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(54) **A PROCESS FOR PRODUCING ALPHA-OLEFINS**

(71) Applicant: **SHELL OIL COMPANY**, Houston (UA)

(72) Inventors: **Cornelius Mark BOLINGER**, Sugar Land, TX (US); **Valerie Anne WILLIAMS**, Monaca, PA (US); **Brent Carl NORRIS**, Houston, TX (US)

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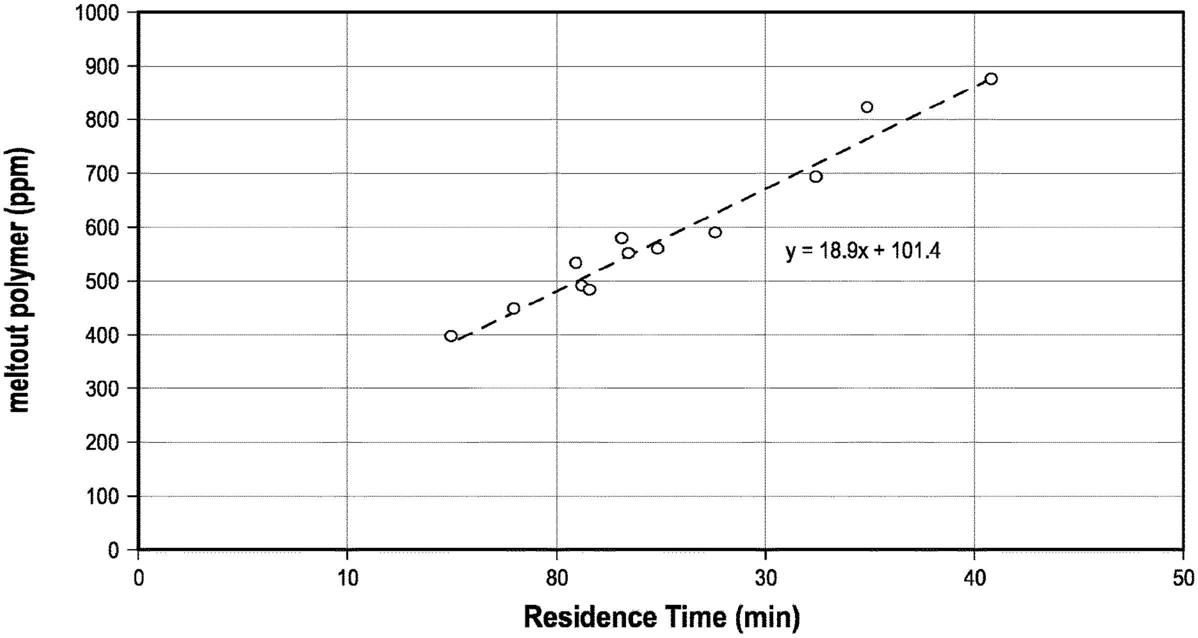
(57) **ABSTRACT**

A process for producing alpha-olefins comprising 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 wherein the catalyst system comprises an iron-ligand complex and a co-catalyst and the residence time in the reaction zone is in the range of from 2 to 40 minutes.



