

Kinetic Monitoring Methods for Ethylene Coordination Polymerization in a Laboratory Reactor

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ABSTRACT: The kinetic performance of metallocene type catalysts as well as their instantaneous activity is determined on line by two independent methods in the semi-batch polymerization of ethylene via metallocenes. The first-principle basis of both methods is described and guidelines for their implementation at a laboratory scale reactor are offered. Polymerization tests were conducted with two heterogenized metallocene catalysts showing that the direct method (based on ethylene flow measurement) and the calorimetric method (based on energy balances and developed here) report equivalent high quality information. This last method can be readily used by the chemical practitioner as the notions and tools required for its implantation are easily grasped; it also has the advantage of requiring a low cost instrumentation (only thermocouples), whereas the direct method needs a relatively more sophisticated equipment (mass flow meter). © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40035.

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INTRODUCTION

The activity of a Ziegler–Natta type catalyst, defined as the polyethylene weight produced per mol of catalyst and per unit time, is an important technological variable that expresses the performance of a catalyst in the operation of an industrial plant of polyethylene. Frequently, mainly in industrial practice, mean activity values are used when comparing different catalysts; however, this information is not enough, because one same mean activity value can result from widely different kinetic behavior. For instance, a multisite catalyst could have the same mean activity as a single-site catalyst.¹ Instantaneous activity values are a better choice to characterize a given catalyst. These are determined experimentally in low scale polymerization tests that report the instantaneous polymerization rate (kinetic curve). The evolution of the polymerization rate, r_p , can be considered the fingerprint of the catalytic system. Additionally to its value as a catalyst characterization means, a kinetic curve can guide the modeling studies, required for a deep understanding of the catalytic medium.^{2,3}

Usually, the metallocene (or Ziegler–Natta) catalyst behavior study is performed in a semi-batch stirred tank reactor provided with a heat transfer jacket, operating at the 0.2–2 L scale of operation. The pressure is maintained constant by means of a pressure regulator. In this way, the addition of ethylene is continuous and governed by the reaction requirements. The

measurement of this flow directly provides the instantaneous polymerization rate assuming that the instantaneous accumulation of ethylene in the system is negligible. The reactor temperature (or jacket temperature) is automatically controlled. In the simplest case, the jacket temperature is maintained constant by means of a controlled temperature circulator connected to the jacket.

An alternative way to the direct ethylene flow measurement for the estimation of the catalytic coordination polymerization rate is through the estimation of the instantaneous heat of reaction. This method (calorimetric) has been used successfully in a variety of polymerization reactions.^{4–9} Rincon et al.⁴ and Espósito et al.⁵ studied the batch and semi-batch emulsion polymerization of vinylacetate in a 5 L calorimetric type reactor. They used a Kalman type filter to estimate the heat transfer coefficient as well as the conversion evolution. Korber et al.^{6,7} working with a commercial calorimeter (RC1 from Mettler-Toledo) in the propylene polymerization via metallocenes, report comparable results between on-line calorimetry and propylene consumption measurement with a mass flowmeter. Altarawneh et al.⁸ investigated the emulsion polymerization of Styrene via RAFT. They were able to monitor the conversion as well as the molecular weight using only calorimetric techniques. However, the reports of the use of calorimetry for monitoring the ethylene polymerization are scarce. In a recent report,⁹ the calorimetric method has been used for the monitoring of ethylene

polymerization via metallocenes in a laboratory reactor. The authors refer successful results when they develop a calorimetric observer and compare it with an estimation of ethylene consumption based on the pressure of an ethylene reservoir.

