Chemical Engineering Science 61 (2006) 4909–4918

Chemical
Engineering Science

www.elsevier.com/locate/ces

Semi-batch reactor for kinetic measurements of catalyzed olefin co-polymerizations in gas and slurry phase

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Received 8 February 2005; received in revised form 8 March 2006; accepted 13 March 2006

Abstract

A multi-purpose setup is presented for homo- and co-polymerizations of ethylene and 1-hexene in slurry and gas phase. Polymerization experiments have been executed semi-batch with a heterogeneous metallocene catalyst under industrial conditions. During the gas phase polymerization, the monomer concentrations have been measured and controlled online. The activities for both monomers have been measured with flow meter technique.

The polymerization kinetics presented have been measured in a very accurate and reproducible way in isothermal (within 0.2 °C) and isobaric mode (within 0.15 bar). The concentrations of monomer and co-monomer have been kept constant within 5% of the set point. The activity for ethylene was 50% higher in the presence of 1-hexene compared to a homo-polymerization.

Keywords: Batch reactor; Control; Kinetics; Polymerization; Metallocene catalyst; Polyolefins; Polyethylene

1. Introduction

1.1. General slurry and gas phase polymerizations

HDPE and LLDPE are produced on industrial scale in solution, slurry or gas phase processes. Most processes can switch between HDPE and LLDPE production by changing co-monomer concentration (Whiteley, 2002). Slurry processes are operated in loop reactors, vertical like the Phillips loop reactors or horizontal like Amoco, and in stirred tank reactors, like Basell's Hostalen slurry process. Slurry processes are still widely used, exhibiting a very efficient heat removal and wide co-monomer range. But the product range is limited due to solubility of the polymer produced, e.g. low molecular weight PE and highly incorporated co-monomer LLDPE. In the late 1960s gas phase reactors were introduced, like fluid bed reactors in the Unipol process, BASF's stirred tank reactors and Amoco's horizontal stirred tank reactors. Gas phase processes can be operated with 1-butene or 1-hexene as co-monomer. Some novel technologies are combinations of gas and slurry phase reactors, like Spherilene (Covezzi, 1995; Galli, 1995) and Borstar PE (Avela et al., 1998). Cascaded processes are suitable for bi-modal polyethylene production.

1.2. State of the art

Although research has been performed for decades on metallocene catalyzed ethylene homo- and co-polymerizations (Hamielec and Soares, 1996; Kaminsky, 1996), only a few academic research groups are able to measure kinetics and produce sufficient amounts of polymer, for property analyses, with good reproducibility at near-industrial, constant process-conditions, i.e., sufficient temperature, pressure and gas phase co-monomer control. Most reports are on slurry polymerizations (Britto et al., 2001; Chien et al., 1998; Kappler et al., 2003). Some gas phase ethylene polymerization kinetics are measured at relative low pressure (5 bar) in a stirred bed 1.0 L glass reactor (Roos et al., 1997) and with optical microscopy in a mini reactor (20 mL) (Kallio et al., 2001). Only a few (Chakravarti and Ray, 2001; Han-Adebekun et al., 1997)

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doi:10.1016/j.ces.2006.03.024

have been able to measure kinetics of highly active metallocene catalysts under near-industrial conditions, i.e., elevated pressures and temperatures at constant process parameters.

Some data has been published on gas phase ethylene 1-hexene co-polymerizations in isoperibolic mode with 1-hexene fed batch wise (Kumkaew et al., 2003; Zhou et al., 2003). In their studies sharp decreases in the reaction rate are observed in the presence of 1-hexene followed by a slower increase compared to homo-polymerizations. They explain this by a temperature dependence on kinetics; temperature increases (2 °C up to 15 °C) are observed over long time periods (15 min). These long-lasting nonisothermal conditions will change kinetics and polymer properties. Another explanation might be the presence of impurities in the 1-hexene. Impurities can react irreversibly and reversibly, so after a certain time a poisoned catalyst site can be reactivated, for example, when poisoning occurs with CO. With large amounts of impurities all sites will be deactivated irreversibly; at high 1-hexene concentrations hardly any reaction rate was observed. However, quasi-isothermal kinetics can be obtained in isoperibolic mode when the temperature remains within ±1 K. This requires a small amount of catalyst, but sufficient activity is required to avoid poisoning effects. In such a way very smooth temperature profiles will be obtained resulting in smooth mass flow meter curves (Weickert, 2004).