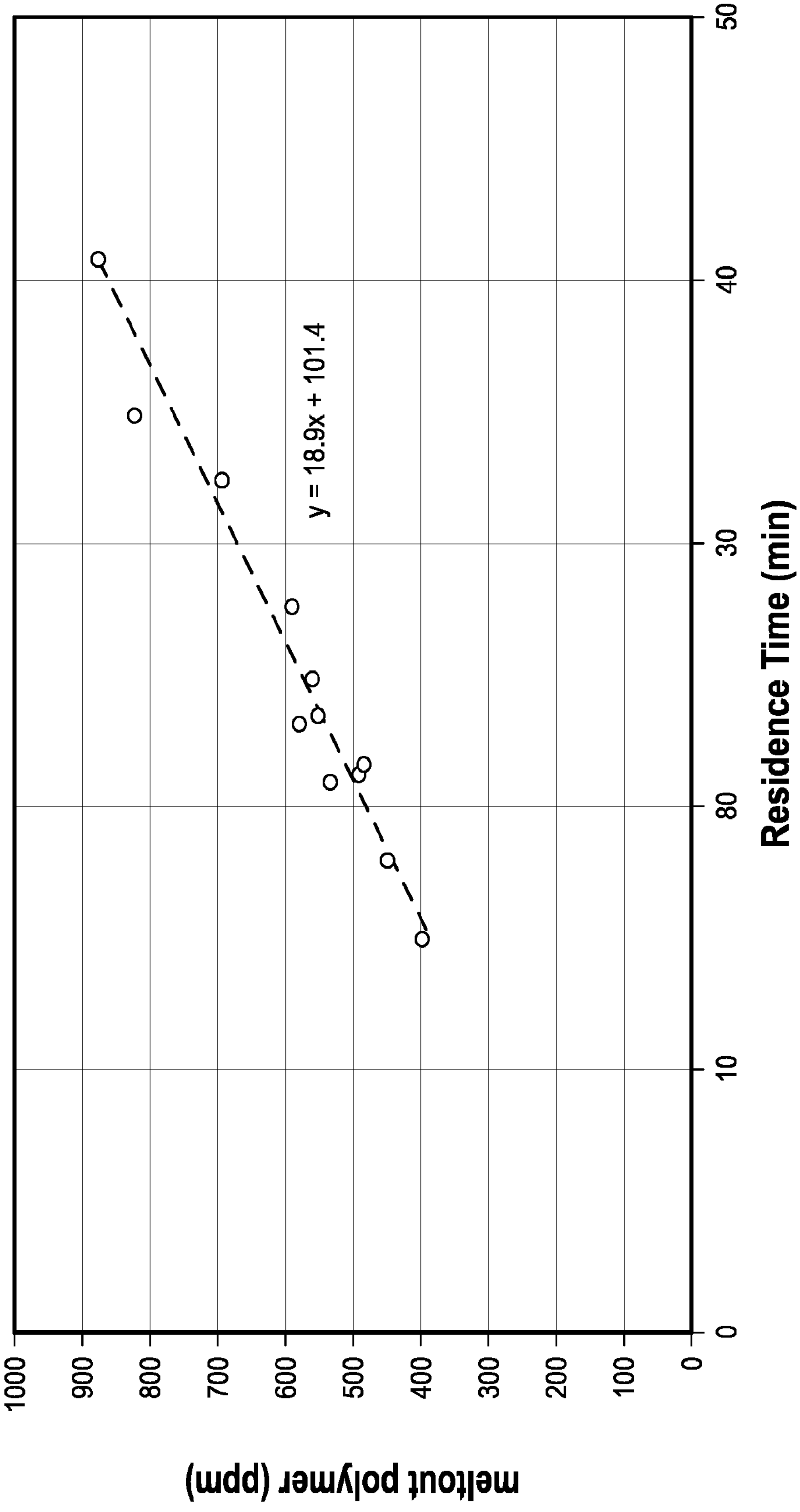

meltout polymer (ppm)
1000
900
800
700
600
500
400
300
200
100
0
0
10
80
30
40
50
Residence Time (min)
y = 18.9x + 101.4

