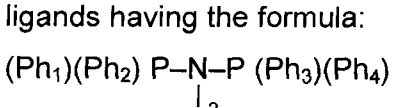
wherein each of Ph_1, Ph_2, Ph_3 and Ph_4 is a phenyl group bonded to a phosphorus atom, with the provisos that:

i) at least one of Ph_1, Ph_2, Ph_3 and Ph_4 is ortho substituted with a halogen selected from the group consisting of fluorine, bromine and chlorine;

ii) at least one of Ph_1, Ph_2, Ph_3 and Ph_4 does not have any substituents in ortho positions; and

iii) R^2 is selected from the group consisting of hydrogen, C_{1-20} hydrocarbyl and silyl; and

(b) P-N-P ligands having the formula:



wherein each of Ph_1, Ph_2, Ph_3 and Ph_4 is a phenyl group bonded to a phosphorus atom, with the provisos that:

i) at least one of Ph_1, Ph_2, Ph_3 and Ph_4 is ortho substituted with a halogen selected from the group consisting of fluorine, bromine and chlorine;

ii) at least one of Ph_1, Ph_2, Ph_3 and Ph_4 is ortho substituted with a polar substituent; and

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iii) R^2 is selected from the group consisting of hydrogen, C_{1-20} hydrocarbyl and silyl.

In a further embodiment in the P-N-P ligand in the trimerization or tetramerization reactor said halogen is fluorine.

In a further embodiment in the P-N-P ligand in the trimerization or tetramerization reactor R^2 is a C_{1-4} hydrocarbyl.

In a further embodiment in the P-N-P ligand in the trimerization or tetramerization reactor R^2 is isopropyl.

In a further embodiment in the P-N-P ligand in the trimerization or tetramerization reactor said polar substituent is a C_{1-3} alkoxy radical.

In a further embodiment in the trimerization or tetramerization reactor the source of chromium is selected from the group consisting of chromium trichloride, chromium (III) 2-ethylhexanoate, chromium (III) acetylacetonate and chromium carboxyl compounds.

In a further embodiment in the trimerization or tetramerization reactor the activator is selected from the group consisting of:

(a) $LiAlH_4$;

(b) aluminum alkyls of the formula $Al(R^3)_a(X)_b$ where R^3 is selected from the group consisting of C_{1-8} alkyl and alkoxide radicals, X is a halogen and a and b are 0 or a positive integer provided the sum of a+b is 3;

(c) an aluminoxane selected from the group consisting of:

(i) linear aluminoxanes having the formula $[R^6AlO]_S$ wherein R^6 is selected from the group consisting of C_{1-6} alkyl radicals and s is a number from 2 to 50;

(ii) cyclic aluminoxanes having the formula $R^7(R^8AlO)_S$ wherein R^7 and R^8 are selected from the group consisting of C_{1-6} alkyl radicals and s is a number from 2 to 50; and

(iii) mixtures thereof;

(d) ionic activators selected from the group consisting of:

(i) compounds of the formula $[R^{13}]^+ [B(R^{14})_4]^-$ wherein B is a boron atom, R^{13} is a cyclic C_{5-7} aromatic cation or a triphenyl methyl cation and each R^{14} is independently selected from the group consisting of phenyl radicals which are unsubstituted or substituted with 3 to 5 substituents selected from the group consisting of a fluorine atom, a C_{1-4} alkyl or alkoxy radical which is unsubstituted or substituted by a fluorine atom; and a silyl radical of the formula $-Si-(R^{15})_3$

wherein each R^{15} is independently selected from the group consisting of a hydrogen atom and a C_{1-4} alkyl radical; and

(ii) compounds of the formula $[(R^{18})_t ZH]^+[B(R^{14})_4]^-$ wherein B is a boron atom, H is a hydrogen atom, Z is a nitrogen atom or phosphorus atom, t is 2 or 3 and R^{18} is selected from the group consisting of C_{1-8} alkyl radicals, a phenyl radical which is unsubstituted or substituted by up to three C_{1-4} alkyl radicals, or one R^{18} taken together with the nitrogen atom may form an anilinium radical and R^{14} is as defined above; and

(iii) compounds of the formula $B(R^{14})_3$ wherein R^{14} is as defined above.

In a further embodiment the molar ratio of Cr to P-N-P ligand is from 100:1 to 1:100 and the molar ratio of Al or B from the activator to Cr is from 0.5 to 1000 :1.

In a further embodiment the trimerization or tetrameraization reactor is operated at a temperature of from 10° C to 300° C and a pressure of from 0.5 MPa (5 atmospheres) to 10MPa (100 atmospheres).

In a further embodiment the complex comprises a steam cracker selected from the group consisting of ethane crackers and naphtha crackers upstream of said trimerization or tetramerization reactor and a C_2 stream from the cracker from which hydrogen, methane and acetylenes have been removed comprising not less than 55%, preferably not less than 60 %, ethylene is fed directly to said trimerization or tetramerization reactor and the ethane recovered from the product stream from said trimerization or tetramerization reactor is recycled back to said steam cracker.

