

A PROCESS FOR PRODUCING ALPHA OLEFINS

Field of the Invention

The invention relates to a process for producing alpha-olefins by oligomerizing an ethylene feed.

5 Background

The oligomerization of olefins, such as ethylene, produces butene, hexene, octene, and other valuable linear alpha olefins. Linear alpha olefins are a valuable comonomer for linear low-density polyethylene and high-density polyethylene. Such olefins are also valuable as a chemical intermediate in the production of plasticizer alcohols, fatty acids, detergent alcohols, polyalphaolefins, oil field
10 drilling fluids, lubricant oil additives, linear alkylbenzenes, alkenylsuccinic anhydrides, alkyl dimethylamines, dialkyl methylamines, alpha-olefin sulfonates, internal olefin sulfonates, chlorinated olefins, linear mercaptans, aluminum alkyls, alkyl diphenylether disulfonates, and other chemicals.

US 6,683,187 describes a bis(arylimino)pyridine ligand, catalyst precursors and catalyst
15 systems derived from this ligand for ethylene oligomerization to form linear alpha olefins. The patent teaches the production of linear alpha olefins with a Schulz-Flory oligomerization product distribution. In such a process, a wide range of oligomers are produced, and the fraction of each olefin can be determined by calculation on the basis of the K-factor. The K-factor is the molar ratio of $(C_n+2)/C_n$, where n is the number of carbons in the linear alpha olefin product.

20 It would be advantageous to develop an improved process that would provide an oligomerization product distribution having a desired K-factor and product quality. Further, it would be advantageous to prevent problems caused by fouling or polymer formation.

Summary of the Invention

The invention provides a process for producing alpha-olefins comprising: a) contacting an
25 ethylene feed with an oligomerization catalyst system in an oligomerization reaction zone under oligomerization reaction conditions to produce a product stream comprising alpha-olefins; and b) cooling at least a portion of the reaction zone using a heat exchange medium having an inlet temperature and an outlet temperature wherein the catalyst system comprises a metal-ligand complex and a co-catalyst; the oligomerization reaction conditions comprise a reaction temperature

of greater than 70 °C; and the difference between the reaction zone temperature and the inlet temperature of the heat exchange medium is from 0.5 to 15 °C.

Brief Description of the Drawings

- Figure 1 depicts the reaction temperature and heat exchange medium temperature of
- 5 Example 1
- Figure 2 depicts the heat transfer coefficient of Example 1
- Figure 3 depicts the reaction temperature, heat exchange medium temperature and the heat transfer coefficient of Example 2.
- Figure 4 depicts the pilot plant configuration used in the Examples.

Detailed Description

- The process comprises converting an olefin feed into a higher oligomer product stream by contacting the feed with an oligomerization catalyst system and a co-catalyst in an oligomerization reaction zone under oligomerization conditions. In one embodiment, an ethylene feed may be contacted with an iron-ligand complex and modified methyl aluminoxane under oligomerization
- 15 conditions to produce a product slate of alpha olefins having a specific k-factor.

Olefin Feed

- The olefin feed to the process comprises ethylene. The feed may also comprise olefins having from 3 to 8 carbon atoms. The ethylene may be pretreated to remove impurities, especially impurities that impact the reaction, product quality or damage the catalyst. In one embodiment, the
- 20 ethylene may be dried to remove water. In another embodiment, the ethylene may be treated to reduce the oxygen content of the ethylene. Any pretreatment method known to one of ordinary skill in the art can be used to pretreat the feed.

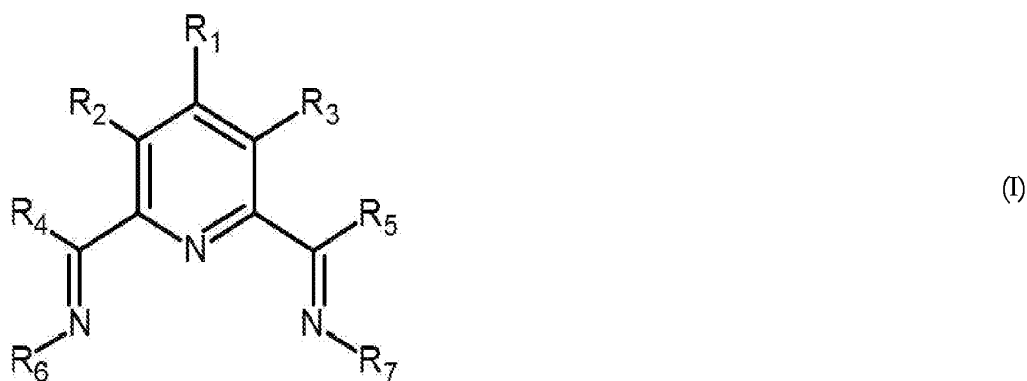
Oligomerization Catalyst

- The oligomerization catalyst system may comprise one or more oligomerization catalysts as
- 25 described further herein. The oligomerization catalyst is a metal-ligand complex that is effective for catalyzing an oligomerization process. The ligand may comprise a bis(arylimino)pyridine compound, a bis(alkylimino)pyridine compound or a mixed aryl-alkyl iminopyridine compound.

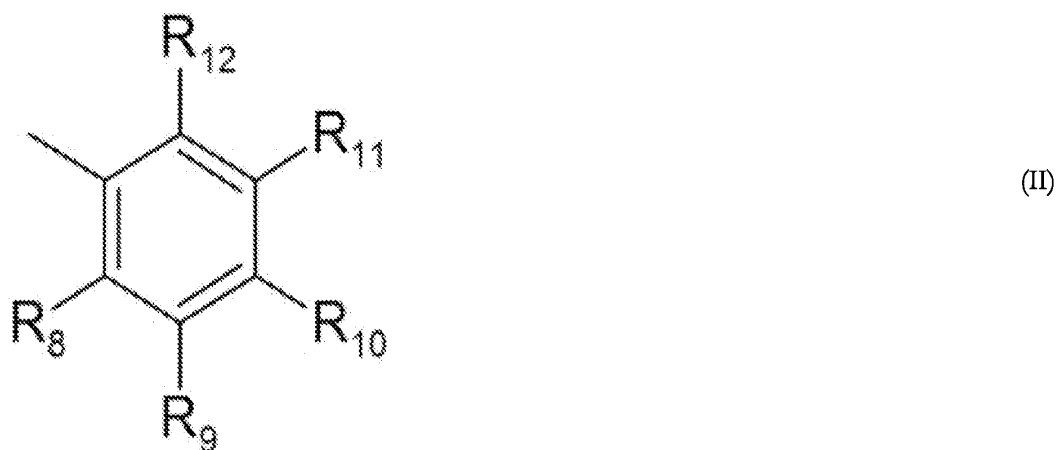
Ligand

In one embodiment, the ligand comprises a pyridine bis(imine) group. The ligand may be a bis(arylimino)pyridine compound having the structure of Formula I.

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- 15 R_1 , R_2 and R_3 are each independently hydrogen, optionally substituted hydrocarbyl, hydroxo, cyano or an inert functional group. R_4 and R_5 are each independently hydrogen, optionally substituted hydrocarbyl, hydroxo, cyano or an inert functional group. R_6 and R_7 are each independently an aryl group as shown in Formula II. The two aryl groups (R_6 and R_7) on one ligand may be the same or different.



- 30 R_8 , R_9 , R_{10} , R_{11} , R_{12} are each independently hydrogen, optionally substituted hydrocarbyl, hydroxo, cyano, an inert functional group, fluorine, or chlorine. Any two of R_1 - R_3 , and R_9 - R_{11} vicinal to one another taken together may form a ring. R_{12} may be taken together with R_{11} , R_4 or R_5 to form a ring. R_2 and R_4 or R_3 and R_5 may be taken together to form a ring.

