ON-LINE TRANSITION BETWEEN INCOMPATIBLE CATALYSTS

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Abstract

It is frequently necessary to transition from one type of catalyst system producing polymers having certain properties and characteristics to another catalyst system capable of producing polymers of different chemical and/or physical attributes. Transitioning between similar Ziegler-Natta catalyst systems for example or compatible catalyst systems generally takes place easily. However, the process is typically complicated when the catalyst systems are incompatible or of different types. For example, when transitioning between two incompatible catalyst systems such as a Ziegler-Natta catalyst system and a chromium based catalyst system, some of the components of the Ziegler-Natta catalyst system act as poisons and prevent polymerization to take place. The developed method of converting between different catalyst types for an olefin polymerization process enabled to reduce the amount of off-grade material produced during the transition process, reduce the transition time, increase the robustness and stability of the transition process and avoid the need to open the reactor.

1. Introduction

During the production of olefin polymers in a polymerization reactor, e.g. a fluidized bed reactor, it will often be necessary to transition from one type of catalyst system producing polymers having certain properties and characteristics to another catalyst system producing polymers having different specifications. Transitioning between similar catalyst systems or compatible catalyst systems is easy and routine activity. Compatible catalysts are those catalysts having similar kinetics of termination and insertion of monomer and comonomer (s) and/or do not detrimentally interact with each other. However, the process is typically complicated when the catalyst systems are incompatible or of different types. Transition between two incompatible catalysts For example, when transitioning between Ziegler-Natta catalyst system and a chromium based catalyst system, in continuous polymerization reaction is typically complicated.

Generally, to accomplish an effective transition between incompatible catalysts, the first catalyzed olefin polymerization process is stopped by various techniques. The reactor is then emptied, recharged and a second catalyst system is introduced into the reactor. Such catalyst conversions are time consuming and costly because of the need for a reactor shut-down for an extended period of time during transition and the off-grade material. There have been many attempts to improve the process for transitioning between incompatible catalysts.

Naturally, in order to inhibit polymerization of a first incompatible catalyst, it is necessary to interrupt catalyst injection into the reactor. Stopping the first catalyst feed into the reactor does not immediately stop polymerization reactions occurring within the reactor because the bed contains catalyst particles which can still polymerize for an extended period of time. Even if one were to allow the polymerization reactions within the reactor to continue for a period of time, the catalyst within the reactor would not be completely deactivated for a considerable period.

Thus, to substantially terminate these polymerization reactions within the reactor, it is known to employ polymerization inhibitors or "catalyst killers"[2]. One transition procedure from a Ziegler-type catalyst to a chromium catalyst involves adding a hydroxyl-containing compound to the reactor containing the Ziegler-type catalyst. These transitions primarily operate by discontinuing the introduction of the components of the Ziegler catalyst system into the polymerization reactor, and adding a hydroxyl-containing silica[1] that reacts with and absorbs components of the Ziegler catalyst system. Such silica injection or catalyst killing gent have showed problems in commercial plants. Such transition mechanism has generally not been reproducible, and periodically, this transition mechanism results in reactor operability problems and shutdowns.

It would be advantageous to provide a catalyst transitioning process without the need for halting the polymerization reaction, emptying the reactor to rid it of the original catalyst system and restarting the polymerization reaction with another catalyst system. In addition, it would be advantageous if the process for transitioning could reduce the amount of off-grade material produced during the transition process, reduce the transition time, increase the robustness and stability of the transition process and avoid the need to open the reactor to charge a seed bed.

It would further be advantageous to provide a catalyst transitioning process which does not require the use of a catalyst killer. In the current paper, the process for

transitioning from a first continuous polymerization reaction of ethylene and a first comonomer for producing a linear low density polyethylene conducted in the presence of a Ziegler-Natta catalyst in a gas phase reactor to a second continuous polymerization reaction of ethylene and a second comonomer for producing a high density polyethylene conducted in the presence of a chromium-based catalyst in the gas phase reactor is described and performed with no discontinuity to the reactor operation.
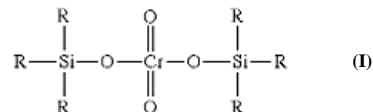
2. Experimental Section

2.1. Materials

Traditional Ziegler-Natta catalysts comprise a transition metal halide, such as titanium, and an organometallic compound of a metal, typically trialkylaluminum compounds (Teal), which serve as an activator or a co-catalyst for the transition metal halide. The Ziegler-Natta catalyst is prepared by contacting a dehydrated solid support having hydroxyl (OH) groups with a magnesium compound to form a solid magnesium containing support material. The solid support for example of such is silica. Preferably, porous silica is used as the support as higher bulk densities and higher catalyst productivities are obtained therewith. The dehydrated solid support can be obtained by drying the solid support in order to remove physically bound water and to reduce the content of hydroxyl groups. The dehydrated support can be slurried, preferably by stirring, in a suitable hydrocarbon solvent in which the individual catalyst components are at least partially soluble. The amount of solvent used is not critical, though the solvent should be used in an amount to provide good mixing of the catalyst components.