In a further embodiment the complex comprises a solution polyethylene plant and a common distillation column for the back end of the polyethylene plant (e.g. for separation of 1-octane and/or C_{10+} components from the polymerization reaction) and the trimerization or tetramerization reactor.

In a further embodiment the complex comprises a conventional linear alpha olefins plant and the product streams from the conventional linear alpha olefins plant and the trimerization or tetramerization reactor after the catalyst removal step are processed in a common separation unit to separate different alpha olefins.

The present invention also contemplates combinations of the foregoing embodiments in whole or in part and singularly and in combinations including an aggregate combination of all the embodiments.

BRIEF DESCRIPTION OF THE DRAWING

Figure 1 is a schematic drawing of a chemical complex comprising an oligomerization plant, a solution polyethylene plant, a steam cracker and a conventional LAO plant.

BEST MODE FOR CARRYING OUT THE INVENTION

PART A: Catalyst System

The catalyst system used in the process of the present invention must contain three essential components, namely:

(i) a source of chromium:

(ii) a defined P-N-P ligand; and

(iii) an activator.

Preferred forms of each of these components are discussed below.

Chromium Source ("Component (i)")

Any source of chromium which allows the oligomerization process of the present invention to proceed may be used. Preferred chromium sources include chromium trichloride; chromium (III) 2-ethylhexanoate; chromium (III) acetylacetonate and chromium carbonyl complexes such as chromium hexacarbonyl.

Component (ii)

Ligand Used in the Tetramerization Process ("Component (ii)")

In one embodiment, the ligand used in the oligomerization process of this invention is defined by the formula:

$$(Ph_1)(Ph_2)\,P\text{–}N(R^2)\text{–}P\,(Ph_3)(Ph_4)$$

wherein each of Ph_1, Ph_2, Ph_3 and Ph_4 is a phenyl group bonded to a phosphorus atom, with the provisos that

i) at least one of Ph_1, Ph_2, Ph_3 and Ph_4 is ortho substituted with a halogen selected from the group consisting of fluorine, bromine and chlorine;

ii) at least one of Ph_1, Ph_2, Ph_3 and Ph_4 does not have any substituents in ortho positions; and

iii) R_2 is selected from the group consisting of hydrogen, $C_{1\text{-}20}$ hydrocarbyl and silyl radicals.

Each halogen is preferably fluorine.

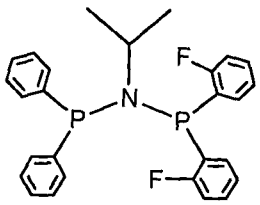
R_2 is preferably a hydrocarbyl radical having from 1 to 20 carbon atoms. The analogous silyl groups may also be employed. The hydrocarbyl groups of R_2 may

contain heteroatom substituents (having a heteroatom selected from O, N, P and S). Simple alkyl groups having from 1 to 12 carbon atoms are preferred. Isopropyl is particularly preferred.

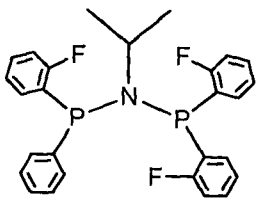
The ortho halogen substituent(s) on the phenyl groups of the ligands of this embodiment are critical to the tetramerization of ethylene to produce a product with a low amount of hexene and internal olefins. Substituents at meta or para positions are generally less important but are contemplated within the scope of the present invention. In addition to the requirement that at least one of the phenyl groups contain an ortho halogen substituent, there is a second requirement that at least one of the other phenyl groups does not contain any substituent in the ortho positions – i.e. neither of the phenyl ring carbon atoms which are adjacent to the carbon atom bonded to phosphorus contains a substituent (they are both bonded only to a single hydrogen atom). In a preferred aspect of this embodiment, the phenyl groups which do not have ortho substituents are further characterized by being completely unsubstituted.

In another embodiment, the substituents on the four phenyl groups satisfy another condition, namely that all of Ph_1, Ph_2, Ph_3 and Ph_4 are either ortho substituted with a halogen (preferably fluorine) or contain no ortho substituents.

Without limiting the scope of the above some ligands of this embodiment include compounds of the structure:



Ligand 1

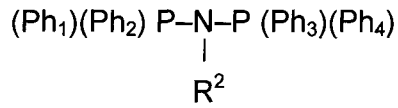


Ligand 2

Ligand Use in the Trimerization Process

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In general, the ligand used in the trimerization process of this invention is defined by the formula:



wherein each of Ph_1, Ph_2, Ph_3 and Ph_4 is a phenyl group bonded to a phosphorus atom, with the provisos that

i) at least one of Ph_1, Ph_2, Ph_3 and Ph_4 is ortho substituted with a halogen selected from the group consisting of fluorine, bromine and chlorine;

ii) at least one of Ph_1, Ph_2, Ph_3 and Ph_4 is ortho substituted with a polar substituent; and

iii) R_2 is selected from the group consisting of hydrogen, C_{1-20} hydrocarbyl and silyl radicals.