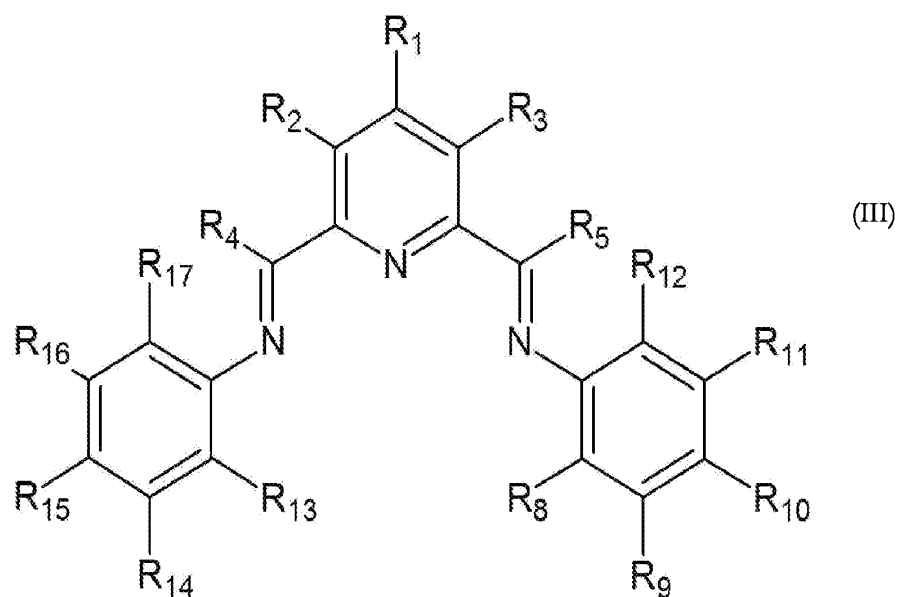
A hydrocarbyl group is a group containing only carbon and hydrogen. The number of carbon atoms in this group is preferably in the range of from 1 to 30.

An optionally substituted hydrocarbyl is a hydrocarbyl group that optionally contains one or more "inert" heteroatom-containing functional groups. Inert means that the functional groups do not interfere to any substantial degree with the oligomerization process. Examples of these inert groups include fluoride, chloride, iodide, stannanes, ethers, hydroxides, alkoxides and amines with adequate steric shielding. The optionally substituted hydrocarbyl group may include primary, secondary and tertiary carbon atoms groups.

Primary carbon atom groups are a $-\text{CH}_2\text{-R}$ group wherein R may be hydrogen, an optionally substituted hydrocarbyl or an inert functional group. Examples of primary carbon atom groups include $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, $-\text{CH}_2\text{Cl}$, $-\text{CH}_2\text{OCH}_3$, $-\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2$, and $-\text{CH}_2\text{Ph}$. Secondary carbon atom groups are a $-\text{CH-R}_2$ or $-\text{CH(R)(R')}$ group wherein R and R' may be optionally substituted hydrocarbyl or an inert functional group. Examples of secondary carbon atom groups include $-\text{CH}(\text{CH}_3)_2$, $-\text{CHCl}_2$, $-\text{CHPh}_2$, $-\text{CH}(\text{CH}_3)(\text{OCH}_3)$, $-\text{CH}=\text{CH}_2$, and cyclohexyl. Tertiary carbon atom groups are a $-\text{C(R)(R')(R'')}$ group wherein R, R', and R'' may be optionally substituted hydrocarbyl or an inert functional group. Examples of tertiary carbon atom groups include $-\text{C}(\text{CH}_3)_3$, $-\text{CCl}_3$, $-\text{C}\equiv\text{CPh}$, 1-Adamantyl, and $-\text{C}(\text{CH}_3)_2(\text{OCH}_3)$.

An inert functional group is a group other than optionally substituted hydrocarbyl that is inert under the oligomerization conditions. Inert has the same meaning as provided above. Examples of inert functional groups include halide, ethers, and amines, in particular tertiary amines.

Substituent variations of $\text{R}_1\text{-R}_5$, $\text{R}_8\text{-R}_{12}$ and $\text{R}_{13}\text{-R}_{17}$ may be selected to enhance other properties of the ligand, for example, solubility in non-polar solvents. Several embodiments of possible oligomerization catalysts are further described below having the structure shown in Formula 3.



In one embodiment, a ligand of Formula III is provided wherein R₁-R₅, R₉-R₁₁ and R₁₄-R₁₆
 15 are hydrogen; and R₈, R₁₂, R₁₃ and R₁₇ are fluorine.

In one embodiment, a ligand of Formula III is provided wherein R₁-R₅, R₈, R₁₀, R₁₂, R₁₄ and
 R₁₆ are hydrogen; R₁₃, R₁₅ and R₁₇ are methyl and R₉ and R₁₁ are tert-butyl.

In one embodiment, a ligand of Formula III is provided wherein R₁-R₅, R₈, R₁₂, R₁₄ and R₁₆
 are hydrogen; R₁₃, R₁₅ and R₁₇ are methyl; R₉ and R₁₁ are phenyl and R₁₀ is an alkoxy.

20 In one embodiment, a ligand of Formula III is provided wherein R₁-R₅, R₈, R₁₀, R₁₁ and R₁₄-
 R₁₆ are hydrogen; R₉ and R₁₂ are methyl; and R₁₃ and R₁₇ are fluorine.

In one embodiment, a ligand of Formula III is provided wherein R₁-R₃, R₉-R₁₁ and R₁₄-R₁₆
 are hydrogen; R₄ and R₅ are phenyl and R₈, R₁₂, R₁₃ and R₁₇ are fluorine.

In one embodiment, a ligand of Formula III is provided wherein R₁-R₅, R₈-R₉, R₁₁-R₁₂, R₁₃-
 25 R₁₄ and R₁₆-R₁₇ are hydrogen; and R₁₀ and R₁₅ are fluorine.

In one embodiment, a ligand of Formula III is provided wherein R₁-R₅, R₈, R₁₀, R₁₂, R₁₃, R₁₅
 and R₁₇ are hydrogen; and R₉, R₁₁, R₁₄ and R₁₆ are fluorine.

In one embodiment, a ligand of Formula III is provided wherein R₁-R₅, R₉, R₁₁-R₁₂, R₁₄ and
 R₁₆-R₁₇ are hydrogen; and R₈, R₁₀, R₁₃ and R₁₅ are fluorine.

30 In one embodiment, a ligand of Formula III is provided wherein R₁-R₅, R₈-R₉, R₁₁-R₁₂, R₁₄
 and R₁₆ are hydrogen; R₁₀ is tert-butyl; and R₁₃, R₁₅ and R₁₇ are methyl.

In one embodiment, a ligand of Formula III is provided wherein R₁-R₅, R₉-R₁₂, R₁₄ and R₁₆ are hydrogen; R₈ is fluorine; and R₁₃, R₁₅ and R₁₇ are methyl.

In one embodiment, a ligand of Formula III is provided wherein R₁-R₅, R₉-R₁₂, R₁₃, R₁₅ and R₁₇ are hydrogen; R₈ is tert-butyl; and R₁₄ and R₁₆ are methyl.

5 In one embodiment, a ligand of Formula III is provided wherein R₁-R₅, R₉-R₁₂, R₁₃-R₁₄ and R₁₆-R₁₇ are hydrogen; and R₈ and R₁₅ are tert-butyl.