As the instrumentation required to implement a calorimetric monitoring technique on or off-line (that is: at the moment of the test or a posteriori) is standard and economically accessible to most laboratories (only temperature sensors in the reactor and the jacket are necessary), it is convenient to consider the applicability of the calorimetric method to the reaction rate monitoring of the ethylene coordination polymerization and compare it with the most standard monitoring method (direct measurement of ethylene flow). The suitability of the calorimetric method for an accurate kinetic characterization should not be taken for granted for a given polymerization system, as it will depend on a number of variables, such as the polymerization enthalpy and reaction rate, as well as the dynamic behavior of the catalyst in the reaction system. In this work, the standard and the calorimetric methods are established and implemented to determine the polymerization rate in the ethylene coordination polymerization. The implementation of the calorimetric method is developed using notions and tools readily accessible to the chemical practitioner. The study is conducted in a bench scale polymerization reactor equipped for the ethylene flow measurement as well as for the reaction heat evolution estimation. Two metallocene type catalysts are used that illustrate the applicability of the kinetic monitoring techniques. It is also demonstrated how these kinetic studies provide essential information for a deeper understanding of the chemical and dynamic nature of the catalytic system and to compare different catalytic systems based on their kinetic performance. The application of the data obtained with these methods to modeling studies of the catalytic system will be a matter of future reports.

BACKGROUND

Determination of r_p Through Calorimetry

The basis for the method to follow the reaction rate through the reaction heat evolution is an energy balance applied to the reactor volume. The reactor is of the stirred type, so it has homogeneous conditions in all the volume of the reaction mixture. Depending on the mode of operation of the reactor with respect to temperature, the calorimetric technique can be classified according to three different types: (i) adiabatic, when there is no control of the temperature and there is no energy exchange between the reactor and its surroundings; (ii) isothermic, when feedback control of the temperature is supplied to regulate it, usually by means of a circulating heat transfer medium flowing through a jacket (see Figure 1); and (iii) isoperibolic, when the temperature of the heat transfer medium is maintained constant, typically using a controlled temperature bath. Each technique presents advantages and drawbacks; the adiabatic and the isoperibolic techniques are easier to implement from the point of view of equipment and control devices required. Conversely, the isothermal technique is more suitable for the study of basic kinetic parameters, as in the case when the values of kinetic rate constants need to be determined at

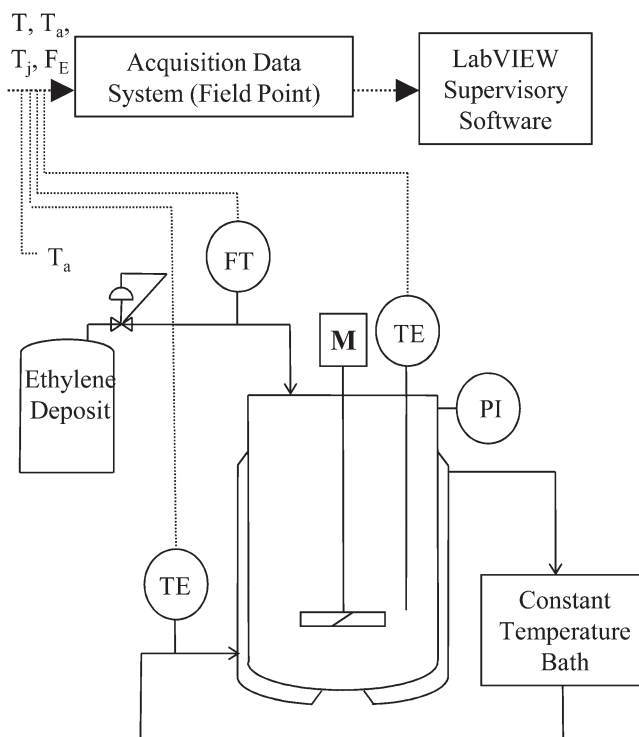


Figure 1. Laboratory reactor arrangement for semi-batch ethylene polymerization using metallocene catalysts.

fixed temperatures. In our case, the mode of operation selected for this study is the isoperibolic type due to its simplicity and low cost of operation and to the fact that the configuration required is one of the most common arrangements at laboratory scale.