FIG. 1

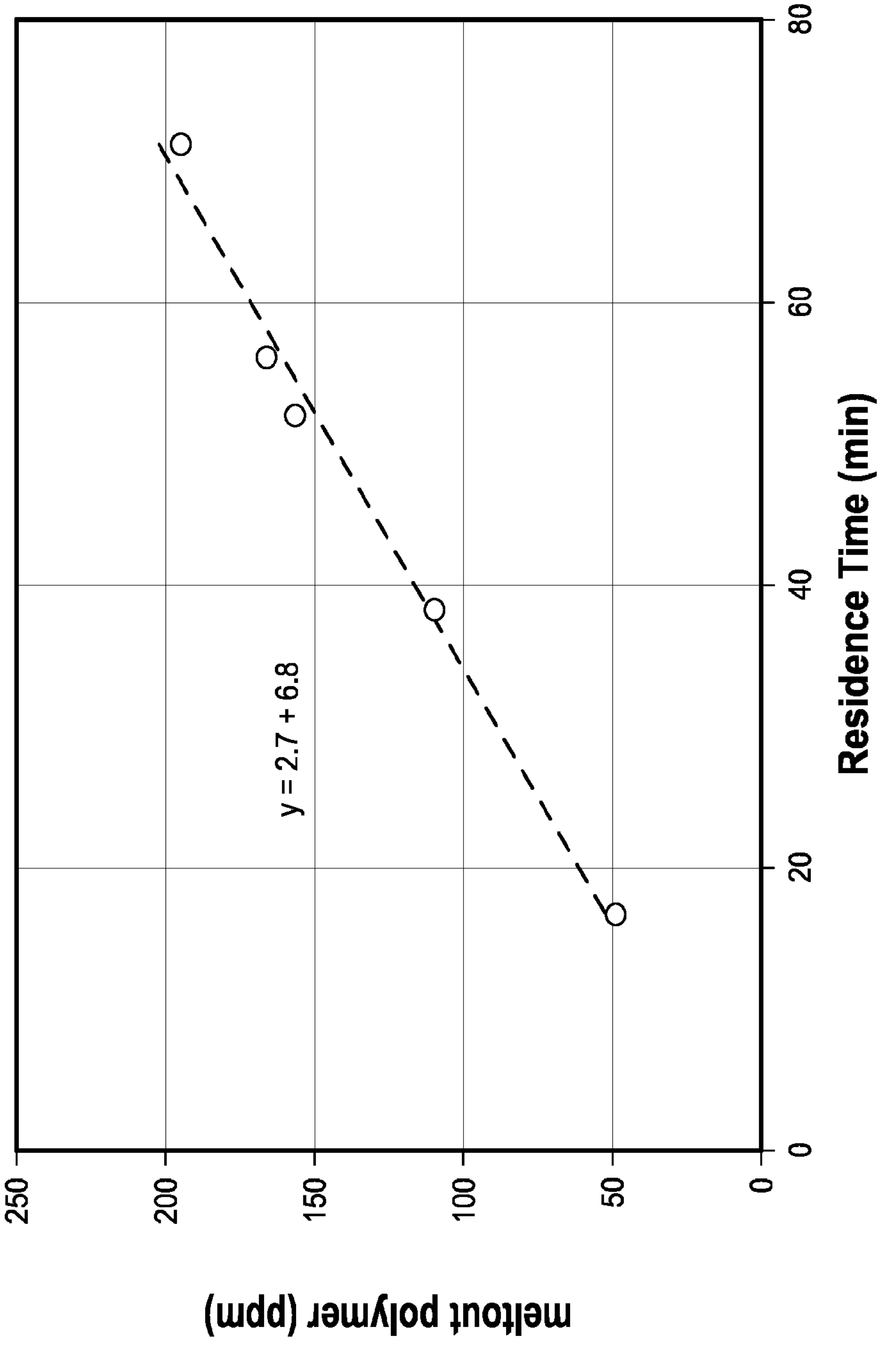

y = 2.7 + 6.8
meltout polymer (ppm)
0
50
100
150
200
250
Residence Time (min)
0
20
40
60
80

FIG. 2

A PROCESS FOR PRODUCING ALPHA-OLEFINS

FIELD OF THE INVENTION

[0001] The invention relates to a process for producing alpha-olefins where the residence time in the reaction zone is limited.

BACKGROUND

[0002] 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 drilling fluids, lubricant oil additives, linear alkylbenzenes, alkenylsuccinic anhydrides, alkyldimethylamines, dialkylmethylamines, alpha-olefin sulfonates, internal olefin sulfonates, chlorinated olefins, linear mercaptans, aluminum alkyls, alkyldiphenylether disulfonates, and other chemicals.

[0003] U.S. Pat. No. 6,683,187 describes a bis(arylimino) pyridine ligand, catalyst precursors and catalyst 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.

[0004] It would be advantageous to develop an improved process that would provide an oligomerization product distribution having a desired K-factor and product quality without forming excessive amounts of polymer that can foul the reactor or other associated equipment.

SUMMARY OF THE INVENTION

[0005] The invention provides a process for producing alpha-olefins comprising 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 wherein the catalyst system comprises an iron-ligand complex and a co-catalyst and the residence time in the reaction zone is in the range of from 2 to 40 minutes.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006] FIG. **1** depicts the results of Example 1.

[0007] FIG. **2** depicts the results of Example 2.

DETAILED DESCRIPTION

[0008] 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 conditions to produce a product slate of alpha olefins having a specific k-factor.

Olefin Feed

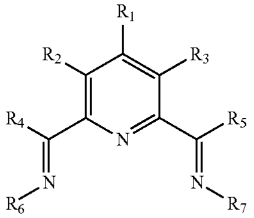
[0009] The olefin feed to the process comprises ethylene. The feed may also comprise olefins having from 3 to 8 carbon atoms. The ethylene may be pretreated to remove impurities, especially impurities that impact the reaction, product quality or damage the catalyst. In one embodiment, the ethylene may 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

[0010] The oligomerization catalyst system may comprise one or more oligomerization catalysts as 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.

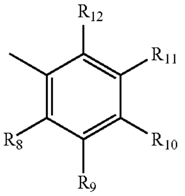
Ligand

[0011] 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.



(I)

[0012] 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.



(II)

[0013] 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.

[0014] 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.

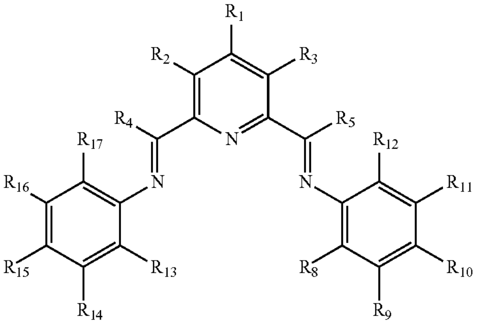
[0015] An optionally substituted hydrocarbyl is a hydrocarbyl group that optionally contains one or more "inert" heteroatom-containing functional groups. Inert means that the functional groups do not interfere to any substantial degree with the oligomerization process. Examples of these inert groups 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.

[0016] Primary carbon atom groups are a —CH_2—R group wherein R may be hydrogen, an optionally substituted hydrocarbyl or an inert functional group. Examples of primary carbon atom groups include —CH_3, —C_2H_5, —CH_2Cl, —CH_2OCH_3, —$CH_2N(C_2H_5)_2$, and —CH_2Ph. Secondary carbon atom groups are a —CH—R_2 or —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 —$CH(CH_3)_2$, —$CHCl_2$, —$CHPh_2$, —$CH(CH_3)(OCH_3)$, —CH=CH_2, and cyclohexyl. Tertiary carbon atom groups are a —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 —$C(CH_3)_3$, —CCl_3, —C≡CPh, 1-Adamantyl, and —$C(CH_3)_2(OCH_3)$

[0017] 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.