In this embodiment each halogen is preferably fluorine.

In this embodiment R_2 is preferably a hydrocarbyl group having from 1 to 20 carbon atoms. The analogous silyl groups may also be employed. The hydrocarbyl groups of R_2 may contain heteroatom substituents (having a heteroatom selected from O, N, P and S). Simple alkyl groups having from 1 to 12 carbon atoms are preferred. Isopropyl is particularly preferred.

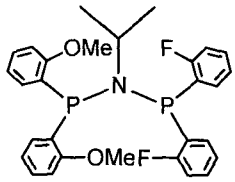
As used in this embodiment, the term "polar" refers to a substituent with a dipole moment. Examples include C_{1-20} alkoxy (with methoxy, ethoxy and isopropoxy being preferred – especially methoxy); phenoxy, hydroxyl, amino, sulfate and the like. Alkoxy substituents are most preferred, especially methoxy.

In a preferred aspect of this embodiment, the substituents on the four phenyl groups satisfy another condition, namely that all of Ph_1, Ph_2, Ph_3 and Ph_4 are either ortho substituted with a halogen (preferably fluorine) or ortho substituted with a polar substituent (especially an alkoxy substituent).

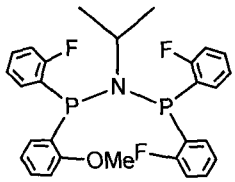
The ortho substituents on the phenyl groups of the ligands of this embodiment are critical to this embodiment of the invention. Substituents at meta or para positions are generally less important but are contemplated within the scope of the present invention.

Without limiting the scope of the above, some ligands of this embodiment include compounds of the structure:

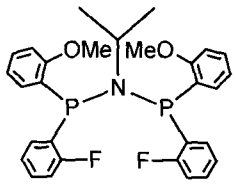
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Ligand A



Ligand B



Ligand C

Activator ("Component (iii)")

The activator (component (iii)) may be any compound that generates an active catalyst for ethylene oligomerization with components (i) and (ii). Mixtures of activators may also be used. Suitable compounds include organoaluminum compounds, organoboron compounds and inorganic acids and salts, such as tetrafluoroboric acid etherate, silver tetrafluoroborate, sodium hexafluoroantimonate and the like. Suitable organoaluminum compounds include compounds of the formula AlR_3, where each R is independently C_1 –C_{12} alkyl, oxygen or halide, and compounds such as $LiAlH_4$ and the like. Examples include trimethylaluminum (TMA), triethylaluminum (TEA), tri-isobutylaluminium (TIBA), tri-n-octylaluminium, methylaluminium dichloride, ethylaluminium dichloride, dimethylaluminium chloride, diethylaluminium chloride, ethylaluminiumsesquichloride, methylaluminiumsesquichloride, and alumoxanes. Alumoxanes are well known in the art as typically oligomeric compounds which can be prepared by the controlled addition of water to an alkylaluminium compound, for example trimethylaluminium. Such compounds can be linear, cyclic, cages or mixtures thereof. Commercially available alumoxanes are generally believed to be mixtures of linear and cyclic compounds. The cyclic alumoxanes can be represented by the formula $[R^6AlO]_S$ and the linear alumoxanes by the formula $R^7(R^8AlO)_S$ wherein s is a number from about 2 to 50, and wherein R^6, R^7, and R^8 represent hydrocarbyl groups,

preferably C_1 to C_6 alkyl groups, for example methyl, ethyl or butyl groups. Alkylalumoxanes especially methylalumoxane (MAO) are preferred. (MAO is also referred to as methalumoxane and methylaluminoxane in the literature).

It will be recognized by those skilled in the art that commercially available alkylalumoxanes may contain a proportion of trialkylaluminium. For instance, commercial MAO usually contains approximately 10 wt % trimethylaluminium (TMA), and commercial "modified MAO" (or "MMAO") contains both TMA and TIBA. Quantities of alkylalumoxane are generally quoted herein on a molar basis of aluminium (and include such "free" trialkylaluminium). The alkylalumoxane and/or alkylaluminium may be added to the reaction media (i.e. ethylene and/or diluent and/or solvent) prior to the addition of the catalyst or at the same time as the catalyst is added. Such techniques are known in the art of oligomerization and are disclosed in more detail in for example, U.S.P. 5,491,272; 5,750,817; 5,856,257; 5,910,619; and 5,919,996.

Examples of suitable organoboron compounds are boroxines, $NaBH_4$, trimethylboron, triethylboron, dimethylphenylammoniumtetra(phenyl)borate, trityltetra(phenyl)borate, triphenylboron, dimethylphenylammonium tetra(pentafluorophenyl)borate, sodium tetrakis[(bis-3,5-trifluoromethyl)phenyl]borate, trityltetra(pentafluorophenyl)borate and tris(pentafluorophenyl) boron.

Activator compound (iii) may also be or contain a compound that acts as a reducing or oxidizing agent, such as sodium or zinc metal and the like, or oxygen and the like.