The energy balance for this kind of reactor can be formulated in two ways: (i) including a secondary energy balance to consider the sensible heat changes in the heat transfer medium,¹⁰ that is, the temperature change of the medium entering and leaving the jacket (the heat balance method); and (ii) considering only one main balance in the reactor (the calibrated heat flow method). In this last method, the heat exchange with the jacket is modeled with a global heat transfer coefficient and the driving force is the difference between the reactor temperature and a characteristic temperature of the heat transfer medium, usually the mean temperature between the inlet and outlet of the jacket. Although in large scale reactors the heat balance method is the preferred one because it has not dependency on a heat transfer coefficient (which can have a variable magnitude and can be difficult to determine), at a laboratory scale the difference of temperatures at the inlet and outlet of the heat transfer medium can be easily masked by the noise of the measurements making the method less precise and prone to error (the heat balance method is better suited for the industrial scale, as the jacket temperature difference is relatively large and easy to measure; which is not the case for laboratory scale reactors). For this reason, the calibrated heat flow method will be used as the basis for this implementation. A commercial calorimetric laboratory reactor setup (RC1 from Mettler Toledo) is also based on the calibrated heat flow method.^{6,7}

The energy balance for the reactor, with the standard terms of inlet (In), outlet (Out), production (Prod), and accumulation (Acc) is as follows¹⁰:

$$\text{In} - \text{Out} + \text{Prod} = \text{Acc} \quad (1)$$

For the arrangement depicted in Figure 1:

$$-F_e C_{pe}(T - T_e) - UA(T - T_j) + r_p V(-\Delta H)M_e = \frac{dm_R C_{pR} T}{dT} \quad (2)$$

where F_e is the ethylene flow, g/s; c_{pe} and C_{pR} are the specific heats of ethylene and the reaction mixtures, respectively, cal/g °C; m_R is the mass of the reaction mixtures in the reactor, g; ΔH is the heat of reaction, cal/mol; T , T_e , and T_j are the reaction, ethylene inlet, and jacket temperature, respectively, °C; UA is the product of heat transfer coefficient and the heat transfer area, cal/s °C; r_p is the polymerization rate, mol/s L; M_e is the molar mass of ethylene, g/mol; V is the volume reactor, L; t is time, s.

Equation (2) can be simplified as the inlet and accumulation terms are 1 or 2 orders of magnitude smaller than the outlet and production terms. The assumption that the accumulation term is zero (quasi-steady state assumption) introduces a slight error when the temperature experiences abrupt changes ($dT/dt \gg 0$) and will be minimized when these changes are smooth. An advantage of this approximation is that less data treatment is required as we are riding off a signal that introduces inaccuracies in the calculations (noise). Otherwise data filtering or adjustment would be required.

The energy balance reduces to:

$$UA(T - T_j) = r_p V(-\Delta H)M_e \quad (3)$$

The polymer weight produced can be precisely known at the end of the test, so we can define a calibration constant that includes all the inaccuracies of the method. Using eq. (3):

$$r_p = \frac{UA}{V(-\Delta H)M_e} (T - T_j) \quad (4)$$

Integration of eq. (4) along the reaction time yields the mass of polymer produced, Pol (g):

$$\text{Pol} = \int_{t_0}^{t_f} r_p V M_e dt = \frac{UA}{-\Delta H} \int_{t_0}^{t_f} (T - T_j) dt = K_{cal} \int_{t_0}^{t_f} (T - T_j) dt \quad (5)$$

where the constant parameters U , A , and ΔH were collected in a single calibration constant K_{cal} .

In this way, assuming ΔH constant, as well as the product UA , the calibration constant value at the end of the test can be known, and eq. (4) enables the calculation of the instantaneous polymerization rate obtained along the run. A caution note regarding the value of the product UA is needed here. On certain operation conditions of the reactor, for example

high monomer conversions (i.e., high solids contents) or a considerable variation in the heat transfer area (the surface wetted by the reactor mixture), the assumption of a constant value for this product is no longer valid. For these cases, the best monitoring strategy is to include the energy balance of the heat transfer medium circulating through the jacket to estimate the variation of the product UA (The heat balance method¹⁰).