[0018] Substituent variations of R_1-R_5, R_8-R_{12} and R_{13}-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.

(III)



[0019] In one embodiment, a ligand of Formula III is provided wherein R_1-R_5, R_9-R_{11} and R_{14}-R_{16} are hydrogen; and R_8, R_{12}, R_{13} and R_{17} are fluorine.

[0020] In one embodiment, a ligand of Formula III is provided wherein R_1-R_5, R_8, R_{10}, R_{12}, R_{14} and R_{16} are hydrogen; R_{13}, R_{15} and R_{17} are methyl and R_9 and R_{11} are tert-butyl.

[0021] In one embodiment, a ligand of Formula III is provided wherein R_1-R_5, R_8, R_{12}, R_{14} and R_{16} are hydrogen; R_{13}, R_{15} and R_{17} are methyl; R_9 and R_{11} are phenyl and R_{10} is an alkoxy.

[0022] In one embodiment, a ligand of Formula III is provided wherein R_1-R_5, R_8, R_{10}, and R_{14}-R_{16} are hydrogen; R_9 and R_{12} are methyl; and R_{13} and R_{17} are fluorine.

[0023] In one embodiment, a ligand of Formula III is provided wherein R_1-R_3, R_9-R_{11} and R_{14}-R_{16} are hydrogen; R_4 and R_5 are phenyl and R_8, R_{12}, R_{13} and R_{17} are fluorine.

[0024] In one embodiment, a ligand of Formula III is provided wherein R_1-R_5, R_{11}-R_{12}, R_{13}-R_{14} and R_{16}-R_{17} are hydrogen; and R_{10} and R_{15} are fluorine.

[0025] In one embodiment, a ligand of Formula III is provided wherein R_1-R_5, R_8, R_{10}, R_{12}, R_{13}, R_{15} and R_{17} are hydrogen; and R_9, R_{11}, R_{14} and R_{16} are fluorine.

[0026] In one embodiment, a ligand of Formula III is provided wherein R_1-R_5, R_9, R_{11}-R_{12}, R_{14} and R_{16}-R_{17} are hydrogen; and R_8, R_{10}, R_{13} and R_{15} are fluorine.

[0027] In one embodiment, a ligand of Formula III is provided wherein R_1-R_5, R_8-R_9, R_{11}-R_{12}, R_{14} and R_{16} are hydrogen; R_{10} is tert-butyl; and R_{13}, R_{15} and R_{17} are methyl.

[0028] In one embodiment, a ligand of Formula III is provided wherein R_1-R_5, R_9-R_{12}, R_{14} and R_{16} are hydrogen; R_8 is fluorine; and R_{13}, R_{15} and R_{17} are methyl.

[0029] In one embodiment, a ligand of Formula III is provided wherein R_1-R_5, R_9-R_{12}, R_{13}, R_{15} and R_{17} are hydrogen; R_8 is tert-butyl; and R_{14} and R_{16} are methyl.

[0030] In one embodiment, a ligand of Formula III is provided wherein R_1-R_5, R_9-R_{12}, R_{13}-R_{14} and R_{16}-R_{17} are hydrogen; and R_8 and R_{15} are tert-butyl.

[0031] In one embodiment, a ligand of Formula III is provided wherein R_1-R_5, R_8-R_{10}, R_{13}-R_{14} and R_{16}-R_{17} are hydrogen; R_{15} is tert-butyl; and R_{11} and R_{12} are taken together to form an aryl group.

[0032] In one embodiment, a ligand of Formula III is provided wherein R_1-R_5, R_{14}-R_{17} are hydrogen; and R_8 and R_{13} are methyl.

[0033] In one embodiment, a ligand of Formula III is provided wherein R_1-R_5, R_8-R_9, R_{11}-R_{12}, R_{14} and R_{16} are hydrogen; R_{10} is fluorine; and R_{13}, R_{15} and R_{17} are methyl.

[0034] In one embodiment, a ligand of Formula III is provided wherein R_1-R_5, R_8, R_{10}, R_{12}, R_{14} and R_{16} are hydrogen; R_9 and R_{11} are fluorine; and R_{13}, R_{15} and R_{17} are methyl.

[0035] In one embodiment, a ligand of Formula III is provided wherein R_1-R_5, R_{11}-R_{12}, R_{14} and R_{16} are hydrogen; R_{10} is an alkoxy; and R_{13}, R_{15} and R_{17} are methyl.

[0036] In one embodiment, a ligand of Formula III is provided wherein R_1-R_5, R_{11}-R_{12}, R_{14} and R_{16} are hydrogen; R_{10} is a silyl ether; and R_{13}, R_{15} and R_{17} are methyl.

[0037] In one embodiment, a ligand of Formula III is provided wherein R_1-R_5, R_8, R_{10}, R_{12}, R_{14}-R_{16} are hydrogen; R_9 and R_{11} are methyl; and R_{13} and R_{17} are ethyl.

[0038] In one embodiment, a ligand of Formula III is provided wherein R_1-R_5, R_9-R_{12}, and R_{14}-R_{17} are hydrogen; and R_8 and R_{13} are ethyl.