In one embodiment, a ligand of Formula III is provided wherein R₁-R₅, R₈-R₁₀, R₁₃-R₁₄ and R₁₆-R₁₇ are hydrogen; R₁₅ is tert-butyl; and R₁₁ and R₁₂ are taken together to form an aryl group.

10 In one embodiment, a ligand of Formula III is provided wherein R₁-R₅, R₉-R₁₂, R₁₄-R₁₇ are hydrogen; and R₈ and R₁₃ are methyl.

In one embodiment, a ligand of Formula III is provided wherein R₁-R₅, R₈-R₉, R₁₁-R₁₂, R₁₄ and R₁₆ are hydrogen; R₁₀ is fluorine; and R₁₃, R₁₅ and R₁₇ are methyl.

In one embodiment, a ligand of Formula III is provided wherein R₁-R₅, R₈, R₁₀, R₁₂, R₁₄ and R₁₆ are hydrogen; R₉ and R₁₁ are fluorine; and R₁₃, R₁₅ and R₁₇ are methyl.

15 In one embodiment, a ligand of Formula III is provided wherein R₁-R₅, R₈-R₉, R₁₁-R₁₂, R₁₄ and R₁₆ are hydrogen; R₁₀ is an alkoxy; and R₁₃, R₁₅ and R₁₇ are methyl.

In one embodiment, a ligand of Formula III is provided wherein R₁-R₅, R₈-R₉, R₁₁-R₁₂, R₁₄ and R₁₆ are hydrogen; R₁₀ is a silyl ether; and R₁₃, R₁₅ and R₁₇ are methyl.

20 In one embodiment, a ligand of Formula III is provided wherein R₁-R₅, R₈, R₁₀, R₁₂, R₁₄-R₁₆ are hydrogen; R₉ and R₁₁ are methyl; and R₁₃ and R₁₇ are ethyl.

In one embodiment, a ligand of Formula III is provided wherein R₁-R₅, R₉-R₁₂, and R₁₄-R₁₇ are hydrogen; and R₈ and R₁₃ are ethyl.

In one embodiment, a ligand of Formula III is provided wherein R₁-R₅, R₉-R₁₁ and R₁₄-R₁₆ are hydrogen; and R₈, R₁₂, R₁₃ and R₁₇ are chlorine.

25 In one embodiment, a ligand of Formula III is provided wherein R₁-R₅, R₉, R₁₁, R₁₄ and R₁₆ are hydrogen; and R₈, R₁₀, R₁₂, R₁₃, R₁₅ and R₁₇ are methyl.

In one embodiment, a ligand of Formula III is provided wherein R₁-R₅, R₉-R₁₀, R₁₂, R₁₄-R₁₅ and R₁₇ are hydrogen; and R₈, R₁₁, R₁₃ and R₁₆ are methyl.

In one embodiment, a ligand of Formula III is provided wherein R₁-R₁₇ are hydrogen.

30 In one embodiment, a ligand of Formula III is provided wherein R₁-R₅, R₈, R₁₀, R₁₂, R₁₃, R₁₅ and R₁₇ are hydrogen; and R₉, R₁₁, R₁₄ and R₁₆ are tert-butyl.

In one embodiment, a ligand of Formula III is provided wherein R₁-R₅, R₈-R₁₂, R₁₄ and R₁₆ are hydrogen; and R₁₃, R₁₅ and R₁₇ are methyl.

In one embodiment, a ligand of Formula III is provided wherein R₁-R₅, R₉, R₁₁-R₁₂, R₁₄ and R₁₆ are hydrogen; R₈ and R₁₀ are fluorine; and R₁₃, R₁₅ and R₁₇ are methyl.

5 In one embodiment, a ligand of Formula III is provided wherein R₁-R₅, R₉, R₁₁-R₁₂, R₁₄ and R₁₆-R₁₇ are hydrogen; and R₈, R₁₀, R₁₃ and R₁₅ are methyl.

In one embodiment, a ligand of Formula III is provided wherein R₁-R₅, R₉-R₁₁ and R₁₄-R₁₆ are hydrogen; R₈ and R₁₂ are chlorine; and R₁₃ and R₁₇ are fluorine.

10 In one embodiment, a ligand of Formula III is provided wherein R₁-R₅, R₈, R₁₀, R₁₂, R₁₄ and R₁₆ are hydrogen; and R₉, R₁₁, R₁₃, R₁₅ and R₁₇ are methyl.

In one embodiment, a ligand of Formula III is provided wherein R₁-R₅, R₉-R₁₁ and R₁₃-R₁₄ and R₁₆-R₁₇ are hydrogen; R₈ and R₁₂ are chlorine; and R₁₅ is tert-butyl.

In one embodiment, a ligand of Formula III is provided wherein R₁-R₅, R₉-R₁₁ and R₁₃-R₁₇ are hydrogen; and R₈ and R₁₂ are chlorine.

15 In one embodiment, a ligand of Formula III is provided wherein R₁-R₅, R₉-R₁₂, and R₁₄-R₁₇ are hydrogen; and R₈ and R₁₃ are chlorine.

In one embodiment, a ligand of Formula III is provided wherein R₁-R₅, R₉, R₁₁-R₁₂, R₁₄ and R₁₆-R₁₇ are hydrogen; and R₈, R₁₀, R₁₃ and R₁₅ are chlorine.

20 In one embodiment, a ligand of Formula III is provided wherein R₁-R₅, R₉, R₁₁-R₁₂, and R₁₄, and R₁₆-R₁₇ are hydrogen; R₁₀ and R₁₅ are methyl; and R₈ and R₁₃ are chlorine.

In one embodiment, a ligand of Formula III is provided wherein R₁-R₅, R₉-R₁₁ and R₁₃-R₁₄ and R₁₆-R₁₇ are hydrogen; R₁₅ is fluorine; and R₈ and R₁₂ are chlorine.

In one embodiment, a ligand of Formula III is provided wherein R₁-R₅, R₈-R₉, R₁₁-R₁₂, R₁₄-R₁₅ and R₁₇ are hydrogen; R₁₀ is tert-butyl; and R₁₃ and R₁₆ are methyl.

25 In one embodiment, a ligand of Formula III is provided wherein R₁-R₅, R₉-R₁₁, R₁₄ and R₁₆ are hydrogen; R₈ and R₁₂ are fluorine; and R₁₃, R₁₅ and R₁₇ are methyl.

In one embodiment, a ligand of Formula III is provided wherein R₁-R₅, R₉-R₁₀, R₁₂, R₁₄-R₁₅ and R₁₇ are hydrogen; R₈ and R₁₃ are methyl; and R₁₁ and R₁₆ are isopropyl.

30 In one embodiment, a ligand of Formula III is provided wherein R₁-R₅, R₉-R₁₂ and R₁₄-R₁₆ are hydrogen; R₈ is ethyl; and R₁₃ and R₁₇ are fluorine.

In one embodiment, a ligand of Formula III is provided wherein R₂-R₅, R₉-R₁₀, R₁₂, R₁₄-R₁₅ and R₁₇ are hydrogen; R₁ is methoxy; and R₈, R₁₁, R₁₃ and R₁₆ are methyl.

In one embodiment, a ligand of Formula III is provided wherein R₂-R₅, R₈-R₁₂, R₁₄ and R₁₆ are hydrogen; R₁ is methoxy; and R₁₃, R₁₅ and R₁₇ are methyl.

In one embodiment, a ligand of Formula III is provided wherein R₂-R₅, R₉-R₁₂, and R₁₄-R₁₇ are hydrogen; R₁ is methoxy; and R₈ and R₁₃ are ethyl.