The instantaneous catalyst activity is given by:

$$A = \frac{r_p M_e}{[C]} \quad (6)$$

where A is the instantaneous catalyst activity, g/mol s; $[C]$ is the catalyst concentration, mol/L.

The method can also be used in predictive form, that is, to determine the polymerization rate as the reaction is conducted if a previous value for K_{cal} is available. In this case, the on-line calculations are as follows:

Initialize the value of Pol as zero at time 0.

1. At time t_i , with the jacket and reactor temperature measurements, T and T_j , calculate r_p using eq. (4) and the calibration constant K_{cal} .
2. Evaluate Pol, by means of eq. (5). The integral can be approximated with a numerical method such as the trapezoidal rule:

$$\text{Pol}_i = \text{Pol}_{i-1} + K_{cal} \frac{(T - T_j)_i + (T - T_j)_{i-1}}{2} (t_i - t_{i-1}) \quad (7)$$

where the subindex $i - 1$ corresponds to the previous time of measuring and i to the actual measurement time.

3. Begin another cycle of measurement (step 1). These calculations are repeated (steps 1–3) until the end of the reaction.

The values, r_p and Pol, can be displayed in graphical form, as profiles of r_p versus t and Pol versus t , during a polymerization run.

r_p Determination by Ethylene Flow Measurement

This technique is broadly used and it is based on the assumption that there is no accumulation of ethylene in the reactor; that is, that as the ethylene is fed into the reactor, it is consumed by the reaction. This stems from the fact that the reactor is operated at constant pressure, avoiding the accumulation in the reactor. The ethylene is fed from a higher pressure reservoir (also constant). The instantaneous polymerization rate is given by a quasi-steady state mass balance for the ethylene where the accumulation term has been neglected, resulting in:

$$r_p = \frac{M_e}{V} F_e \quad (8)$$

As in the case of the calorimetric method, the relationship between catalyst activity and polymerization rate is obtained with eq. (6).

EXPERIMENTAL

Polymerization Reactor

The experimental arrangement used is shown in Figure 1. It consists of a metallic-top, 600 mL glass PARR reactor provided with a glass jacket for heat exchange. The agitation is provided with a magnetically sealed mechanic drive. The reactor operation can operate at vacuum or light pressures (<150 psig) at 150°C or lower temperatures. A constant temperature circulating bath is connected to the reactor jacket. The temperature measurements are taken with type T thermocouples. The system has three temperature sensors: the first at the reactor interior through a thermo-well; the second at the reactor jacket inlet; the third is exposed to the ambient.

Ethylene Flow Measurement

The ethylene flow entering the reactor is measured via an Aalborg gas flow-meter of 0–500 mL/min flow range. The measuring principle of this instrument is based on the heat capacity determination of a small fraction of the total stream flowing through the apparatus. This flow fraction enters to a capillary provided with an electric resistance injecting a constant heat flow to the stream. Two high precision temperature sensors are located at the inlet and outlet of the capillary to determine the heat capacity of the stream. This heat capacity is directly related to the mass flow of gases flowing through the capillary and, by means of standardized constants, the ethylene mass flow can be obtained.

Data Acquisition System

It is a National Instruments Field Point 2000 bank, consisting of an Ethernet module containing a microprocessor with associated peripherals; a thermocouple module; and an analog input signal module (configurable as current or voltage inputs). Optionally, a digital output module to implement feedback control can be added. The signals proceeding from the process (temperatures and ethylene flow) are transmitted to the data acquisition system where they are digitalized and directed to the supervisory control system (PC computer running LabVIEW software) as depicted in Figure 1.

Supervisory Control System

The supervisory control system implemented is based on the National Instruments LabVIEW 9 Software. It runs on a conventional personal computer with MS Windows environment. Conceptually, it constitutes the interface between the operator and the process. The operator actions and the process responses are performed and visualized through the supervisory control system. Its main functions are: (i) communication with the data acquisition system to update in real time all the variables of the process; (ii) display of the main variables of interest by means of windows and graphical objects; (iii) register of the process variables in the computer hard disk.