In the preparation of the catalyst systems used in the present invention, the quantity of activating compound to be employed is easily determined by simple testing, for example, by the preparation of small test samples which can be used to oligimerize small quantities of ethylene and thus to determine the activity of the produced catalyst. It is generally found that the quantity employed is sufficient to provide 0.5 to 1000 moles of aluminium (or boron) per mole of chromium. MAO is the presently preferred activator. Molar Al/Cr ratios of from 1/1 to 500/1 are preferred.

PART B: Process Conditions

The chromium (component (i)) and ligand (component (ii)) may be present in any molar ratio which produces oligomer, preferably between 100:1 and 1:100, and most preferably from 10:1 to 1:10, particularly 3:1 to 1:3. Generally the amounts of (i) and (ii) are approximately equal on a molar basis, i.e. a ratio of between 1.5:1 and 1:1.5.

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Components (i)-(iii) of the catalyst system utilized in the present invention may be added together simultaneously or sequentially, in any order, and in the presence or absence of ethylene in any suitable solvent, so as to give an active catalyst. For example, components (i), (ii) and (iii) and ethylene may be contacted together simultaneously, or components (i), (ii) and (iii) may be added together simultaneously or sequentially in any order and then contacted with ethylene, or components (i) and (ii) may be added together to form an isolable metal-ligand complex and then added to component (iii) and contacted with ethylene, or components (i), (ii) and (iii) may be added together to form an isolable metal-ligand complex and then contacted with ethylene. Suitable solvents for contacting the components of the catalyst or catalyst system include, but are not limited to, hydrocarbon solvents such as heptane, toluene, 1-hexene, 1-octene, xylenes, C_5-C_{12} paraffinic and cycloparaffinic hydrocarbons and the like.

The catalyst components (i), (ii) and (iii) utilized in the present invention are typically unsupported. The catalyst components may be mixed in any order in a solvent or diluent as noted above.

If desired the catalyst may be supported on a support material, for example, silica, alumina, $MgCl_2$ or zirconia, or on a polymer, for example polyethylene, polypropylene, polystyrene, or poly(aminostyrene). The catalysts may be formed in situ in the presence of the support material, or the support material may be pre-impregnated or premixed, simultaneously or sequentially, with one or more of the catalyst components. The quantity of support material employed can vary widely, for example from 100,000 to 1 grams per gram of metal present in the transition metal compound. In some cases, the support material may also act as, or as a component of, the activator compound (iii). Examples include supports containing alumoxane moieties.

The oligomerization may be conducted under solution phase, slurry phase, gas phase or bulk phase conditions. Suitable temperatures range from 10° C to +300° C preferably from 10° C to 100° C, especially from 30°C to 85° C. Suitable pressures are from 0.1 MPa (atmospheric) to 80MPa (800 atmospheres) preferably from 0.5 MPa (5 atmospheres) to 10 MPa (100 atmospheres), especially from 1MPa to 8 MPa (10 to 80 atmospheres).

Irrespective of the process conditions employed, the oligomerization is typically carried out under conditions that substantially exclude oxygen, water, and other materials that act as catalyst poisons. Also, oligomerization can be carried out in the

presence of additives to control selectivity, enhance activity and reduce the amount of polymer formed in the oligomerization processes. Potentially suitable additives include, but are not limited to, hydrogen or a halide source.

There exist a number of options for the oligomerization process including batch, semi-batch, and continuous operation. The reactions of the present invention can be performed under a range of process conditions that are readily apparent to those skilled in the art: as a homogeneous liquid phase reaction in the presence or absence of an inert hydrocarbon diluent such as toluene or heptanes; as a two-phase liquid/liquid reaction; as a slurry process where the catalyst is in a form that displays little or no solubility; as a bulk process in which essentially neat reactant and/or product olefins serve as the dominant medium; as a gas-phase process in which at least a portion of the reactant or product olefin(s) are transported to or from a supported form of the catalyst via the gaseous state. Evaporative cooling from one or more monomers or inert volatile liquids is one method that can be employed to effect the removal of heat from the reaction. The reactions may be performed in the known types of gas-phase reactors, such as circulating bed, vertically or horizontally stirred-bed, fixed-bed, or fluidized-bed reactors, liquid-phase reactors, such as plug-flow, continuously stirred tank, or loop reactors, or combinations thereof. In accordance with the present invention distillation is used to separate products, reactants and catalyst separation and/or purification.

Also advantageous may be a process which includes more than one reactor, a catalyst kill system between reactors or after the final reactor, or an integrated reactor/separator/purifier. While all catalyst components, reactants, inerts and products could be employed in the present invention on a once-through basis, it is often economically advantageous to recycle one or more of these materials; in the case of the catalyst system, this might require reconstituting one or more of the catalysts components to achieve the active catalyst system. It is within the scope of this invention that an oligomerization product might also serve as a solvent or diluent. Mixtures of inert diluents or solvents also could be employed. The preferred diluents or solvents are aliphatic and aromatic hydrocarbons such as, for example, isobutane, pentane, toluene, xylene, ethylbenzene, cumene, mesitylene, heptane, cyclohexane, methylcyclohexane, 1-hexene, 1-octene, tetrahydronaphthalene, 1-decene and the like, and mixtures such as Isopar™.