5 In one embodiment, a ligand of Formula III is provided wherein R₂-R₅, R₉, R₁₁-R₁₂, R₁₄ and R₁₆-R₁₇ are hydrogen; R₁ is tert-butyl; and R₈, R₁₀, R₁₃ and R₁₅ are methyl.

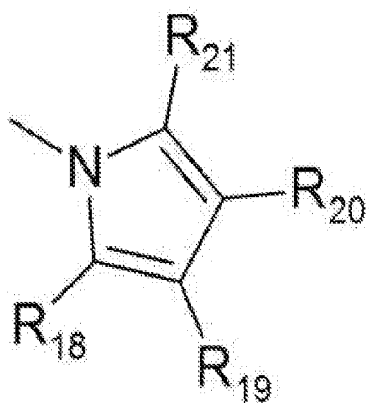
In one embodiment, a ligand of Formula III is provided wherein R₂-R₅, R₈-R₁₂, R₁₄ and R₁₆ are hydrogen; R₁ is tert-butyl; and R₁₃, R₁₅ and R₁₇ are methyl.

10 In one embodiment, a ligand of Formula III is provided wherein R₂-R₅, R₉, R₁₁, R₁₄ and R₁₆ are hydrogen; R₁ is methoxy; and R₈, R₁₀, R₁₂, R₁₃, R₁₅ and R₁₇ are methyl.

In one embodiment, a ligand of Formula III is provided wherein R₂-R₅, R₉, R₁₁, R₁₄ and R₁₆ are hydrogen; R₁ is alkoxy; and R₈, R₁₀, R₁₂, R₁₃, R₁₅ and R₁₇ are methyl.

In one embodiment, a ligand of Formula III is provided wherein R₂-R₅, R₉, R₁₁, R₁₄ and R₁₆ are hydrogen; R₁ is tert-butyl; and R₈, R₁₀, R₁₂, R₁₃, R₁₅ and R₁₇ are methyl.

15 In another embodiment, the ligand may be a compound having the structure of Formula I, wherein one of R₆ and R₇ is aryl as shown in Formula II and one of R₆ and R₇ is pyridyl as shown in Formula IV. In another embodiment, R₆ and R₇ may be pyrrolyl.

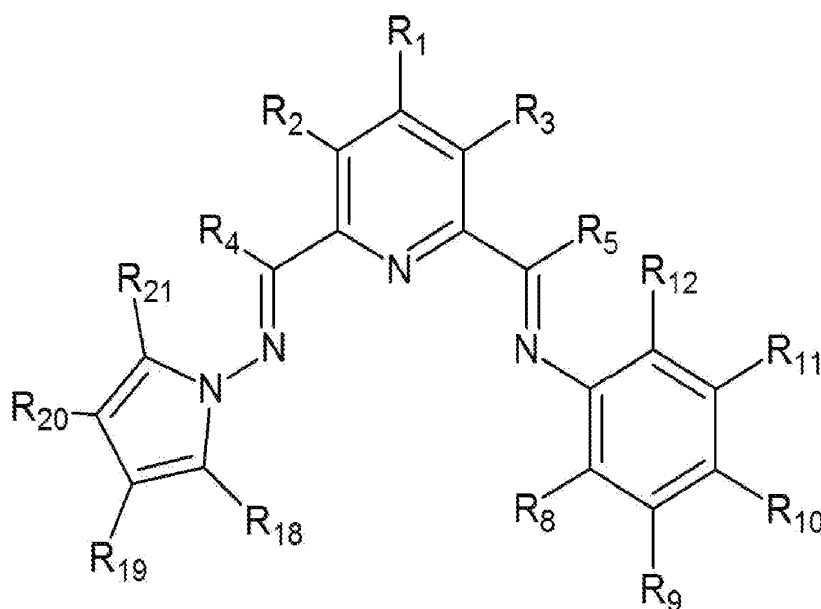


(IV)

30 R₁, R₂ and R₃ are each independently hydrogen, optionally substituted hydrocarbyl, hydroxo, cyano or an inert functional group. R₄ and R₅ are each independently hydrogen, optionally substituted hydrocarbyl, hydroxo, cyano or an inert functional group. R₈-R₁₂ and R₁₈-R₂₁ are each independently hydrogen, optionally substituted hydrocarbyl, hydroxo, cyano, an inert functional

group, fluorine, or chlorine. Any two of R₁-R₃, and R₉-R₁₁ vicinal to one another taken together may form a ring. R₁₂ may be taken together with R₁₁, R₄ or R₅ to form a ring. R₂ and R₄ or R₃ and R₅ may be taken together to form a ring.

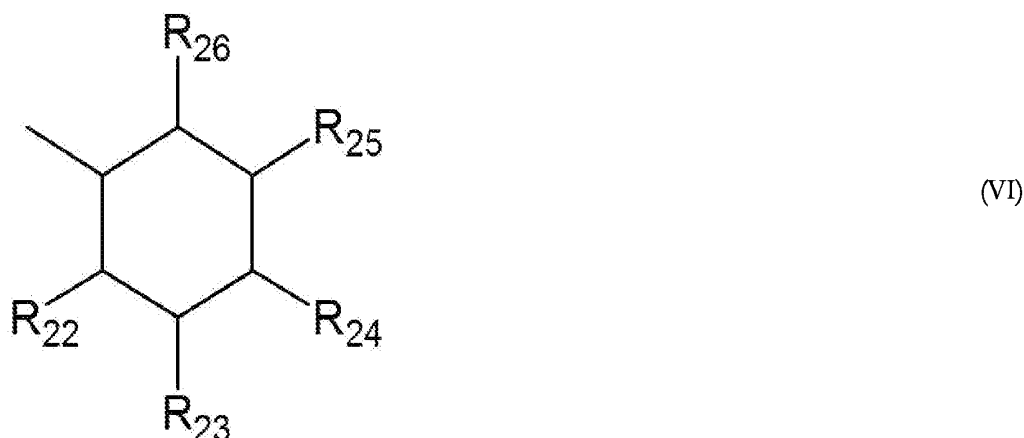
(V)



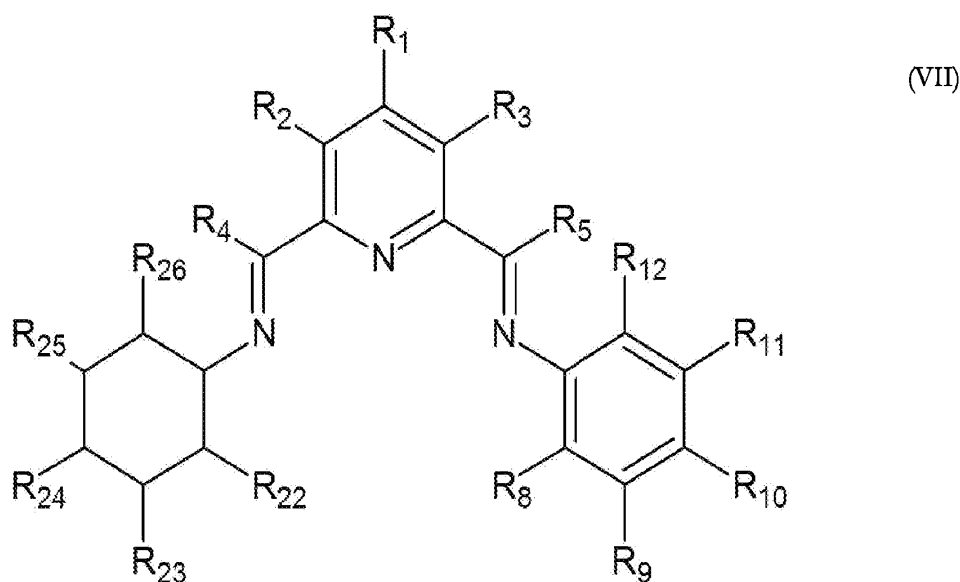
In one embodiment, a ligand of Formula V is provided wherein R₁-R₅, R₉, R₁₁ and R₁₈-R₂₁ are hydrogen; and R₈, R₁₀, and R₁₂ are methyl.