The titanium halide compound is represented by the general formula TiX4, wherein Ti is a titanium atom and X is a halide atom. Suitable titanium halide compounds include titanium tetrachloride, as higher catalyst productivity is obtained. The molar ratio of the titanium halide compound to magnesium may be in the range of about 0.05 to about 1.0, as a better balance of high catalyst productivity and high bulk density is obtained.

Chromium based catalyst can be chosen from, for example, chromium oxide based catalysts and silyl chromate based catalysts. The chromium oxide catalysts may be CrO3, or any compound convertible to CrO3 under the activation conditions employed. Generally, chromium based catalysts are prepared by using commercially available silica, to which a chrome source has been added. The silica substrate may be treated with a titanium ester (titanium tetraisopropylate or titanium tetraethoxide are typically used) either, after the Cr compound is deposited, or prior to this deposition.

Generally, the Cr compound, which is convertible to Cr+6, has already been added to the support. The support is then converted into active catalyst by calcination in air. Among the preferred compounds for Cr are the bis-trihydrocarbylsilylchromates of Formula I below:

$$R-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Si}}-O-\underset{\underset{O}{\parallel}}{\overset{\overset{O}{\parallel}}{Cr}}-O-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Si}}-R \qquad \textbf{(I)}$$

The Ziegler-Natta catalyst used for the first polymerization and the chromium-based catalyst used for the second polymerization are incompatible. For the purposes of this paper, the term "incompatible catalysts" are understood as those that satisfy one or more of the following: 1) those catalysts that in each other's presence reduce the productivity of at least one of the catalysts by greater than 50%; 2) those catalysts that under the same reactive conditions one of the catalysts produces polymers having a molecular weight (Mw) greater than two times higher than any other catalyst in the system; and 3) those catalysts that differ in comonomer incorporation or reactivity ratio under the same conditions by more than about 30%

Productivity is herein understood as kg of product per kg of catalyst over a certain period of time. Mw is herein understood as the weight average molecular weight as measured using SEC (Size Exclusion Chromatography using 1,2,4-trichlorobenzene as an eluent, and calibrated using linear polyethylene standards. The comonomer incorporation is measured by the analytical temperature rising elution fractionation (aTREF)[3].

Therefore, the transitioning will be conducted in the presence of a Ziegler- Natta catalyst in a continuous polymerization reaction of ethylene and a first comonomer for producing a linear low density polyethylene (LLDPE) to a second continuous polymerization reaction of ethylene and a second comonomer for producing a high density polyethylene (HDPE) in the presence of a chromium-based catalyst in the gas phase reactor.

2.2. Experimental Setup

A gas phase polymerization process in a fluidized bed reactor is used in this experiment. In a typical continuous gas fluidized bed polymerization process for the production of polymer from monomer, a gaseous stream comprising monomer is passed through a fluidized bed reactor in the presence of a catalyst under reactive conditions. The fluidized bed reactor contains a bed of growing polymer particles in the polymerization zone. The polymerization catalyst is continuously introduced into the polymerization zone while the monomer is fed and the polymer is withdrawn. Gas fluidized bed polymerization system

generally employ a continuous gas cycle. In one part of the cycle, in a reactor a cycling gas stream is heated by the heat of polymerization. This heat is removed in another part of the cycle by a cooling system external to the reactor. An example of a gas phase fluidized bed reactor (FBR) is shown in FIG. 1
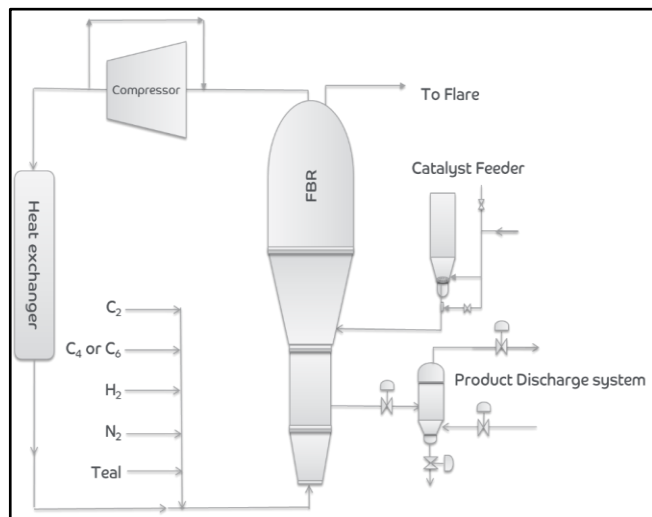

Figure 1. Shows a fluidized bed reactor (FBR) system.

3. Results and Discussion

The gas phase reactor system as schematically shown in FIG. 1 was used for the transition process. The Ziegler-Natta catalyst used for the first polymerization and the chromium-based catalyst used for the second polymerization are incompatible. The Ziegler-Natta **(ZN)** catalyst was used to produce 1-butene-copolymerized low linear density polyethylene (LLDPE) having a density of 918 kg/m^3 and a melt index of 1.0. The LLDPE obtained is suitable for processing by blown film extrusion process. While the chromium-based catalyst was used for 1-hexene-copolymerized high density polyethylene (HDPE) having a density of 0.952 g/cm3 and a flow index (measured at 21.6 kg) of 10 g/10 min.