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Techniques for varying the distribution of products from the oligomerization reactions include controlling process conditions (e.g. concentration of components (i)-(iii), reaction temperature, pressure, residence time) and properly selecting the design of the process and are well known to those skilled in the art.

The preferred oligomerization process of this invention is also characterized by producing very low levels of internal olefins (i.e. low levels of hexene-2, hexene-3, octene-2, octene-3 etc.), with preferred levels of less than 10 weight% (especially less than 5 weight%) of the hexenes and octenes being internal olefins. Low levels of internal olefins (e.g. hexene-2 and/or hexene-3 octene-2, octane -3 and/ or octent-4) are highly desirable because:

a) internal olefins generally have boiling points that are very close to the boiling point of the alpha olefin (and hence are difficult to separate from the alpha olefin by distillation); and

b) internal olefins are difficult to copolymerize with ethylene using conventional catalysts (in comparison to alpha olefins) and hence are not desired for use in most copolymerizations.

It is generally preferred to deactivate the oligomerization catalyst at the end of the oligomerization reaction. In general, many polar compounds (such as water, alcohols, amines and carboxcylic acids) will deactivate the catalyst. The use of alcohols and/or carboxcylic acids is preferred – and combinations of both are contemplated.

It is also preferred to remove the catalyst (and by-product polymer, if any) from the liquid product stream. Techniques for catalyst deactivation/product recovery that are known for use with other oligomerization catalysts should also be generally suitable for use with the present catalysts (see for example, U.S. 5,689,208 and 5,340,785).

Integration

There are a number of ways the oligomerization (trimerization or tetramerization) process may be integrated in a chemical complex, using one or more common distillation columns or separators.

Solution Polymerization

Solution processes for the (co)polymerization of ethylene are well known in the art. These processes are conducted in the presence of an inert hydrocarbon solvent typically a C_{5-12} hydrocarbon which may be unsubstituted or substituted by a C_{1-4} alkyl group, such as pentane, methyl pentane, hexane, heptane, octane, cyclohexane,

methylcyclohexane and hydrogenated naphtha. An example of a suitable solvent which is commercially available is "Isopar E" (C_{8-12} aliphatic solvent, Exxon Chemical Co.).

The polymerization temperature in a conventional solution process is from about 80°C to about 300°C (preferably from about 120° C to 250° C). The upper temperature limit will be influenced by considerations which are well known to those skilled in the art, such as a desire to maximize operating temperature (so as to reduce solution viscosity) while still maintaining good polymer properties (as increased polymerization temperatures generally reduce the molecular weight of the polymer). In general, the upper polymerization temperature will preferably be between 200° C and 300° C (especially 220° C to 250° C). The most preferred reaction process is a "medium pressure process", meaning that the pressure in the reactor is preferably less than about 42 MPa (420 atmospheres). Preferred pressures are from 10 to 40 MPa, most preferably from 14-22 MPa (about 140 to 220 atmospheres).

Suitable monomers for copolymerization with ethylene include 1-hexene and 1-octene, preferably 1-octene which may be prepared by the oligomerization process described above.

In the solution polyethylene process after the solution of polyethylene leaves the last reactor most of the solvent and unreacted monomer is flashed off in a lower pressure drum. This results in a mixture of solvent typically C_{6-10} alphatic or aromatic solvents, ethylene and the comonomer typically 1-octene. The ethylene is recovered from the flash drum as a vapor phase. The liquid phase is fed to a distillation column to separate the solvent from the co-monomer, particularly 1-octene.

In one aspect of the present invention both a solution phase olefins polymerization reactor and a ethylene trimeriztion or tetramerization reactor are integrated with a common column used to separate 1-octene (boiling point ≅ 121° C) and optionally 1-hexene (boiling point ≅ 63° C) from solvent used in the solution phase olefins polymerization plant. The solvent may be selected so that it has a boiling point at least 5° C, preferably 10° C or more different from the boiling point of the 1-olefin (1-octene or 1-hexene). In the integrated operation of the common distillation column for a solution polymerization plant and an oligomerization plant preferably the distillation load (in terms of volume of feed to the column) from the polymerization unit should not exceed about 40 vol% of the feed preferably less than 25 vol% of the feed. This is preferred so that if the polymerization plant has an up set there is sufficient capacity to handle the load without excessive loss of feed to for example a flare stack.

