CLAIMS

What is claimed is:

1. An oligomerization process comprising:

A) introducing ethylene, a transition metal-based catalyst system or catalyst system components, an organic reaction medium, and optionally hydrogen, into an oligomerization reactor, the transition metal-based catalyst system or catalyst system components containing a co-catalyst comprising an aluminoxane and optionally an alkylaluminum;

B) forming an oligomer product in the oligomerization reactor, the oligomer product comprising hexenes and octenes;

C) discharging an effluent stream from the oligomerization reactor, the effluent stream comprising unreacted ethylene, the oligomer product, a residual transition metal-based catalyst system containing the co-catalyst comprising the aluminoxane and optionally the alkylaluminum, and the organic reaction medium; and

D) contacting the effluent stream with a C_4-C_{18} alcohol co-catalyst deactivating agent at a molar amount of OH of the co-catalyst deactivating agent in a range from 0.5 to 1.5 times {(moles of aluminum of the aluminoxane) + (moles aluminum of the alkylaluminum) + (moles aluminum of the alkylaluminum)}.

2. The process of claim 1, wherein the effluent stream is contacted with the co-catalyst deactivating agent before the effluent stream is introduced into a separator to remove at least a portion of the unreacted ethylene.

3. The process of claim 1, wherein the effluent stream is contacted with the co-catalyst deactivating agent after at least a portion of the unreacted ethylene has been removed from the effluent stream in a separator.

4. The process of claim 1, wherein:

the co-catalyst comprises the alkylaluminum;

the alkylaluminum comprises trimethylaluminum (TMA), triethylaluminum (TEA), tri-n-propylaluminum (TNPA), tri-n-butylaluminum (TNBA), triisobutylaluminum (TIBA), tri-n-hexylaluminum, tri-n-octylaluminum, or any combination thereof; and

the aluminoxane comprises methylaluminoxane (MAO), modified methylaluminoxane (MMAO), ethylaluminoxane, n-propylaluminoxane, iso-propyl-

aluminoxane, n-butylaluminoxane, t-butylaluminoxane, sec-butylaluminoxane, iso-butylaluminoxane, 1-pentylaluminoxane, 2-pentylaluminoxane, 3-pentylaluminoxane, isopentylaluminoxane, neopentylaluminoxane, or any combination thereof.

5. The process of claim 1, wherein the co-catalyst deactivating agent has a boiling point at a pressure of 1 atm of at least 150 ℃.

6. The process of claim 1, wherein the co-catalyst deactivating agent comprises 2-ethyl-1-hexanol.

7. The process of claim 1, wherein the transition metal-based catalyst system or catalyst system components comprise (i) a heteroatomic ligand chromium compound complex and the co-catalyst, or (ii) a heteroatomic ligand, a chromium compound, and the co-catalyst.

8. The process of claim 1, wherein the oligomer product comprises from 30 to 87.5 wt. % octenes, based on the total amount of oligomers in the oligomer product.

9. The process of claim 1, wherein the oligomer product comprises from 20 to 60 wt. % hexenes, based on the total amount of oligomers in the oligomer product.

10. The process of claim 1, wherein hydrogen is present in step A).

11. The process of claim 1, further comprising the steps of:

(i) determining an amount of catalytic activity remaining after addition of the co-catalyst deactivating agent; and

(ii) adjusting the amount of the co-catalyst deactivating agent based on the catalytic activity.

12. The process of claim 1, wherein the molar amount of OH is from 0.6 to 1.4 times {(moles of aluminum of the aluminoxane) + (moles aluminum of the alkylaluminum) + (moles aluminum of the alkylaluminum)}.

13. The process of claim 1, wherein the co-catalyst does not contain the alkylaluminum.

14. The process of claim 1, wherein a molar ratio of aluminoxane:alkylaluminum based on aluminum is from 10:1 to 1:10.

15. A method for deactivating a residual transition metal-based catalyst system containing a co-catalyst comprising an aluminoxane and optionally an alkylaluminum in an effluent stream from an oligomerization reactor, the method comprising:

contacting the effluent stream, the effluent stream comprising unreacted ethylene, an oligomer product, the residual transition metal-based catalyst system containing the co-catalyst comprising the aluminoxane and optionally the alkylaluminum, and an organic reaction medium, with a C_4-C_{18} alcohol co-catalyst deactivating agent at a molar amount of OH of the co-catalyst deactivating agent in a range from 0.5 to 1.5 times {(moles of aluminum of the aluminoxane) + (moles aluminum of the alkylaluminum) + (moles aluminum of the alkylaluminum)}.

16. The method of claim 15, wherein the molar amount of OH is from 0.6 to 1.3 times {(moles of aluminum of the aluminoxane) + (moles aluminum of the alkylaluminum) + (moles aluminum of the alkylaluminum)}.

17. The method of claim 15, wherein the catalyst system comprises chromium, iron, cobalt, vanadium, titanium, zirconium, hafnium, or a combination thereof.

18. A method for deactivating a transition metal-based catalyst system containing a co-catalyst comprising an aluminoxane and optionally an alkylaluminum, the method comprising:

contacting the catalyst system with a C_4-C_{18} alcohol co-catalyst deactivating agent at a molar amount of OH of the co-catalyst deactivating agent in a range from 0.5 to 1.5 times {(moles of aluminum of the aluminoxane) + (moles aluminum of the alkylaluminum) + (moles aluminum of the alkylaluminum)}.

19. The method of claim 18, wherein the molar amount of OH is from 0.6 to 1.5 times {(moles of aluminum of the aluminoxane) + (moles aluminum of the alkylaluminum) + (moles aluminum of the alkylaluminum)}.

20. The method of claim 18, wherein:

the co-catalyst comprises the alkylaluminum; and

the co-catalyst deactivating agent comprises a butanol, a pentanol, a hexanol, a heptanol, an octanol, a nonanol, a decanol, an undecanol, or mixtures thereof.

21. The process of claim 2, wherein the co-catalyst deactivating agent comprises 2-ethyl-1-hexanol.

22. The process of claim 21, further comprising the steps of:

(i) determining an amount of catalytic activity remaining after addition of the co-catalyst deactivating agent; and

(ii) adjusting the amount of the co-catalyst deactivating agent based on the catalytic activity.

23. The process of claim 21, wherein a molar ratio of aluminoxane:alkylaluminum based on aluminum is from 10:1 to 1:10.

24. The process of claim 3, wherein the co-catalyst deactivating agent comprises 2-ethyl-1-hexanol.