Isoperibolic Operation

The reactor is operated with a constant jacket temperature (isoperibolic operation). This form of operation conveys the advantage of ease of implementation, as feedback control of the reactor temperature is not required, only control of the jacket temperature. This jacket temperature control can be simply accomplished using a bath of controlled temperature integrated

to the reactor jacket; the relatively large reservoir of the bath provides enough capacitance to absorb small disturbances that could create a deviation from the set point temperature. Also, in this operation modality, the reactor temperature evolution is a direct evidence of the thermal effect of the reaction, as described in the previous section.

Notice that, to the extent of our knowledge, the only other application of calorimetry⁹ that has been reported for ethylene polymerization uses the isothermal instead of the isoperibolic modes, requiring a more elaborated control scheme than the simple one used here (isoperibolic) which only requires a constant temperature circulating bath that is a standard equipment in most laboratories.

Ethylene Polymerization via Metallocenes

Homogeneous and heterogeneous ethylene polymerizations were performed in the 600 mL semi-batch reactor, equipped as described above in Figure 1.

Prior to each polymerization the glass vessel of the reactor was cured at 90°C using 200 mL of a 1M solution of trimethylaluminum (TMA) in toluene. Once the TMA solution was transferred from the reactor to another cylinder, the reactor was heated at 90°C under vacuum, and then purged with Ar. Then 200 mL of isooctane was charged to the reactor and the temperature was set up to 70°C. The polymerization temperature was maintained at 70°C ± 2°C. Other reaction conditions used were: 42 psig of ethylene pressure and a stirring rate of 500 rpm. At the end of the polymerization time (1 or 2 h), ethylene feed in the reactor was blocked, the reactor was rapidly vented, and then 20 mL of 2 wt % of hydrochloric acid in ethanol was added to the polymer contents inside the reactor. Then the polymer was washed with ethanol, filtered, and dried under vacuum at 50°C.

Two catalytic systems were used to test and compare the kinetic monitoring methods.

The catalytic system 1 (S₁) consisted of bis-pentamethylcyclopentadienyl zirconocene aluminohydride (Cp*ZrH₃AlH₂). S₁ was activated with MAO in homogeneous phase for ethylene polymerization, using or not molecular hydrogen (H₂) as chain transfer agent. Catalyst S₁ synthesized as reported in the literature¹¹ was previously activated with MAO, before adding to the polymerization reactor, using constant ratios of Al/Zr = 2000. Zirconium molar concentration in the order of 10⁻⁶ mol/L was used for all the polymerizations performed in homogeneous phase.

Catalytic system 2 (S₂) consisted of bis-pentamethylcyclopentadienyl zirconocene aluminohydride supported on silica previously treated with MAO, as reported by the indirect supported method onto porous silica,¹² (Cp*ZrH₃AlH₂/SiO₂/MAO). Additional amount of MAO was used for activation of the supported catalysts in ratios of Al/Zr = 2000, having zirconium concentrations around 3 × 10⁻⁶ M in the polymerization reactions. The effect of molecular hydrogen as chain transfer agent was also evaluated in the heterogeneous polymerization reactions using two concentrations of H₂, mixed before in the ethylene stream.

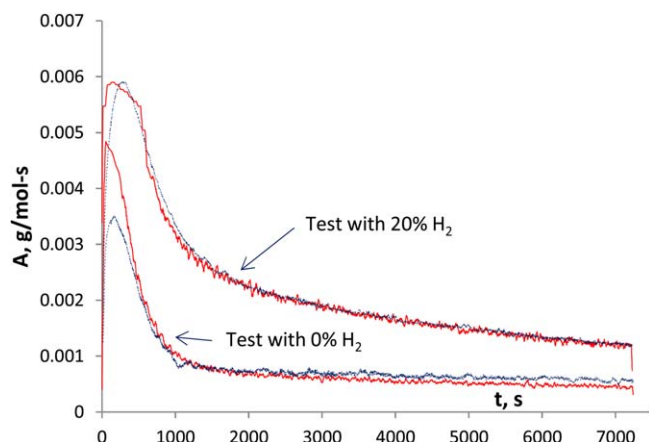


Figure 2. Comparison of calorimetry (—) and direct method (ethylene flow measurement) (---) in monitoring the catalytic activity, A , of system S_1 . Results of both monitoring methods applied to two different polymerization reactions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