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In a further aspect of the present invention an ethylene trimerization or tetramerization plant may be integrated with a conventional linear alpha olefins plant and a common column(s) may be used to separate C_6 and C_8 olefins. "Conventional linear alpha olefin plants" includes i) those processes which produce alpha olefins by a chain growth process using an aluminum alkyl catalyst, ii) the "SHOP" process and iii) the production of olefins from synthesis gas using the Lurgi process have a series of distillation columns to separate the "crude alpha product" (i.e. a mixture of alpha olefins) into alpha olefins (such as butene-1, hexene-1 and octene-1). The mixed hexene-octene product which is produced in accordance with the present invention is highly suitable for addition/mixing with a crude alpha olefin product from a conventional linear alpha olefin plant (or a "cut" or fraction of the product from such a plant) because the mixed hexene-octene product produced in accordance with the present invention can have very low levels of internal olefins. Thus, the hexene-octene product of the present invention can be readily separated in the existing distillation columns of conventional linear alpha olefin plants (without causing the large burden on the operation of these distillation columns which would otherwise exist if the present hexene-octene product stream contained large quantities of internal olefins). As used herein a linear alpha olefins plant refers to a plant to oligomerize ethylene in the presence of a metal alkyl (typically aluminum) compound such as trimethyl or triethyl aluminum or a homogeneous catalyst containing for e.g. Ti, Zr, Cr, complexes alternatively, in the presence of an organometallic nickel catalyst (in the so called Shell Higher Olefins, or "SHOP" process). The product from the tetramerization or trimerization plant produced using a source of chromium, a P-N-P ligand and an activator, could be fed to common column(s) to separate 1-hexene and 1-octene. In one instance the product from the trimerization or dimerization plant produced using a source of chromium, a P-N-P ligand and an activator, which produces a significant amount of 1-hexene would be fed into the bottom stream coming from the column in the conventional linear alpha olefins plant that separates 1-butene as an overhead stream from the product stream of the conventional linear alpha olefins plant. This strategy would also be useful for a mixed stream of 1- hexene and 1-octene.

The resulting streams of 1-octene and 1-hexene could for example be fed to a polymerization reactor such as a solution phase process or a gas phase process, respectively.

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The trimerization and tetramerization unit operation (plant) using a source of chromium, a P-N-P ligand and an activator, could be integrated with a steam cracker. In particular a portion of the ethane–ethylene feed stream to the C_2 splitter could be fed directly to the trimerization or tetramerization unit operation as a feed stream. Preferably the stream would be relatively rich in ethylene and comprise not more than 40 volume %, preferably less than 30 volume%, most preferably less than 25 volume %, of ethane and corresponding at least 60 volume % , preferably at least 70 volume %, most preferably at least 75 volume %, of ethylene (i.e. a stream of dilute ethylene). The dilute ethylene feed stream would pass through the reactor and the ethylene component would be trimerized or tetramerized to 1-hexene or 1-octene respectively. On exiting the trimerization or tetramerization reactor the product stream is degassed prior to feeding to a (common) separation column for 1-hexene or 1-octene. The off gas from the degassed product is largely ethane which may be recycled back to the cracker.

One embodiment of the present invention will now be described in accordance with Figure 1. Figure 1 is a schematic diagram of a chemical complex comprising a cracker, preferably ethane, but it could be a naphtha cracker or a flexi cracker which also uses ethane as a feedstock; a de-ethanizer 3 at the back end of the cracker; a conventional linear alpha olefins plant 5; a common separation or distillation column 8; a solution polyethylene plant 10; and an ethylene trimerization or tetramerization plant 12.

The complex of Figure 1 is arranged so that the ethane/ethylene stream from the back end of the cracker 1 is fed to a de-ethanizer 3 by line 2. However, there is an off take line 13 upstream of the de-ethanizer that feeds the ethylene trimerization or tetramerization reactor 12. The mixed ethane/ethylene feed from the cracker is reacted in the trimerizer tetramerizer to produce a product stream of 1-hexene or 1-octene. The unconsumed ethane is then recycled back to the cracker by line 14. In an embodiment not shown in Figure 1 the feed for the trimerizer or tetramerizer could be taken after the de-ethanizer or C_2 splitter however, that does not reduce the load on the de-ethanizer or C_2 splitter. The ethylene from the de-ethanizer or C_2 splitter is fed by line 4 to a conventional linear alpha olefins plant. The C_{6-8} product stream from the linear alpha olefins plant is feed to common separation column 8 by line 7. Typically the pure 1-octene stream from the common separation column 8 is fed to the solution polyethylene plant 10. Not shown in the drawing is a feed line for ethylene from the de-ethanizer to

the solution polyethylene plant 10. Line 11 from the back end of the solution polyethylene plant feeds a relatively small stream typically containing 1-octene and a solvent such as a C_{4-8} paraffin to the common separation column 8. The product from the ethylene trimerization or tetramerization plant (e.g. 1-hexene or 1-octene) is fed by line 15 to the common separation column 8. The alpha olefin, preferably 1-octene from the common separation column is then fed via line 9 to the solution polyethylene plant 10.