In one embodiment, a ligand of Formula V is provided wherein R₁-R₅, R₉-R₁₁ and R₁₈-R₂₁ are
 20 hydrogen; and R₈ and R₁₂ are ethyl.

In another embodiment, the ligand may be a compound having the structure of Formula I, wherein one of R₆ and R₇ is aryl as shown in Formula II and one of R₆ and R₇ is cyclohexyl as shown in Formula VI. In another embodiment, R₆ and R₇ may be cyclohexyl.



R₁, R₂ and R₃ are each independently hydrogen, optionally substituted hydrocarbyl, hydroxo, cyano or an inert functional group. R₄ and R₅ are each independently hydrogen, optionally substituted hydrocarbyl, hydroxo, cyano or an inert functional group. R₈-R₁₂ and R₂₂-R₂₆ are each independently hydrogen, optionally substituted hydrocarbyl, hydroxo, cyano, an inert functional group, fluorine, or chlorine. Any two of R₁-R₃, and R₉-R₁₁ vicinal to one another taken together may form a ring. R₁₂ may be taken together with R₁₁, R₄ or R₅ to form a ring. R₂ and R₄ or R₃ and R₅ may be taken together to form a ring.



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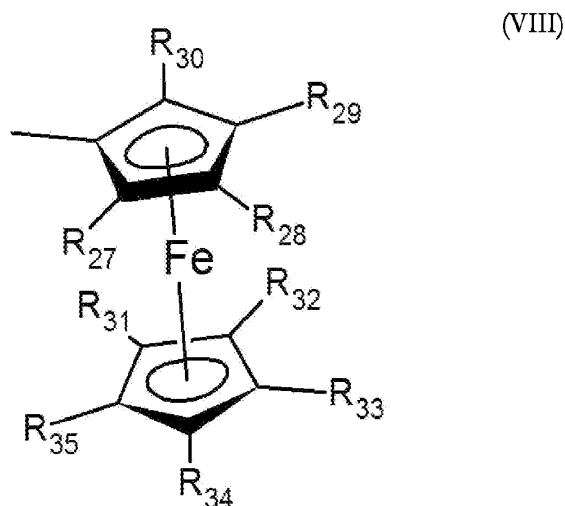
In one embodiment, a ligand of Formula VII is provided wherein R₁-R₅, R₉, R₁₁ and R₂₂-R₂₆ are hydrogen; and R₈, R₁₀, and R₁₂ are methyl.

In another embodiment, R_6 and R_7 may be adamantyl or another cycloalkane.

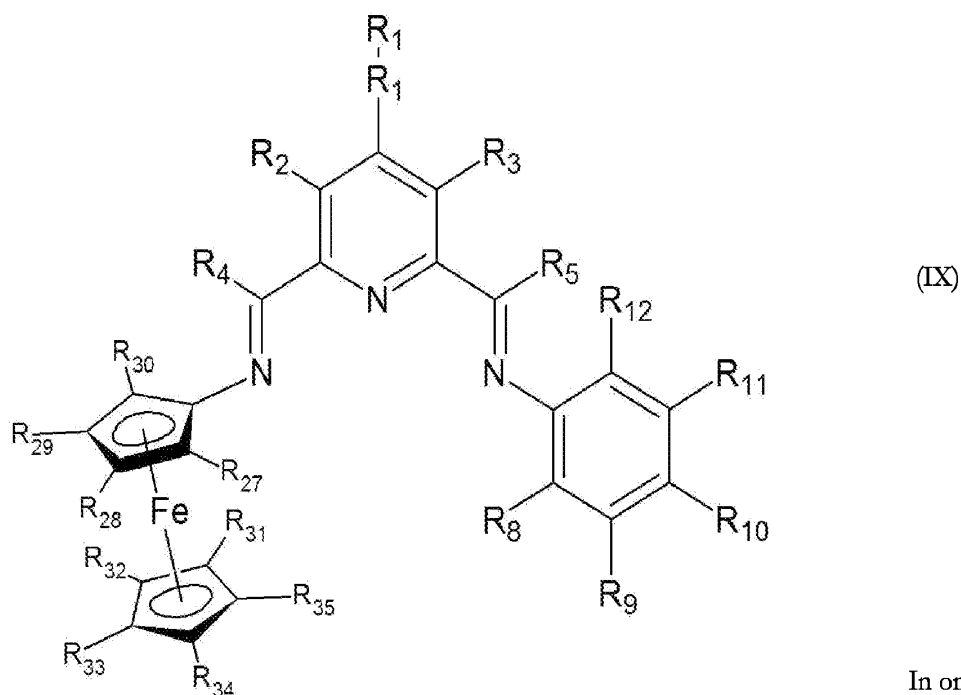
In another embodiment, the ligand may be a compound having the structure of Formula I, wherein one of R_6 and R_7 is aryl as shown in Formula II and one of R_6 and R_7 is ferrocenyl as shown in Formula VIII. In another embodiment, R_6 and R_7 may be ferrocenyl.

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R_1 , R_2 and R_3 are each independently hydrogen, optionally substituted hydrocarbyl, hydroxo, cyano or an inert functional group. R_4 and R_5 are each independently hydrogen, optionally substituted hydrocarbyl, hydroxo, cyano or an inert functional group. R_8 - R_{12} and R_{27} - R_{35} are each independently hydrogen, optionally substituted hydrocarbyl, hydroxo, cyano, an inert functional group, fluorine, or chlorine. Any two of R_1 - R_3 , and R_9 - R_{11} vicinal to one another taken together may form a ring. R_{12} may be taken together with R_{11} , R_4 or R_5 to form a ring. R_2 and R_4 or R_3 and R_5 may be taken together to form a ring.



embodiment, a ligand of Formula IX is provided wherein R₁-R₅, R₉, R₁₁ and R₂₇-R₃₅ are hydrogen; and R₈, R₁₀, and R₁₂ are methyl.

In one embodiment, a ligand of Formula IX is provided wherein R₁-R₅, R₉-R₁₁, and R₂₇-R₃₅ are hydrogen; and R₈ and R₁₂ are ethyl.

In another embodiment, the ligand may be a bis(alkylamino)pyridine. The alkyl group may have from 1 to 50 carbon atoms. The alkyl group may be a primary, secondary, or tertiary alkyl group. The alkyl group may be selected from the group consisting of methyl, ethyl, propyl, isopropyl, butyl, sec-butyl, isobutyl, and tert-butyl. The alkyl group may be selected from any n-alkyl or structural isomer of an n-alkyl having 5 or more carbon atoms, e.g., n-pentyl; 2-methyl-butyl; and 2,2-dimethylpropyl.

In another embodiment, the ligand may be an alkyl-alkyl iminopyridine, where the two alkyl groups are different. Any of the alkyl groups described above as being suitable for a bis(alkylamino)pyridine are also suitable for this alkyl-alkyl iminopyridine.

In another embodiment, the ligand may be an aryl alkyl iminopyridine. The aryl group may be of a similar nature to any of the aryl groups described with respect to the bis(arylimino)pyridine compound and the alkyl group may be of a similar nature to any of the alkyl groups described with respect to the bis(alkylamino)pyridine compound.