[0039] In one embodiment, a ligand of Formula III is provided wherein R_1-R_5, R_9-R_{11} and R_{14}-R_{16} are hydrogen; and R_8, R_{12}, R_{13} and R_{17} are chlorine.

[0040] In one embodiment, a ligand of Formula III is provided wherein R_1-R_5, R_9, R_{11}, R_{14} and R_{16} are hydrogen; and R_8, R_{10}, R_{12}, R_{13}, R_{15} and R_{17} are methyl.

[0041] In one embodiment, a ligand of Formula III is provided wherein R_1-R_5, R_9-R_{10}, R_{12}, R_{14}-R_{15} and R_{17} are hydrogen; and R_8, R_{11}, R_{13} and R_{16} are methyl.

[0042] In one embodiment, a ligand of Formula III is provided wherein R_1-R_{17} are hydrogen.

[0043] In one embodiment, a ligand of Formula III is provided wherein R_1-R_5, R_8, R_{10}, R_{12}, R_{13}, R_{15} and R_{17} are hydrogen; and R_9, Rn, R_{14} and R_{16} are tert-butyl.

[0044] In one embodiment, a ligand of Formula III is provided wherein R_1-R_5, R_8-R_{12}, R_{14} and R_{16} are hydrogen; and R_{13}, R_{15} and R_{17} are methyl.

[0045] In one embodiment, a ligand of Formula III is provided wherein R_1-R_5, R_9, R_{11}-R_{12}, R_{14} and

[0046] R_{16} are hydrogen; R_8 and R_{10} are fluorine; and R_{13}, R_{15} and R_{17} are methyl.

[0047] In one embodiment, a ligand of Formula III is provided wherein R_1-R_5, R_9, R_{11}-R_{12}, R_{14} and R_{16}-R_{17} are hydrogen; and R_8, R_{10}, R_{13} and R_{15} are methyl.

[0048] In one embodiment, a ligand of Formula III is provided wherein R_1-R_5, R_9-R_{11} and R_{14}-R_{16} are hydrogen; R_8 and R u are chlorine; and R_{13} and R_{17} are fluorine.

[0049] In one embodiment, a ligand of Formula III is provided wherein R_1-R_5, R_8, R_{10}, R_{12}, R_{14} and R_{16} are hydrogen; and R_9, R_{11}, R_{13}, R_{15} and R_{17} are methyl.

[0050] In one embodiment, a ligand of Formula III is provided wherein R_1-R_5, R_9-R_{11} and R_{13}-R_{14} and R_{16}-R_{17} are hydrogen; R_8 and R_{12} are chlorine; and R_{15} is tert-butyl.

[0051] In one embodiment, a ligand of Formula III is provided wherein R_1-R_5, R_9-R_{11} and R_{13}-R_{17} are hydrogen; and R_8 and R_{12} are chlorine.

[0052] In one embodiment, a ligand of Formula III is provided wherein R_1-R_5, R_9-R_{12}, and R_{14}-R_{17} are hydrogen; and R_8 and R_{13} are chlorine.

[0053] In one embodiment, a ligand of Formula III is provided wherein R_1-R_5, R_9, R_{11}-R_{12}, R_{14} and R_{16}-R_{17} are hydrogen; and R_8, R_{10}, R_{13} and R_{15} are chlorine.

[0054] In one embodiment, a ligand of Formula III is provided wherein R_1-R_5, R_9, R_{11}-R_{12}, and R_{14}, and R_{16}-R_{17} are hydrogen; R_{10} and R_{15} are methyl; and R_8 and R_{13} are chlorine.

[0055] In one embodiment, a ligand of Formula III is provided wherein R_1-R_5, R_9-R_{11} and R_{11}-R_{14} and R_{16}-R_{17} are hydrogen; R_{15} is fluorine; and R_8 and R_{12} are chlorine.

[0056] In one embodiment, a ligand of Formula III is provided wherein R_1-R_5, R_8-R_9, R_{11}-R_{12}, R_{14}-R_{15} and R_{17} are hydrogen; R_{10} is tert-butyl; and R_{13} and R_{16} are methyl.

[0057] In one embodiment, a ligand of Formula III is provided wherein R_1-R_5, R_9-R_{11}, R_{14} and R_{16} are hydrogen; R_8 and R_{12} are fluorine; and R_{13}, R_{15} and R_{17} are methyl.

[0058] In one embodiment, a ligand of Formula III is provided wherein R_1-R_5, R_9-R_{10}, R_{12}, R_{14}-R_{15} and R_{17} are hydrogen; R_8 and R_{13} are methyl; and R_{11} and R_{16} are isopropyl.

[0059] In one embodiment, a ligand of Formula III is provided wherein R_1-R_5, R_9-R_{12} and R_{14}-R_{16} are hydrogen; R_8 is ethyl; and R_{13} and R_{17} are fluorine.

[0060] In one embodiment, a ligand of Formula III is provided wherein R_2-R_5, R_9-R_{10}, R_{12}, R_{14}-R_{15} and R_{17} are hydrogen; R_1 is methoxy; and R_8, R_{11}, R_{13} and R_{16} are methyl.