EXAMPLES

Example 1

Using modeling software and programs which have been adapted to closely simulate NOVA Chemicals ethylene cracker at Joffre and its solution polymerization plants simulations were run to compare the mass balance of the integration of an ethane steam cracker and an ethane steam cracker integrated with a 1-octene plant. The demethanizer tends to be a pinch point. The models were operated using a fixed capacity for the secondary demethanizer of 160 tons per hour. The current sequence in the cracker is deethanizer, acetylene reactor (to remove acetylenes) , driers, secondary demethanizer, C_2 splitter, ethylene, (product) ethane and other recycle. In the model according to the present invention, a side stream of ethylene, ethane and methane is taken prior the secondary demethanizer and is fed to a 1-octene plant (tetramerization plant) in accordance with the present invention. The results are set forth in Table 1.

TABLE 1

Unit operation	Stand Alone Cracker C2 production rate	Cracker Integrated with a 1-octene plant production rate	1-octene plant Additional products production rate
Deethanizer	C_2 1345 ktpa	C_2 1468ktpa	
Acetylene reactor	C_2 160 tph	C_2 176 tph	
Driers	C_2 160 tph	C_2 176 tph	
Sec. Demethanizer	C_2 160 tph	C_2 160 tph	
C_2 Splitter	C_2 160 tph	C_2 160 tph	
Ethylene	780 kpha	780 kpha	
Ethane, other recycle	565 ktpa	565ktpa	
1-octene			50 ktpa
1-hexene			15 ktpa
C_{10+} inc. polyethylene			7.5 ktpa
Ethane recycle			51 ktpa

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Note: ktpa =kilotons per annum; tph = tons per hour

The table shows by integrating a 1-octene plant with an ethylene cracker the same ethylene output can be maintained but the crude output coming from the deethanizer is significantly increased and this additional capacity is consumed in the production of the 1-octene plant without going through the demethanizer or the C_2 splitter. The integration maintains a constant load on the demethanizer and the C_2 splitter.

Example 2

Using the same software and programs the outputs for a stand alone solution polymerization, a solution polymerization integrated with an octane plant and the octane plant per se (stand alone) were compared.

The results are set forth in table 2 below.

TABLE 2

Unit operation	Stand Alone Solution Polymerization	Solution Polymerization rate Integrated with a 1-octene plant production rate	1-octene plant Additional products production rate
Production Rate	PE 385 KTA	PE 385 KTA	
Average 1-Octene consumption	6 tph	6 tph	
1-Octene column flow	30 tph	30 tph	
C10 plus Column flow	30.5 tph	35 tph	
C10 plus Column Purge	0.5 tph	5 tph	
1-octene			50 ktpa
1-hexene			15 ktpa
C_{10+} inc. polyethylene			4.5

The table shows that with "right sizing" the column for C_{10+} column it is possible to eliminate a second column at the 1-octene plant (e.g. 30.5 +4.5 = 35) reducing the capital and operating costs of the integrated system over the non integrated system. It is estimated this will result in about a 25% reduction in the capital costs for the distillation requirements for the integrated complex.

INDUSTRIAL APPLICABILITY

The present invention provides an integrated process for the production of higher alpha olefins in conjunction at least with an ethylene cracker and optionally with other production facilities such as an ethylene polymerization plant, preferably a solution process, and provides for common separation units, such as separation columns resulting in capital and operational cost savings.

CLAIMS

1. In a chemical complex comprising one or more unit operations selected from the group consisting of a steam cracker comprising a C_2 splitter, a linear alpha olefin plant and a solution or slurry polyethylene plant the improvement comprising integrating into the complex a reactor for the trimerization or tetramerization ethylene in the presence of a catalyst system comprising:

   i) a source of chromium;

   ii) a defined P-N-P ligand; and

   iii) an activator

and a distillation column to separate one or more of ethylene, 1-hexene, 1-octene which olefins containing less than 1.5 weight % of internal olefins.

2. The complex according to claim 2, wherein the reactor for trimerization or tetramerization of ethylene produces a liquid product stream which contains linear octenes, linear hexanes or both

3. The complex according to claim 2, wherein the P-N-P ligand in the trimerization or tetramerization reactor is selected from the group consisting of:

(a) P-N-P ligands having the formula:

$$(Ph_1)(Ph_2)\,P\text{–}N(R^2)\text{–}P\,(Ph_3)(Ph_4)$$

wherein each of Ph_1, Ph_2, Ph_3 and Ph_4 is a phenyl group bonded to a phosphorus atom, with the provisos that:

   i) at least one of Ph_1, Ph_2, Ph_3 and Ph_4 is ortho substituted with a halogen selected from the group consisting of fluorine, bromine and chlorine;

   ii) at least one of Ph_1, Ph_2, Ph_3 and Ph_4 does not have any substituents in ortho positions; and

   iii) R^2 is selected from the group consisting of hydrogen, $C_{1\text{-}20}$ hydrocarbyl and silyl; and

(b) P-N-P ligands having the formula:

$$(Ph_1)(Ph_2)\,P\text{–}N(R^2)\text{–}P\,(Ph_3)(Ph_4)$$

wherein each of Ph_1, Ph_2, Ph_3 and Ph_4 is a phenyl group bonded to a phosphorus atom, with the provisos that:

   i) at least one of Ph_1, Ph_2, Ph_3 and Ph_4 is ortho substituted with a halogen selected from the group consisting of fluorine, bromine and chlorine;

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ii) at least one of Ph_1, Ph_2, Ph_3 and Ph_4 is ortho substituted with a polar substituent; and

iii) R^2 is selected from the group consisting of hydrogen, C_{1-20} hydrocarbyl and silyl.