In addition to the ligand structures described hereinabove, any structure that combines features of any two or more of these ligands can be a suitable ligand for this process. Further, the oligomerization catalyst system may comprise a combination of one or more of any of the described oligomerizations catalysts.

5 The ligand feedstock may contain between 0 and 10 wt.% bisimine pyridine impurity, preferably 0-1 wt.% bisimine pyridine impurity, most preferably 0-0.1 wt.% bisimine pyridine impurity. This impurity is believed to cause the formation of polymers in the reactor, so it is preferable to limit the amount of this impurity that is present in the catalyst system.

10 In one embodiment, the bisimine pyridine impurity is a ligand of Formula II in which three of R_8 , R_{12} , R_{13} , and R_{17} are each independently optionally substituted hydrocarbyl.

 In one embodiment, the bisimine pyridine impurity is a ligand of Formula II in which all four of R_8 , R_{12} , R_{13} , and R_{17} are each independently optionally substituted hydrocarbyl.

Metal

15 The metal may be a transition metal, and the metal is preferably present as a compound having the formula MX_n , where M is the metal, X is a monoanion and n represents the number of monoanions (and the oxidation state of the metal).

 The metal can comprise any Group 4-10 transition metal. The metal can be selected from the group consisting of titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, iron, cobalt, nickel, palladium, platinum, ruthenium and
20 rhodium. In one embodiment, the metal is cobalt or iron. In a preferred embodiment, the metal is iron. The metal of the metal compound can have any positive formal oxidation state of from 2 to 6 and is preferably 2 or 3.

 The monoanion may comprise a halide, a carboxylate, a β -diketonate, a hydrocarboxide, an optionally substituted hydrocarbyl, an amide or a hydride. The hydrocarboxide may be an alkoxide,
25 an aryloxy or an aralkoxide. The halide may be fluorine, chlorine, bromine or iodine.

 The carboxylate may be any C_1 to C_{20} carboxylate. The carboxylate may be acetate, a propionate, a butyrate, a pentanoate, a hexanoate, a heptanoate, an octanoate, a nonanoate, a decanoate, an undecanoate, or a dodecanoate. In addition, the carboxylate may be 2-ethylhexanoate or trifluoroacetate.

30 The β -diketonate may be any C_1 to C_{20} β -diketonate. The β -diketonate may be acetylacetonate, hexafluoroacetylacetonate, or benzoylacetonate.

The hydrocarboxide may be any C₁ to C₂₀ hydrocarboxide. The hydrocarboxide may be a C₁ to C₂₀ alkoxide, or a C₆ to C₂₀ aryloxy. The alkoxide may be methoxide, ethoxide, a propoxide (e.g., iso-propoxide) or a butoxide (e.g., tert-butoxide). The aryloxy may be phenoxide

Generally, the number of monoanions equals the formal oxidation state of the metal atom.

5 Preferred embodiments of metal compounds include iron acetylacetonate, iron chloride, and iron bis(2-ethylhexanoate). In addition to the oligomerization catalyst, a co-catalyst is used in the oligomerization reaction.

Co-catalyst

The co-catalyst may be a compound that is capable of transferring an optionally substituted
10 hydrocarbyl or hydride group to the metal atom of the catalyst and is also capable of abstracting an X⁻ group from the metal atom M. The co-catalyst may also be capable of serving as an electron transfer reagent or providing sterically hindered counterions for an active catalyst.

The co-catalyst may comprise two compounds, for example one compound that is capable of transferring an optionally substituted hydrocarbyl or hydride group to metal atom M and another
15 compound that is capable of abstracting an X⁻ group from metal atom M. Suitable compounds for transferring an optionally substituted hydrocarbyl or hydride group to metal atom M include organoaluminum compounds, alkyl lithium compounds, Grignards, alkyl tin and alkyl zinc compounds. Suitable compounds for abstracting an X⁻ group from metal atom M include strong
20 neutral Lewis acids such as SbF₅, BF₃ and Ar₃B wherein Ar is a strong electron-withdrawing aryl group such as C₆F₅ or 3,5-(CF₃)₂C₆H₃. A neutral Lewis acid donor molecule is a compound which may suitably act as a Lewis base, such as ethers, amines, sulfides and organic nitrites.

The co-catalyst is preferably an organoaluminum compound which may comprise an alkylaluminum compound, an aluminoxane or a combination thereof.

The alkylaluminum compound may be trialkylaluminum, an alkylaluminum halide, an
25 alkylaluminum alkoxide or a combination thereof. The alkyl group of the alkylaluminum compound may be any C₁ to C₂₀ alkyl group. The alkyl group may be methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl or octyl. The alkyl group may be an iso-alkyl group.

The trialkylaluminum compound may comprise trimethylaluminum (TMA), triethylaluminum (TEA), tripropylaluminum, tributylaluminum, tripentylaluminum,
30 trihexylaluminum, triheptylaluminum, trioctylaluminum or mixtures thereof. The trialkylaluminum compound may comprise tri-n-propylaluminum (TNPA), tri-n-butylaluminum (TNBA), tri-iso-butylaluminum (TIBA), tri-n-hexylaluminum, tri-n-octylaluminum (TNOA).

The halide group of the alkylaluminum halide may be chloride, bromide or iodide. The alkylaluminum halide may be diethylaluminum chloride, diethylaluminum bromide, ethylaluminum dichloride, ethylaluminum sesquichloride or mixtures thereof.

The alkoxide group of the alkylaluminum alkoxide may be any C₁ to C₂₀ alkoxy group. The
5 alkoxy group may be methoxy, ethoxy, propoxy, butoxy, pentoxy, hexoxy, heptoxy or octoxy. The alkylaluminum alkoxide may be diethylaluminum ethoxide.

The aluminoxane compound may be methylaluminoxane (MAO), ethylaluminoxane, modified methylaluminoxane (MMAO), n-propylaluminoxane, iso-propyl-aluminoxane, n-butylaluminoxane, sec-butylaluminoxane, iso-butylaluminoxane, t-butylaluminoxane, 1-pentyl-
10 aluminoxane, 2-pentyl-aluminoxane, 3-pentyl-aluminoxane, iso-pentyl-aluminoxane, neopentylaluminoxane, or mixtures thereof.

The preferred co-catalyst is modified methylaluminoxane. The synthesis of modified methylaluminoxane may be carried out in the presence of other trialkylaluminum compounds in addition to trimethylaluminum. The products incorporate both methyl and alkyl groups from the
15 added trialkylaluminum and are referred to as modified methyl aluminoxanes, MMAO. The MMAO may be more soluble in nonpolar reaction media, more stable to storage, have enhanced performance as a cocatalyst, or any combination of these. The performance of the resulting MMAO may be superior to either of the trialkylaluminum starting materials or to simple mixtures of the two starting materials. The added trialkylaluminum may be triethylaluminum, triisobutylaluminum or
20 triisooctylaluminum. In one embodiment, the co-catalyst is MMAO, wherein preferably about 25% of the methyl groups are replaced with iso-butyl groups.

In one embodiment, the co-catalyst may be formed in situ in the reactor by providing the appropriate precursors into the reactor.

Solvent

25 One or more solvents may be used in the reaction. The solvent(s) may be used to dissolve or suspend the catalyst or the co-catalyst and/or keep the ethylene dissolved. The solvent may be any solvent that can modify the solubility of any of these components or of reaction products. Suitable solvents include hydrocarbons, for example, alkanes, alkenes, cycloalkanes, and aromatics. Different solvents may be used in the process, for example, one solvent can be used for the catalyst and
30 another for the co-catalyst. It is preferred for the solvent to have a boiling point that is not substantially similar to the boiling point of any of the alpha olefin products as this will make the product separation step more difficult.