1.3. This work

The kinetic behavior of a catalyst is important for reactor design, process optimization, control and polymer properties like molecular weight, molecular weight distributions, density, co-polymer composition, etc. Yield measurements, often used to characterize catalyst performance, are not sufficient, because very different polymerization rate profiles can result in the same yield (Weickert, 2004).

Laboratory scale reactors are required to measure polymerization rate profiles of HDPE and LLDPE in slurry and gas phase under industrial conditions. For gas phase polymerizations this means the presence of an inert gas (e.g. nitrogen, propane). Inert gases are used in industrial reactors to improve heat transfer on the particle and reactor scale. Because of scaling-up requirements, these reactors should produce PEs at constant reaction conditions within a 10% reproducibility of polymerization rate and reaction conditions (Böhm et al., 1990).

In this work, we present a reactor system including temperature, pressure and gas composition control, which allows us to measure rate profiles in a reproducible and accurate way at industrial conditions. Some polymerizations with an impurity-sensitive metallocene catalyst will be presented in order to demonstrate the “kinetic potential” of the equipment.

2. Experimental

2.1. Setup

The experimental setup for gas phase polymerizations is represented in Fig. 1. The reactor is a jacketed, stainless steel 1600 mL reactor from Büchi, which operates at up to pressures of 40 bar and temperatures of 120 °C. The setup is equipped with two automatic catalyst injection systems, suitable for dry powder and slurry injections. The suspended catalyst injection system described by Samson et al. (1998, 1999) has been automated and can be used for catalyst and/or scavenger injections.

The dry catalyst injection consists of a tube with a valve on both ends. The tube is connected to the reactor lid and the dead ends are flushed with nitrogen. The catalyst is injected by pressurizing the tube, up to maximum 60 bar, and opening the bottom valve. A 100 mL vessel is placed on the reactor for adding an inert seedbed to the reactor, to prevent the catalyst particles from sticking to the wall and to each other (Meier et al., 2001). This bed injection vessel can also be used for adding large amounts of pre-polymerized catalyst into the reactor. The seedbed and polymer produced are mixed with a helical stirrer combined with a propeller on the tip, to obtain good powder circulation along the wall. This forced circulation improves the heat transfer from the polymerizing particles to the cooled reactor wall. The stirrer speed can be varied up to 2000 rpm. The reaction temperature is measured above the helical stirrer, in contact with the circulating powder.

Ethylene, nitrogen and hydrogen can be added to the reactor by thermal mass flow controllers (Bronkhorst Hi-Tec); 1-hexene is fed to the reactor by a thermal liquid mass flow controller (Bronkhorst Hi-Tec). All components flow into the reactor via a controlled evaporator mixer (CEM, Bronkhorst Hi-Tec), wherein 1-hexene is dosed by a control valve in the gas mixture flow and evaporated in this CEM system. A continuous flow can be withdrawn from the reactor over a pressure reducer via thermal mass flow controllers (Brooks instruments) to analyzers. Three analyzers are used for the continuous online measuring of the monomers and the hydrogen concentrations. The ethylene and 1-hexene concentrations are measured with two infrared analyzers (Xendos 2550 and 2500, Servomex). The monomer gas can be diluted with nitrogen in order to get the component concentrations in the working range of the analyzers. This nitrogen is added to the sample flow by a thermal mass flow controller. The real concentration in the reactor is calculated with the ratio of the sample flow, the dilution with nitrogen and the concentration measured. The hydrogen concentration is measured by a modified thermal conductivity detector (TCD; Thermor 615, Maihak). After measuring the thermal conductivity of the sample in the measurement cell, the sample flows through a hydrogenation reactor; here all the hydrogen is converted by hydrogenating to a small part of the ethylene on a palladium catalyst. This hydrogen-free sample is measured in the reference cell and the original hydrogen concentration is calculated via a Wheatstone bridge. Note the conductivity of ethylene and ethane differs only slightly and the conductivity of hydrogen is seven times higher, for which see Table 1 (Daubert et al., 1999). This is also the case for most other common olefins and their hydrogenated products. This enables the measuring of the hydrogen concentration in a multi-component system independent of the ethylene and co-monomer concentrations. Besides the monomers and hydrogen the reaction gas also contains nitrogen (about 50 vol%).