4. The complex according to claim 3, wherein in the P-N-P ligand in the trimerization or tetramerization reactor said halogen is fluorine.

5. The complex according to claim 4, wherein in the P-N-P ligand in the trimerization or tetramerization reactor R^2 is a C_{1-4} hydrocarbyl.

6. The complex according to claim 5, wherein in the P-N-P ligand in the trimerization or tetramerization reactor R^2 is isopropyl.

7. The complex according to claim 6, wherein in the P-N-P ligand in the trimerization or tetramerization reactor said polar substituent is a C_{1-3} alkoxy radical.

8. The complex according to claim 7, wherein in the trimerization or tetramerization reactor the source of chromium is selected from the group consisting of chromium trichloride; chromium (III) 2-ethylhexanoate; chromium (III) acetylacetonate and chromium carboxyl complexes.

9. The complex according to claim 7, wherein in the trimerization or tetramerization reactor the activator is selected from the group consisting of:

(a) $LiAlH_4$;

(b) aluminum alkyls of the formula $Al(R^3)_a(X)_b$ where R^3 is selected from the group consisting of C_{1-8} alkyl and alkoxide radicals, X is a halogen and a and b are 0 or a positive integer provided the sum of a+b is 3;

(c) an aluminoxane selected from the group consisting of:

(i) linear aluminoxanes having the formula $[R^6AlO]_S$ wherein R^6 is selected from the group consisting of C_{1-6} alkyl radicals and s is a number from 2 to 50;

(ii) cyclic aluminoxanes having the formula $R^7(R^8AlO)_S$ wherein R^7 and R^8 are selected from the group consisting of C_{1-6} alkyl radicals and s is a number from 2 to 50; and

(iii) mixtures thereof;

(d) ionic activators selected from the group consisting of

(i) compounds of the formula $[R^{13}]^+ [B(R^{14})_4]^-$ wherein B is a boron atom, R^{13} is a cyclic C_{5-7} aromatic cation or a triphenyl methyl cation and each R^{14} is independently selected from the group consisting of phenyl radicals which are

unsubstituted or substituted with 3 to 5 substituents selected from the group consisting of a fluorine atom, a C_{1-4} alkyl or alkoxy radical which is unsubstituted or substituted by a fluorine atom; and a silyl radical of the formula $-Si-(R^{15})_3$; wherein each R^{15} is independently selected from the group consisting of a hydrogen atom and a C_{1-4} alkyl radical; and

(ii) compounds of the formula $[(R^{18})_t ZH]^+[B(R^{14})_4]^-$ wherein B is a boron atom, H is a hydrogen atom, Z is a nitrogen atom or phosphorus atom, t is 2 or 3 and R^{18} is selected from the group consisting of C_{1-8} alkyl radicals, a phenyl radical which is unsubstituted or substituted by up to three C_{1-4} alkyl radicals, or one R^{18} taken together with the nitrogen atom may form an anilinium radical and R^{14} is as defined above; and

(iii) compounds of the formula $B(R^{14})_3$ wherein R^{14} is as defined above.

10. The complex according to claim 9, wherein the molar ratio of Cr to P-N-P ligand is from 100:1 to 1:100 and the molar ratio of Al or B from the activator to Cr is from 0.5 to 1000 :1.

11. The complex according to claim 9, wherein the trimerization or dimeraization reactor is operated at a temperature of from 10° C to 300° C and a pressure of from 0.5 to 10 MPa (5 to 100 atmospheres).

12. The complex according to claim 11, comprising a steam cracker comprising a C_2 splitter upstream of said trimerization or tetramerization reactor and a C_2 stream from the cracker from which methane and acetylenes have been removed comprising not less than 60 vol.% ethylene is fed directly to said trimerization or tetramerization reactor and the ethane recovered from the product stream from said trimerization or tetramerization reactor is recycled back to said steam cracker.

13. The complex according to claim 11 further comprising a solution polyethylene plant and a common distillation column for the back end of the polyethylene plant and the trimerization or tetramerization reactor.

14. The complex according to claim 11, further comprising a conventional linear alpha olefins plant and the product streams from the conventional linear alpha olefins plant and the trimerization or tetramerization reactor are treated in a common separation unit to separate different alpha olefins.

15. The complex according to claim 9, wherein the unit operations are integrated with the reactor for the trimerization or tetramerization of ethylene to reduce capital or operating costs or both, in the complex by:

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(i) using common distillation columns for the separation C_{6-8} olefins; or

(ii) passing at least a portion of the feed to the C_2 splitter of the steam cracker to the tetramerization or trimerization reactor(s) or both and recycling unconsumed ethane to the cracker; or

(iii) both (i) and (ii).

Figure 1

