Claims

1. Method for oligomerization of ethylene, comprising the steps:

a) feeding ethylene, solvent and a catalyst composition comprising catalyst and cocatalyst into a reactor,

b) oligomerizing ethylene in the reactor,

c) discharging a reactor effluent comprising linear alpha-olefins including 1-butene, solvent, unconsumed ethylene dissolved in the reactor effluent, and catalyst composition from the reactor,

d) separating ethylene and 1-butene collectively from the remaining reactor effluent, and

e) recycling at least a part of the ethylene and the 1-butene separated in step d) into the reactor.

2. Method according to claim 1, wherein the recycling stream of ethylene and 1-butene of step e) is purged at least partly by a purge stream.

3. Method according to claim 1 or 2, wherein the amount of 1-butene in the reactor is at least 1 weight percent, more preferably 5 weight percent, more preferably 10 weight percent, more preferably 25 weight percent, based on the total weight of liquids in the reactor.

4. Method according to any of the preceding claims, wherein 1-butene is present in the reactor in a maximum amount of 30 weight percent, based on the total weight of liquids in the reactor.

5. Method according to any of the preceding claims, wherein step b) is carried out at a temperature of 10-100°C, preferably 30-70°C, and/or a pressure of about 10-100 bar.

6. Method according to any of the preceding claims, wherein additional 1-butene is fed into the reactor, from an external source, preferably at an initial start-up period of the method for oligomerization.

7. Method according to any of the preceding claims, wherein the separation of step d) is carried out at a pressure below reaction pressure of step b).

8. Method according to any of the preceding claims, wherein ethylene and 1-butene are recycled into the reactor in liquid form.

9. Method according to any of the preceding claims, which is a trimerisation.

10. Method according to any of the preceding claims, wherein the catalyst composition comprises a catalyst comprising a chromium compound and a ligand of the general structure (A) $R_1R_2P\text{-}N(R_3)\text{-}P(R_4)\text{-}N(R_5)\text{-}H$ or (B) $R_1R_2P\text{-}N(R_3)\text{-}P(R_4)\text{-}N(R_5)\text{-}PR_6R_7$, wherein R_1-R_7 are independently selected from halogen, amino, trimethylsilyl, C_1-C_{10}-alkyl, C_6-C_{20} aryl or any cyclic derivatives of (A) and (B), wherein at least one of the P or N atoms of the PNPN-unit or PNPNP-unit is a member of a ring system, the ring system being formed from one or more constituent compounds of structures (A) or (B) by substitution.

11. Method according to claim 10, wherein the chromium compound is selected from or ganic or inorganic salts, coordination complexes and organometallic complexes of Cr(II) or Cr(III), preferably $CrCl_3(THF)_3$, Cr(III)acetyl acetonate, Cr(III)octanoate, chromium hexacarbonyl, Cr(III)-2-ethylhexanoate, benzene(tricarbonyl)-chromium or Cr(III)chloride.

12. Method according to any of the preceding claims, wherein the co-catalyst is selected from trimethylaluminum, triethylaluminum, triisopropylaluminum, triisobutyl-aluminum, ethylaluminumsesquichloride, diethylaluminumchloride, ethylaluminumdi chloride, methylaluminoxane (MAO) or mixtures thereof.

13. Method according to any of the preceding claims, wherein the catalyst composition additionally comprises a modifier containing organic or inorganic halide.

14. Method according to any of the preceding claims 10-13, wherein the ligand is selected from Ph_2P-N(i-Pr)-P(Ph)-N(i-Pr)-H, Ph_2P-N(i-Pr)-P(Ph)-N(Ph)-H, Ph_2P-N(i-Pr)-P(Ph)-N(tert-butyl)-H and Ph_2P-N(i-Pr)-P(Ph)-N($CH(CH_3)$(Ph))-H.

15. Method according to any of the preceding claims, wherein the solvent is selected from aromatic hydrocarbons, straight chain and cyclic aliphatic hydrocarbons, and ethers, preferably toluene, benzene, ethylbenzene, cumen, xylenes, mesitylene, hexane, octane, cyclohexane, methylcyclohexane, diethylether, tetrahydrofurane, and mixtures thereof, most preferably toluene.