The gaseous feed streams are mixed together in a mixing tee arrangement and enters the reactor from the bottom. Then, it passes through a perforated distribution plate. The unreacted gas stream is separated from the entrained polymer particles, and is then compressed, cooled, and recycled back into the reactor. Product properties are controlled by adjusting reaction conditions (temperature, pressure, flow rates, etc.)

The individual flow rates of ethylene, hydrogen and comonomer were controlled to maintain fixed composition targets. The ethylene concentration was controlled to maintain a constant ethylene partial pressure. The hydrogen/ethylene flow ratio was well controlled to maintain a relatively steady melt index of the final resin. The concentrations of all the gases were measured by an on-line gas chromatograph to ensure relatively constant composition in the recycle gas stream.

The reacting bed of growing polymer particles was maintained in a fluidized state by the continuous flow of the make-up feed and recycle gas through the reaction zone. A superficial gas velocity of 0.40 m/sec was used to achieve this. The conditions for this first polymerization are shown in below Table#1.

Table 1. Conditions for first polymerization

Reactor Conditions	
Bed temperature (° C.)	85
Reactor pressure (barg)	20.7
C2 partial pressure (bara)	7.0
Bed level (mbar)	35
Superficial velocity (mis)	0.40
H/C2 volume ratio	0.140
C4/C2 volume ratio	0.40
TEAL flow (kg/h)	0.08

After running the reactor at steady state for producing the LLDPE, the feed of 1-butene flow to the reactor was stopped until the C4/C2 volume ratio was down to 0.1 or less.

Subsequently the feeding of the ZN catalyst was stopped. After the ZN catalyst feed was stopped, the feeding of the co-catalyst TEAL was maintained for an additional 30 minutes before it was stopped. The reactor conditions, i.e. the conditions of Table 1 except that C4/C2 volume ratio and TEAL flow were zero, were maintained until the reaction died. All feeds were stopped when the reaction died by first stopping the ethylene feed and subsequently stopping H2 feed within 5-10 minutes after the ethylene feed was stopped.

The reactor was depressurized to 7 barg. Subsequently the reactor was flow-purged with N2 for 4 hours at a reactor temperature of 85° C. The bed temperature was subsequently decreased to 80° C.

The C2 partial pressure was increased to the target pressure in two steps. The C2 partial pressure was gradually increased up to 10 bara by feeding 10 kg/hr flow rate of C2 while maintaining the bed temperature to 80° C. In the second step, the C2 partial pressure was gradually increased up to 15 bara by feeding 5 kg/hr flow rate of C2 while maintaining the bed temperature to 80° C. When the target C2 partial pressure of 15 bara was reached, H2 was introduced to reach the H2/C2 volume ratio of 0.02.

Subsequently, the bed temperature was gradually increased to 95° C. by increasing 2° C. per hour.

The chromium-based catalyst was charged to the reactor. The chromium-based catalyst comprises a chromium oxide on a silica support, which was titanated by drying and then treating with tetra-isopropyltitanate prior to activation of the catalyst.

This was followed by the introduction of 1-hexene. The final reactor conditions for the polymerization using the chromium-based catalyst is as listed below in Table#2.

Table 2. Conditions for second polymerization

Reactor Conditions	Target
Bed temperature (° C.)	100
Reactor pressure (barg)	20.7
C2 partial pressure (bara)	15
Bed level (mbar)	35
Superficial velocity (mis)	0.40
H/C2 volume ratio	0.02
C6/C2 volume ratio	0.0015
TEAL flow (kg/h)	0

HDPE having a density of 0.952 g/cm3 and a flow index of 10 g/10 min was successfully obtained. A successful transitioning was achieved from a Ziegler-Natta catalyst to a chromium-based catalyst with no operational upsets.

4. Conclusions

In the current paper, a developed process for transitioning from an olefin polymerization reaction utilizing a Ziegler-Natta catalyst system to an olefin polymerization reaction utilizing a chromium based catalyst system in a gas phase fluidized bed reactor was demonstrated and found that the transitioning process can be performed without the use of a catalyst killer or enforcing to halt operation. A successful transitioning can therefore be performed in a short time.

Author Biography

Nayef Enazi is currently a senior scientist with SABIC company in Saudi Arabia. Has experience in oil and gas industries and during the past 10 years his work has focused upon polyolefins reaction engineering and process development, focusing in ethylene catalyst polymerization. Working in projects development that have NPV's of several million USD. Published several patents in polyolefins reaction engineering.

1. Fripiat et al.; "Hydroxyl Content in Silica Gel 'Aerosil'"; Journal of Physical Chemistry; vol. 66, Issue 5; 1962; pp. 800-805.
2. Burdett et al (2004); *U.S. Pat. No. 6,858,684.* Retrieved from *https://patents.google.com/patent/US6858684B2/en?oq=US+9%2c914%2c794+B2*
3. Wilde, L.; Ryle, T. R.; Knobeloch, D. C; Peat, L R.; Determination of Branching Distributions in Polyethylene and Ethylene Copolymers, J. Polym. ScL, 20, 441-455 (1982)