RESULTS AND DISCUSSION

Ethylene polymerizations using homogeneous (S_1) and silica (SiO_2) supported heterogeneous (S_2) catalytic systems, were conducted as described in the experimental part, to test the suitability of the calorimetric monitoring technique in ethylene coordination polymerizations run under a variety of kinetic conditions. Both homogeneous and heterogeneous systems were also studied in the presence of hydrogen as chain transfer agent to test if the calorimetric measurements could detect the rate-acceleration hydrogen effect previously reported for metallocene-based catalysts.¹³ The kinetic behavior at different polymerization conditions could then be compared by calorimetric measures transformed to activity (A), as discussed above.

Results of the kinetic monitoring realized in two polymerization tests with the catalytic system S_1 are shown in Figure 2. For the experiments using hydrogen, a mixture of hydrogen with ethylene with partial pressures corresponding to H_2/C_2 of 50 psig/1000 psig was previously prepared in the ethylene cylinder. The kinetic behavior of the system in solution or homogeneous phase showed a high initial activation rate of the catalyst, exhibiting the highest rate of monomer consumption during the first hour of reaction, and then decaying in the second hour, suggesting the deactivation step of the catalyst. This high initial activation rate is characteristic of highly active single-site catalytic systems, commonly observed for metallocene-based catalysts in homogeneous polymerizations.¹⁴ The polymerizations with H_2 showed higher ethylene consumption, as expected due to the hydrogen effect on the activity of the system.¹³ It is observed that both methods, the calorimetric and the direct measuring of ethylene flow, give almost identical results, even in those polymerizations containing the chain transfer agent. A slight discrepancy between the two measures can be observed at the start of the reaction free of H_2 , which can be attributed to the way of catalyst addition to the reactor, which conducts to a variable saturation time with ethylene in the reaction medium. This could be reflected also in the ethylene consumption.

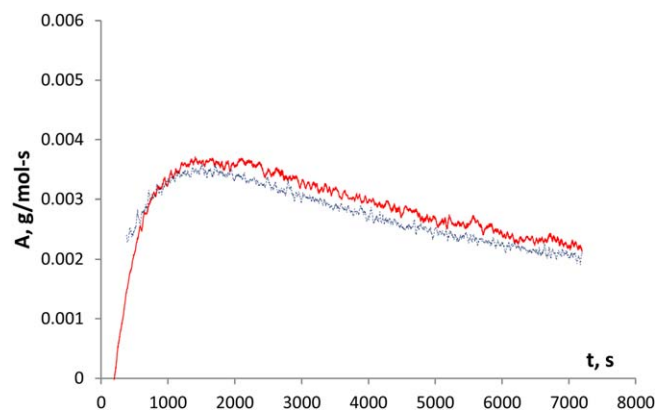


Figure 3. Catalytic activity, A , in the polymerization with the catalytic system S_2 using 20% of H_2 in the ethylene inlet stream. Calorimetric method (—) and direct method (---). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

It is important to mention that due to their bridged hydride bonds, zirconocene aluminohydrides are more sensitive complexes compared to the classical metallocenes, and this instability can provide higher reactivity and therefore higher activity in this kind of heterobimetallic complexes than in classical metallocenes. Given the higher activity of these catalytic systems which leads to fast dynamics, they represent a good testing system for the calorimetric method, demonstrating that this is capable of tracking such fast reactions.

Figures 3 and 4 exhibit the results of two kind of heterogeneous polymerizations performed with the supported catalytic system (S_2) using 20% of H_2 in the ethylene stream feed (Figure 3) or without H_2 in the ethylene feed stream (Figure 4).