Aromatics

Aromatic solvents can be any solvent that contains an aromatic hydrocarbon, preferably having a carbon number of 6 to 20. These solvents may include pure aromatics, or mixtures of pure aromatics, isomers as well as heavier solvents, for example C₉ and C₁₀ solvents. Suitable aromatic
5 solvents include benzene, toluene, xylene (including ortho-xylene, meta-xylene, para-xylene and mixtures thereof) and ethylbenzene.

Alkanes

Alkane solvents may be any solvent that contains an alkyl hydrocarbon. These solvents may include straight chain alkanes and branched or iso-alkanes having from 3 to 20 carbon atoms and
10 mixtures of these alkanes. The alkanes may be cycloalkanes. Suitable solvents include propane, isobutane, n-butane, butane (n-butane or a mixture of linear and branched C₄ acyclic alkanes), pentane (n-pentane or a mixture of linear and branched acyclic alkanes), hexane (n-hexane or a mixture of linear and branched C₆ acyclic alkanes), heptane (n-heptane or a mixture of linear and branched C₇ acyclic alkanes), octane (n-octane or a mixture of linear and branched C₈ acyclic alkanes) and
15 isooctane. Suitable solvents also include cyclohexane and methylcyclohexane. In one embodiment, the solvent comprises C₆, C₇ and C₈ alkanes, that may include linear, branched and iso-alkanes.

Catalyst System

The catalyst system may be formed by mixing together the ligand, the metal, the co-catalyst and optional additional compounds in a solvent. The feed may be present in this step.

20 In one embodiment, the catalyst system may be prepared by contacting the metal or metal compound with the ligand to form a catalyst precursor mixture and then contacting the catalyst precursor mixture with the co-catalyst in the reactor to form the catalyst system.

In some embodiments, the catalyst system may be prepared outside of the reactor vessel and fed into the reactor vessel. In other embodiments, the catalyst system may be formed in the reactor
25 vessel by passing each of the components of the catalyst system separately into the reactor. In other embodiments, one or more catalyst precursors may be formed by combining at least two components outside of the reactor and then passing the one or more catalyst precursors into the reactor to form the catalyst system.

Reaction Conditions

30 The oligomerization reaction is a reaction that converts the olefin feed in the presence of an oligomerization catalyst and a co-catalyst into a higher oligomer product stream.

Temperature

Typical oligomerization reactions may be conducted over a range of temperatures of from - 100 °C to 300 °C. The oligomerization reaction conditions of the present invention comprise a reaction temperature of at least 70 °C. The reaction temperature is preferably in the range of from
5 70 °C to 127 °C.

The oligomerization reaction described herein is an exothermic reaction, and the reaction temperature is controlled by contacting the reaction zone and/or the process streams with a heat exchange medium to remove heat. The heat exchange medium may be any medium known to one of ordinary skill in the art as being useful for transferring heat. The heat exchange medium is
10 preferably water.

The inlet temperature of the heat exchange medium is important in the overall heat transfer capacity of the system. The inlet temperature of the heat exchange medium is especially important in reactor configurations where the heat transfer surface area may be limited.

The temperature of the heat exchange medium should not be too low. In addition to the
15 alpha-olefins produced in this process, the oligomerization reaction described herein also produces higher olefins (having a carbon number of greater than 26) and possibly some polyethylene by a side reaction. These higher olefins and polyethylene can foul the physical surfaces in the reactor and the oligomerization system, and it has been found that additional fouling is caused by too large of a difference between the reaction zone temperature and the inlet temperature of the heat exchange
20 medium.

The difference between the reaction zone temperature and the inlet temperature of the heat exchange medium is from 0.5 to 15 °C, preferably from 0.5 to 10 °C.

Without this invention, the reactor would have to be regularly shut down to clean out the higher olefins and polyethylene, resulting in significant shutdown time.

25 When starting up the oligomerization reaction system, the reaction temperature will be lower than normal and the difference between the reaction temperature and the inlet temperature of the heat exchange medium may be within this range, but this invention requires that the temperature difference stays in this range while the system is operating, especially when it is operating under steady state conditions and the reaction zone has achieved the desired operating temperature.

30

Pressure

The oligomerization reaction may be conducted at a pressure of from 0.01 to 15 MPa and more preferably from 1 to 10 MPa.

5 The optimum conditions of temperature and pressure used for a specific catalyst system, to maximize the yield of oligomer, and to minimize the impact of competing reactions, for example dimerization and polymerization can be determined by one of ordinary skill in the art. The temperature and pressure are selected to yield a product slate with a K-factor in the range of from 0.40 to 0.90, preferably in the range of from 0.45 to 0.80, more preferably in the range of from 0.5 to 0.7.

10 *Residence Time*

Residence times in the reactor of from 3 to 60 min have been found to be suitable, depending on the activity of the catalyst. In one embodiment, the reaction is carried out in the absence of air and moisture.

15 *Gas Phase, Liquid Phase or Mixed Gas-Liquid Phase*

The oligomerization reaction can be carried out in the liquid phase or mixed gas-liquid phase, depending on the volatility of the feed and product olefins at the reaction conditions.

Reactor type

20 The oligomerization reaction may be carried out in a conventional fashion. It may be carried out in a stirred tank reactor, wherein solvent, olefin and catalyst or catalyst precursors are added continuously to a stirred tank and solvent, product, catalyst, and unused reactant are removed from the stirred tank with the product separated and the unused reactant recycled back to the stirred tank.

In another embodiment, the oligomerization reaction may be carried out in a batch reactor, 25 wherein the catalyst precursors and reactant olefin are charged to an autoclave or other vessel and after being reacted for an appropriate time, product is separated from the reaction mixture by conventional means, for example, distillation.

In another embodiment, the oligomerization reaction may be carried out in a gas lift reactor. This type of reactor has two vertical sections (a riser section and a downcomer section) and a gas 30 separator at the top. The gas feed (ethylene) is injected at the bottom of the riser section to drive circulation around the loop (up the riser section and down the downcomer section). This type of

reactor may be especially sensitive to the formation of fouling and web-like polymers and the formation of those polymers in the reactor system can reduce the circulation flow significantly.

In another embodiment, the oligomerization reaction may be carried out in a pump loop reactor. This type of reactor has two vertical sections, and it uses a pump to drive circulation around the loop. A pump loop reactor can be operated at a higher circulation rate than a gas lift reactor.

In another embodiment, the oligomerization reaction may be carried out in a once-through reactor. This type of reactor feeds the catalyst, co-catalyst, solvent and ethylene to the inlet of the reactor and/or along the reactor length and the product is collected at the reactor outlet. One example of this type of reactor is a plug flow reactor.

Some of these reactor types provide for flows of the feed, catalyst system and products through a reactor. In these embodiments, the heat exchange medium will likely also be flowing through a heat exchange zone. These flows may be in a co-current or counter current direction. One of ordinary skill in the art will be able to determine which flow directions are most useful for the design of the specific reactor.

Catalyst Deactivation

The higher oligomers produced in the oligomerization reaction contains catalyst from the reaction step. To stop further reactions that can produce byproducts and other undesired components, it is important to deactivate the catalyst downstream from the reactor.

In one embodiment, the catalyst is deactivated by addition of an acidic species having a $pK_A(aq)$ of less than 25. The deactivated catalyst can then be removed by water washing in a liquid/liquid extractor.

Product Separation

The resulting alpha-olefins have a chain length of from 4 to 100 carbon atoms, preferably 4 to 30 carbon atoms and most preferably 4 to 20 carbon atoms. The alpha-olefins are even-numbered alpha-olefins.