[0061] In one embodiment, a ligand of Formula III is provided wherein R_2-R_5, R_8-R_{12}, R_{14} and R_{16} are hydrogen; R_1 is methoxy; and R_{13}, R_{15} and R_{17} are methyl.

[0062] In one embodiment, a ligand of Formula III is provided wherein R_2-R_5, R_9-R_{12}, and R_{14}-R_{17} are hydrogen; R_1 is methoxy; and R_8 and R_{13} are ethyl.

[0063] In one embodiment, a ligand of Formula III is provided wherein R_2-R_5, R_9, R_{11}-R_{12}, R_{14} and R_{16}-R_{17} are hydrogen; R_1 is tert-butyl; and R_8, R_{10}, R_{13} and R_{15} are methyl.

[0064] In one embodiment, a ligand of Formula III is provided wherein R_2-R_5, R_8-R_{12}, R_{14} and R_{16} are hydrogen; R_1 is tert-butyl; and R_{13}, R_{15} and R_{17} are methyl.

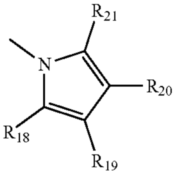
[0065] In one embodiment, a ligand of Formula III is provided wherein R_2-R_5, R_9, R_{11}, R_{14} and R_{16} are hydrogen; R_1 is methoxy; and R_8, R_{10}, R_{12}, R_{13}, R_{15} and R_{17} are methyl.

[0066] In one embodiment, a ligand of Formula III is provided wherein R_2-R_5, R_9, R_{11}, Rn and R_{16} are hydrogen; R_1 is alkoxy; and R_8, R_{10}, R_{12}, R_{13}, R_{15} and R_{17} are methyl.

[0067] In one embodiment, a ligand of Formula III is provided wherein R_2-R_5, R_9, R_{11}, R_{14} and R_{16} are hydrogen; R_1 is tert-butyl; and R_8, R_{10}, R_{12}, R_{13}, R_{15} and R_{17} are methyl.

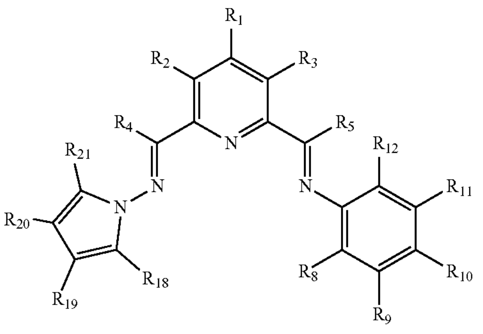
[0068] In another embodiment, the ligand may be a compound having the structure of Formula I, wherein one of R_6 and R_7 is aryl as shown in Formula II and one of R_6 and R_7 is pyridyl as shown in Formula IV. In another embodiment, R_6 and R_7 may be pyrrolyl.

(IV)



[0069] 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_{18}-R_{21} 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.

(V)

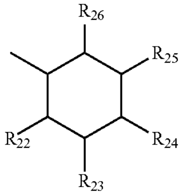


[0070] In one embodiment, a ligand of Formula V is provided wherein R_1-R_5, R_9, R_{11} and R_{18}-R_{21} are hydrogen; and R_8, R_{10}, and R_{12} are methyl.

[0071] In one embodiment, a ligand of Formula V is provided wherein R_1-R_5, R_9-R_{11} and R_{18}-R_{21} are hydrogen; and R_8 and R u are ethyl.

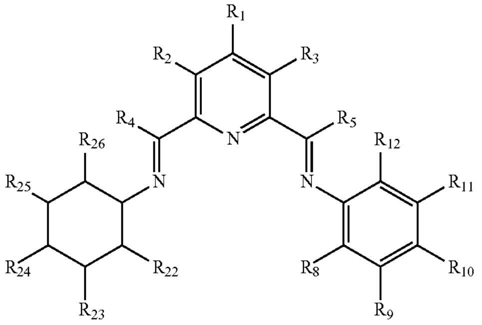
[0072] In another embodiment, the ligand may be a compound having the structure of Formula I, wherein one of R_6 and R_7 is aryl as shown in Formula II and one of R_6 and R_7 is cyclohexyl as shown in Formula VI. In another embodiment, R_6 and R_7 may be cyclohexyl.

(VI)



[0073] 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_{22}-R_{26} 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.

(VII)

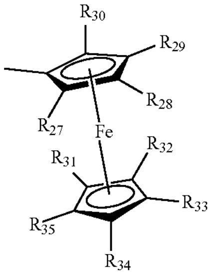


[0074] In one embodiment, a ligand of Formula VII is provided wherein R_1-R_5, R_9, R_{11} and R_{22}-R_{26} are hydrogen; and R_8, R_{10}, and R_{12} are methyl.

[0075] In another embodiment, R_6 and R_7 may be adamantyl or another cycloalkane.