First, from the point of view of the catalyst activity, the two measuring techniques show (Figures 3 and 4) that ethylene polymerizations using the supported catalytic systems exhibited lower initial activation rates compared to the corresponding homogeneous polymerizations (Figure 2). It is usually observed that supported catalysts exhibit lower activities than

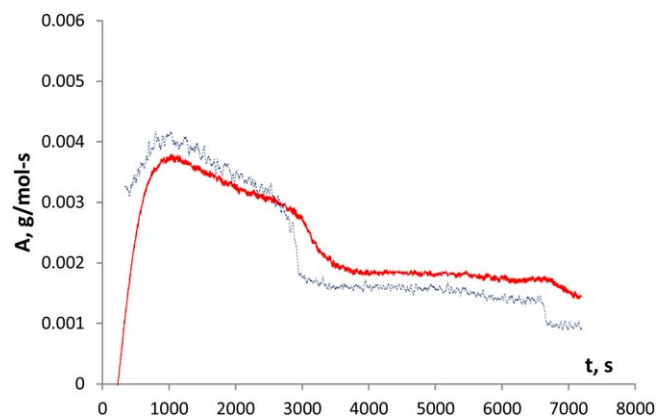


Figure 4. Catalytic activity, A , in the ethylene polymerization with catalytic system S_2 without H_2 in the ethylene inlet stream. Calorimetric method (—) and direct method (---). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

homogeneous systems and this is due to the higher steric hindrance provided by the support to the metallocene and, conversely, to the fact that strong electrostatic interactions of the catalyst with the support could help to stabilize the catalytic system during the polymerization reactions.^{14,15}

As shown in Figure 3, the S₂ catalytic system exhibits a longer period of stability reflected in the fact that its activity decays less markedly than in the corresponding homogeneous polymerizations (Figure 2). Similarly to the behavior of the homogeneous polymerizations with the S₁ catalyst, the use of hydrogen in the polymerizations led to higher activities, but in the heterogeneous case several peaks in the kinetic curve are observed (Figure 4), suggesting that more than one active species could be present in the polymerization reaction. For supported catalysts the desorption or lixiviation of the metallocene has been widely reported as a drawback,^{16–18} promoting simultaneous polymerization in the supported catalyst (heterogeneous) and in solution (homogeneous). In the kinetic behavior depicted in Figure 4, the first peak (1000 s) could be attributed to the heterogenized catalyst, which it is then desorbed to the continuous phase, showing another peak at around 3000 s.

With respect to the on-line measurement of the polymerization rate, it can be seen that both methods yield similar kinetic curves. In Figure 4, the calorimetric method renders very well the kinetic response, although with a slight delay. This delay of the dynamic behavior obeys to the elimination of the accumulation term in the energy balance [eq. (2)]. If more precise calorimetric calculations were needed, the accumulation term should be considered in the balance and data filtering for the numerical estimation of the derivative would be required.

It is worth noticing that previous works reporting the application of calorimetric techniques to the reaction rate measurement in coordination catalysis polyolefin synthesis have mostly dealt with polypropylene synthesis, which in general results in slower reactions than those involved in ethylene polymerization. Also, the only previous work in which calorimetry was used to study ethylene polymerization kinetics was done using a catalytic system of lower activity than the one used here. Here, a simple calorimetric technique captures the essential kinetic features of a more challenging ethylene polymerization with a high activity catalyst.

CONCLUSIONS

It can be stated that calorimetry and direct measuring of ethylene flow are methods conveying essentially the same kind of information about the instantaneous activity of Ziegler–Natta catalysts. The results presented in this study support the intuitive idea that in the isoperibolic operation, the reaction temperature excursion is an indicator of the activity of the

catalyst. Also, this work presents enough information to guide the implementation of the techniques in a reactor laboratory, to follow online the instantaneous activity of Ziegler–Natta catalysts.

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