The product olefins can be recovered by distillation or other separation techniques depending on the intended use of the products. The solvent(s) used in the reaction preferably have a boiling point that is different from the boiling point of any of the alpha-olefin products to make the separation easier.

In one embodiment, the distillation steps comprise columns for separating ethylene and the main linear alpha olefin products, for example, butene, hexene, and octene.

Product qualities and characteristics

The products produced by the process may be used in a number of applications. The olefins produced by this process may have improved qualities as compared to olefins produced by other processes. In one embodiment, the butene, hexene and/or octene produced may be used as a comonomer in making polyethylene. In one embodiment, the octene produced may be used to produce plasticizer alcohols. In one embodiment, the decene produced may be used to produce polyalphaolefins. In one embodiment, the dodecene and/or tetradecene produced may be used to produce alkylbenzene and/or detergent alcohols. In one embodiment, the hexadecene and/or octadecene produced may be used to produce alkenyl succinates and/or oilfield chemicals. In one embodiment, the C20+ products may be used to produce lubricant additives and/or waxes.

Recycle

A portion of any unreacted ethylene that is removed from the reactor with the products may be recycled to the reactor. This ethylene may be recovered in the distillation steps used to separate the products. The ethylene may be combined with the fresh ethylene feed or it may be fed separately to the reactor.

A portion of any solvent used in the reaction may be recycled to the reactor. The solvent may be recovered in the distillation steps used to separate the products.

Examples

The following example shows the negative effects that occur when operating an ethylene oligomerization pilot plant with a heat exchange medium that is at too low of a temperature. The examples were carried out with an ethylene feed, an iron-ligand catalyst where the ligand was X, and an MMAO co-catalyst. These examples were carried out in a gas-lift reactor depicted in Figure 4 and further described herein.

Figure 4 depicts the ethylene oligomerization reactor that was operated with continuous feed as a gas-lift loop reactor to produce alpha olefins (AO). The reactor volume was 9.5 L and the typical circulation velocity is from 0.6 to 1.1 m/sec. Circulation for the gas lift reactor is provided by injecting ethylene at the bottom of the riser 110. The gas holdup in the riser creates a differential head pressure between the riser 110 and the downcomer 120 that drives liquid circulation down the downcomer and up the riser.

The riser and downcomer each are coaxial pipes with an outer heat exchanger shell for heat removal from the exothermic oligomerization reaction. The heat transfer fluid in the exchangers is

water and each exchanger has an internal temperature indicator probe at the inlet and outlet as well as a mass flow controller to quantify the heat of reaction. Reactor temperature is controlled by a jacketed water heating system to preheat the reactor for startup or remove heat of reaction from the oligomerization reaction. The temperature of the gas lift reactor can be controlled from 60 to 99° C.

5 The heating system is also able to operate in a melt out mode at a temperature of 121 to 154° C.

Ethylene feed is pretreated in a carbon bed, a molecular sieve bed, and then an oxygen removal bed (not shown) and then compressed to about 345 kPa above the reactor operating pressure and fed to the reactor through a control valve. The ethylene is supplied on pressure demand to maintain the reactor operating pressure from 2.8 MPa to 6.2 MPa. A regulated 0-18
10 kg/hr fresh ethylene feed 200 provides ethylene to the reaction zone by feeding at the reactor bottom through an injection nozzle 130. The ethylene recycle compressor 140 circulates ethylene for the gas lift and operates between 0.45 and 18 kg/hr.

Solvent feed is provided at a flow rate of 4.5 to 11.3 kg/hr. Solvent is fed through a diaphragm pump and then through two control valves before mixing with the catalyst feed solutions
15 and entering the reactor. The solvent flow is divided between the two catalyst feed streams using the control valves.

The reactor can use separate feed lines for ligand, iron, and MMAO catalyst solutions fed to the reactor zone. In Figure 4, the ligand and iron are precomplexed and added as a single feed stream 210. The MMAO is added through line 220. Each catalyst stream is fed through an ISCO
20 pump that is supplied by a catalyst supply feed vessel. The ISCO pump outlet operates at reactor pressure and the feed rate range for the pump is from 0.001 to 100 ml/min. MMAO and ligand/iron catalyst feeds are each blended with part of the total solvent recycle feed before entering the reactor.

The reactor top has an overhead separator 160 that allows for liquid to overflow into a heat traced pipe to control level. A downstream valve controls the level in the overflow pipe and this
25 downstream product flow 170 is distilled to separate AO products from the solvent which is recycled back to the reactor. The liquid reactor outlet and downstream lines are heat traced with steam to maintain a temperature of 127° C to 160° C.

The gas phase that exits the top of the overhead separator goes through a cooler and then a
30 gas/liquid separator to remove liquid upstream of the recycle compressor 140. This gas phase is recycled back to the reactor bottom via recycle line 180 and the liquid feeds forward to distillation.

Example 1

This example was conducted in the gas-lift reactor shown in Figure 4. In this example, the pilot plant was started up and the oligomerization reaction started to produce alpha olefins. The heat exchange medium temperature was reduced to 60 °C and subsequently the heat exchange medium was reduced further to maintain temperature control. Figure 1 shows the alpha olefin production, the oligomerization reaction zone temperature and the temperature of the heat exchange medium. Figure 2 shows the decrease in the heat transfer coefficient when the heat exchange medium temperature was reduced. Due to the decrease in the heat transfer coefficient, the temperature of the heat exchange medium was further reduced to enable control of the temperature.

Example 2

This example was conducted in the gas-lift reactor shown in Figure 4. In this example, the pilot plant reactor temperature was 250 °F (121 °C) and pressure was 650 psig (4.48 MPa). The heat exchange medium temperature was maintained 20 °F (11.1 °C) lower than the reactor temperature after startup and subsequently the heat exchange medium was maintained 10 °F (5.56 °C) lower than the reactor temperature during the steady state. Figure 3 shows the alpha olefin production and the temperature difference (DT) between the reactor temperature and the heat exchange medium temperature and the heat transfer coefficient. The heat transfer coefficient in Example 2 stayed higher than in Example 1.

CLAIMS

1. A process for producing alpha-olefins comprising:
 - a. contacting an ethylene feed with an oligomerization catalyst system in an oligomerization reaction zone under oligomerization reaction conditions to produce a product stream comprising alpha-olefins; and
 - b. cooling at least a portion of the reaction zone using a heat exchange medium having an inlet temperature and an outlet temperaturewherein the catalyst system comprises a metal-ligand complex and a co-catalyst; the oligomerization reaction conditions comprise a reaction temperature of greater than 70 °C; and the difference between the reaction zone temperature and the inlet temperature of the heat exchange medium is from 0.5 to 15 °C.
2. The process of claim 1 wherein the metal is iron and the co-catalyst comprises modified methyl aluminoxane (MMAO).
3. The process of any of claims 1-2 wherein the reaction zone temperature is in a range of from 70 to 127 °C.
4. The process of any of claims 1-3 wherein the difference between the reaction zone temperature and the inlet temperature of the heat exchange medium is from 0.5 to 10 °C.
5. The process of any of claims 1-4 wherein the difference between the reaction zone temperature and the inlet temperature of the heat exchange medium is measured when the reaction is operating under steady state conditions.
6. The process of any of claims 1-5 wherein the reaction zone temperature is the average temperature in the reaction zone.
7. The process of any of claims 1-6 wherein the feed, catalyst system and product stream in the reaction zone flow in a first direction and the heat exchange medium flows in a second direction.
8. The process of claim 7 wherein the first direction and second direction are the same, such that the flows are co-current.
9. The process of claim 7 wherein the first direction and second direction are opposite, such that the flows are counter current.