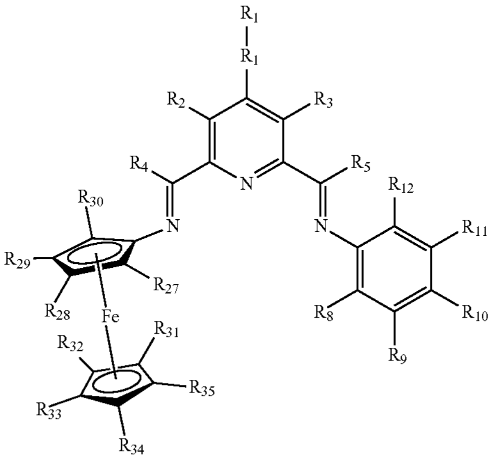
[0076] In another embodiment, the ligand may be a compound having the structure of Formula I, wherein one of R_6 and R_7 is aryl as shown in Formula II and one of R_6 and R_7 is ferrocenyl as shown in Formula VIII. In another embodiment, R_6 and R_7 may be ferrocenyl.

(VIII)



[0077] 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.

(IX)



[0078] In one embodiment, a ligand of Formula IX is provided wherein R_1-R_5, R_9, R_{11} and R_{27}-R_{35} are hydrogen; and R_8, R_{10}, and R_{12} are methyl.

[0079] In one embodiment, a ligand of Formula IX is provided wherein R_1-R_5, R_9-R_{11}, and R_{27}-R_{35} are hydrogen; and R_8 and R_{12} are ethyl.

[0080] 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.

[0081] 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.

[0082] 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.

[0083] 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.

[0084] 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.

[0085] 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.

[0086] 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

[0087] 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).

[0088] 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 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.

[0089] 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, an aryloxide or an aralkoxide. The halide may be fluorine, chlorine, bromine or iodine.

[0090] 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.

[0091] The β-diketonate may be any C_1 to C_{20} β-diketonate. The β-diketonate may be acetylacetonate, hexafluoroacetylacetonate, or benzoylacetonate.

[0092] The hydrocarboxide may be any C_1 to C_{20} hydrocarboxide. The hydrocarboxide may be a C_1 to C_{20} alkoxide, or a C_6 to C_{20} aryloxide. The alkoxide may be methoxide, ethoxide, a propoxide (e.g., iso-propoxide) or a butoxide (e.g., tert-butoxide). The aryloxide may be phenoxide

[0093] Generally, the number of monoanions equals the formal oxidation state of the metal atom.

[0094] 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

[0095] The co-catalyst may be a compound that is capable of transferring an optionally substituted 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.

[0096] 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 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 neutral Lewis acids such as SbF_5, BF_3 and Ar_3B wherein Ar is a strong electron-withdrawing aryl group such as C_6F_5 or $3,5\text{-}(CF_3)_2C_6H_3$. 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.

[0097] The co-catalyst is preferably an organoaluminum compound which may comprise an alkylaluminum compound, an aluminoxane or a combination thereof.

[0098] The alkylaluminum compound may be trialkylaluminum, an alkylaluminum halide, an alkylaluminum alkoxide or a combination thereof. The alkyl group of the alkylaluminum compound may be any C_1 to C_{20} 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.

[0099] The trialkylaluminum compound may comprise trimethylaluminum (TMA), triethylaluminum (TEA), tripropylaluminum, tributylaluminum, tripentylaluminum, 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).

[0100] 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.

[0101] The alkoxide group of the alkylaluminum alkoxide may be any C_1 to C_{20} alkoxy group. The alkoxy group may be methoxy, ethoxy, propoxy, butoxy, pentoxy, hexoxy, heptoxy or octoxy. The alkylaluminum alkoxide may be diethylaluminum ethoxide.

[0102] 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-aluminoxane, 2-pentyl-aluminoxane, 3-pentyl-aluminoxane, iso-pentyl-aluminoxane, neopentylaluminoxane, or mixtures thereof.

[0103] 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 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 triisooctylaluminum. In one embodiment, the co-catalyst is MMAO, wherein preferably about 25% of the methyl groups are replaced with iso-butyl groups.

[0104] In one embodiment, the co-catalyst may be formed in situ in the reactor by providing the appropriate precursors into the reactor.

Solvent

[0105] 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 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

[0106] 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 C_9 and C_{10} solvents. Suitable aromatic solvents include benzene, toluene, xylene (including ortho-xylene, meta-xylene, para-xylene and mixtures thereof) and ethylbenzene.

Alkanes

[0107] 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 mixtures of these alkanes. The alkanes may be cycloalkanes. Suitable solvents include propane, iso-butane, n-butane, butane (n-butane or a mixture of linear and branched C_4 acyclic alkanes), pentane (n-pentane or a mixture of linear and branched acyclic alkanes), hexane (n-hexane or a mixture of linear and branched C_6 acyclic alkanes), heptane (n-heptane or a mixture of linear and branched C_7 acyclic alkanes), octane (n-octane or a mixture of linear and branched C_8 acyclic alkanes) and isooctane. Suitable solvents also include cyclohexane and methylcyclohexane. In one embodiment, the solvent comprises C_6, C_7 and C_8 alkanes, that may include linear, branched and iso-alkanes.