CLAIMS

1. Method for trimerisation or tetramerisation of ethylene, comprising the steps:

a) feeding ethylene, solvent and a catalyst composition comprising catalyst and cocatalyst into a reactor,

b) oligomerizing ethylene in the reactor,

c) discharging a reactor effluent comprising linear alpha-olefins including 1-butene, solvent, unconsumed ethylene dissolved in the reactor effluent, and catalyst composition from the reactor,

d) separating ethylene and 1-butene collectively from the remaining reactor effluent, and

e) recycling at least a part of the ethylene and the 1-butene separated in step d) into the reactor,

wherein the amount of 1-butene in the reactor is at least 1 weight percent, based on the total weight of liquids in the reactor. (cf. previous claim 3)

2. Method according to claim 1, wherein the recycling stream of ethylene and 1-butene of step e) is purged at least partly by a purge stream.

3. Method according to claim 1, wherein the amount of 1-butene is at least 5 weight percent based on the total weight of liquids in the reactor.

4. Method according to claim 3, wherein the amount of 1-butene is at least 10 weight percent based on the total weight of liquids in the reactor.

5. Method according to any one of claims 1 to 4, wherein 1-butene is present in the reactor in a maximum amount of 30 weight percent, based on the total weight of liquids in the reactor.

6. Method according to any one of claims 1 to 5, wherein step b) is carried out at a temperature of 10-100°C, and/or a pressure of about 10-100 bar.

7. Method according to claim 6, wherein the temperature is 30-70 °C.

8. Method according to any one of claims 1 to 7, wherein additional 1-butene is fed into the reactor from an external source at an initial start-up period of the method for oligomerization.

9. Method according to any one of claims 1 to 8, wherein the separation of step d) is carried out at a pressure below reaction pressure of step b).

10. Method according to any one of claims 1 to 9, wherein ethylene and 1-butene are recycled into the reactor in liquid form.

11. Method according to any one of claims 1 to 10, wherein the oligomerization is a trimerisation.

12. Method according to any one of claims 1 to 11, wherein the catalyst composition comprises a catalyst comprising a chromium compound and a ligand of the general structure (A) R_1R_2P-$N(R_3)$-$P(R_4)$-$N(R_5)$-H or (B) R_1R_2P-$N(R_3)$-$P(R_4)$-$N(R_5)$-PR_6R_7, wherein R_1-R_7 are independently selected from halogen, amino, trimethylsilyl, C_1-C_{10}-alkyl, C_6-C_{20} aryl or any cyclic derivatives of (A) and (B), wherein at least one of the P or N atoms of the PNPN-unit or PNPNP-unit is a member of a ring system, the ring system being formed from one or more constituent compounds of structures (A) or (B) by substitution.

13. Method according to claim 12, wherein the chromium compound is selected from organic or inorganic salts, coordination complexes and organometallic complexes of Cr(II) or Cr(III).

14. Method according to claim 13, wherein the chromium compound is selected from $CrCl_3(THF)_3$, Cr(III)acetyl acetonate, Cr(III)octanoate, chromium hexacarbonyl, Cr(III)-2-ethylhexanoate, benzene(tricarbonyl)-chromium or Cr(III)chloride.

15. Method according to any one of claims 1 to 14, wherein the co-catalyst is selected from trimethylaluminum, triethylaluminum, triisopropylaluminum, triisobutyl-aluminum, ethylaluminumsesquichloride, diethylaluminumchloride, ethylaluminumdichloride, methylaluminoxane (MAO) or mixtures thereof.

16. Method according to any one of claims 1 to 15, wherein the catalyst composition additionally comprises a modifier containing organic or inorganic halide.

17. Method according to any of the preceding claims 12-14, wherein the ligand is selected from Ph_2P-N(i-Pr)-P(Ph)-N(i-Pr)-H, Ph_2P-N(i-Pr)-P(Ph)-N(Ph)-H, Ph_2P-N(i-Pr)-P(Ph)-N(tert-butyl)-H and Ph_2P-N(i-Pr)-P(Ph)-N($CH(CH_3)$(Ph))-H.

18. Method according to any one of claims 1 to 17, wherein the solvent is selected from aromatic hydrocarbons, straight chain and cyclic aliphatic hydrocarbons, and ethers.

19. Method according to claim 18, wherein the solvent is selected from toluene, benzene, ethylbenzene, cumene, xylenes, mesitylene, hexane, octane, cyclohexane, methylcyclohexane, diethylether, tetrahydrofurane, and mixtures thereof.