Catalyst System

[0108] 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.

[0109] 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.

[0110] 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 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

[0111] 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

[0112] The oligomerization reaction may be conducted over a range of temperatures of from −100° C. to 300° C., preferably in the range of from 0° C. to 200° C., and more preferably in the range of from 50° C. to 150° C. In one embodiment, the temperature is at most 135° C., preferably at most 121° C. and more preferably in the range of from 88 to 121° C.

Pressure

[0113] The oligomerization reaction may be conducted at a pressure of from 0.01 to 15 MPa and more preferably from 1 to 10 MPa.

[0114] 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.

Residence Time

[0115] Residence times in the reactor of from 3 to 60 min have been found to be suitable, depending on the lifetime of the catalyst. The residence time in the reaction zone had a significant impact on the polymer produced in the reactor per unit ethylene converted. This impact was consistent across multiple different reaction conditions and ligands. It is believed that this may be caused by one or both of two possible reasons. First, the catalyst that forms the polymer has a longer activation time than the alpha-olefin catalyst. This means that the longer the components stay in the reactor, the higher the relative concentration of polymer catalyst. Second, the polymer catalyst may be a result of the decomposition of the alpha-olefin catalyst. In this sequential reaction, the catalyst pre-cursors first make the alpha-olefin catalyst, and then after a deactivation reaction, form the catalyst that produces polymer. It is not clear from the experimental results which reason is the cause, but it has been found that reducing residence time reduces polymer formation.

[0116] In one embodiment, the residence time in the reaction zone is at most 40 minutes. In one embodiment, the residence time is in the range of from 2 minutes to 40 minutes, preferably from 2 to 35 minutes, and more preferably from 2 to 30 minutes. In one embodiment, the residence time is in the range of from 10 to 25 minutes.

Gas Phase, Liquid Phase or Mixed Gas-Liquid Phase

[0117] 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. In one embodiment, the reaction is carried out in the absence of air and moisture.

Reactor Type

[0118] 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.

[0119] In another embodiment, the oligomerization reaction may be carried out in a batch reactor, 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.

[0120] 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 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).

[0121] 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.

[0122] 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.

Catalyst Deactivation

[0123] 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.

[0124] In one embodiment, the catalyst is deactivated by addition of an acidic species having a pKA(aq) of less than 25. The deactivated catalyst can then be removed by water washing in a liquid/liquid extractor.

Product Separation

[0125] 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.

[0126] 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.

[0127] 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

[0128] 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

[0129] 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.

[0130] 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

Example 1

[0131] This example was conducted in a 600 mL stirred Parr reactor. The reactor was fed ethylene, solvent, iron-ligand complex catalyst and MMAO continuously throughout the examples.

[0132] The amount of polymer was calculated by collecting a mass of polymer and normalizing it to the amount of ethylene consumed during the run. The numbers are reported as ppmw (mass of polymer/mass of ethylene consumed x (1×10^6). The meltout polymer shown in FIG. **1** for the different residence time runs is the polymer collected from the reactor after the run. This polymer was collected by passing xylene through the reaction zone and associated equipment, first at reaction temperature to remove residual AO's and then twice at elevated temperatures to recover the polymer.

[0133] The residence time is calculated based on liquid feed flow through the reactor plus the alpha-olefins produced. The calculation assumes that all of the produced alpha-olefin stays in the liquid phase even though some of the butene likely goes into the gas phase. Residence time is calculated as follows:

$$\text{Residence time (min)} = \frac{\text{reactor volume (mL)}^{*}\text{reactor density}\left(\text{g/mL}\right)^{*}\text{run time (min)}}{\text{total Solvent mass (g)}+\text{total ethylene converted(g)}}$$

[0134] In this example, various residence times were tested at 76.7° C. using an iron-ligand complex catalyst and an MMAO cocatalyst.

Example 2

[0135] In this example, all of the conditions were the same except that the reaction zone was at a temperature of 93.3° C. The results are shown in FIG. **2**.

1. A process for producing alpha-olefins comprising 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 wherein the catalyst system comprises an iron-ligand complex and a co-catalyst and the residence time in the reaction zone is in the range of from 2 to minutes.

2. The process of claim **1** wherein the co-catalyst comprises modified methyl aluminoxane (MMAO).

3. The process of claim **1** wherein the residence time in the reaction zone is in the range of from 2 to 35 minutes.

4. The process of claim **1** wherein the residence time in the reaction zone is in the range of from 2 to 30 minutes.

5. The process of claim **1** wherein the residence time in the reaction zone is in the range of from 10 to 25 minutes.

6. The process of claim **1** wherein the temperature in the reaction zone is at most 135° C.

7. The process of claim **1** wherein the temperature in the reaction zone is at most 121° C.

8. The process of claim **1** wherein the temperature in the reaction zone is in the range of from 70 to 121° C.

9. The process of claim **1** wherein the reaction zone is a continuous stirred tank reactor, a plug flow reactor or a loop reactor.

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