

Polymerization of Olefins Through Heterogeneous Catalysis. XVI. Design and Control of a Laboratory Stirred Bed Copolymerization Reactor

G. C. HAN-ADEBEKUN, J. A. DEBLING, W. H. RAY

Department of Chemical Engineering, University of Wisconsin, 1415 Johnson Drive, Madison, Wisconsin 53706

Received 7 August 1996; accepted 29 August 1996

ABSTRACT: A novel lab-scale stirred bed gas phase reactor system has been designed and constructed for investigating the kinetic behaviour of olefin copolymerization reactions using heterogeneous catalysts. The system, equipped for basic temperature and pressure control, also includes an on-line composition control system which maintains close control of reactor composition for gaseous and liquid monomers as well as for hydrogen. With this apparatus, it is now possible to investigate the fundamental kinetic features of the catalyst system with high precision. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 373–382, 1997

Key words: olefin polymerization; gas phase; reactor design; composition control

INTRODUCTION

Since the discovery of transition metal catalysts for olefin polymerization, intensive research efforts have been directed toward obtaining a comprehensive understanding of their structure and kinetic behaviour. In spite of their successful applications in industry, a complete knowledge of the kinetic mechanism of this group of catalysts is still lacking.

The dearth of fundamental kinetic models is related to the difficulty in obtaining high-precision kinetic data. A complete kinetic study requires extensive experiments due to the vast number of combinations of important operating parameters (temperature, pressure, hydrogen level, monomer composition) which influence these reactions. High precision in the experiments demands close control of these parameters for the duration of reaction. This poses a challenging problem.

In this work, a lab-scale stirred bed gas phase reactor system which addresses the basic control problem is designed and constructed. This apparatus is capable of producing various polyolefins using heterogeneous transition metal catalysts. Emphasis is placed on the reliability of the system in obtaining instantaneous kinetic data, its versatility in producing different types of polyolefins, as well as its flexibility in changing the reactor operating parameters on-line.

This article describes the reactor system, the temperature control system, the pressure control system, the gas composition controller, and results from kinetic studies conducted with this apparatus; detailed results of complete mechanistic studies of some catalyzed polymerization systems will be reported in subsequent publications.

REACTOR SYSTEM

The reactor (Fig. 1) is a 1-L stainless steel vessel manufactured by Parr Instrument Co. The gas phase reactor system was originally designed by Choi as a vertical reactor for propylene polymerization studies using unsupported catalysts.¹ It

Correspondence to: W. H. Ray.

Contract grant sponsors: the National Science Foundation and the University of Wisconsin Polymerization Reaction Engineering Laboratory (UWPREL).

© 1997 John Wiley & Sons, Inc. CCC 0021-8995/97/020373-10

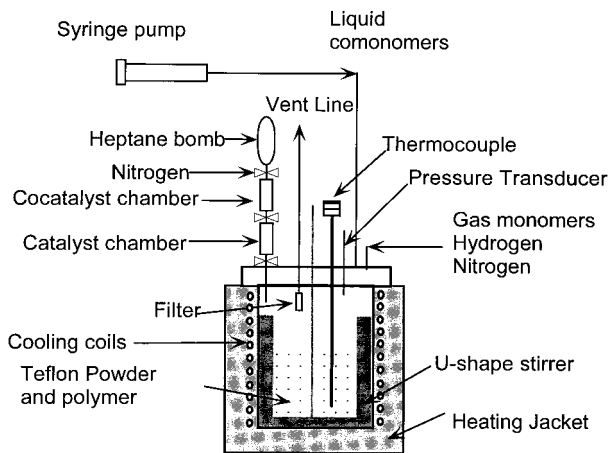


Figure 1 The stirred bed reactor.

was modified by Chen for ethylene/propylene copolymerization studies using feedback control of temperature, pressure, and composition using on-line gas chromatography (GC).² Chen also found that horizontal operation provided better particle agitation and improved reactor heat transfer. More recently, the reactor system was redesigned and newly constructed to allow for feeding liquid monomers, rapid response monomer composition control using on-line Fourier transform infrared spectrometry (FTIR),³ and hydrogen partial pressure control using on-line thermal conductivity. The reactor operates in a horizontal position for better particle temperature control.

A schematic diagram of the feed system is shown in Figure 2. As indicated in the figure, gaseous feeds are fed through the three-stage purification trains prior to injection into the reactor. The current scheme for gas purification is shown in Table I. Gas feed flow rates are measured and controlled with Teledyne Hastings mass flow controllers. These controllers may be manually operated as fully open, or the set point may be supplied from a digital/analog convertor installed in a microcomputer.

To purify the liquid monomers, vacuum distillation is carried out under a nitrogen atmosphere, and the distillate is collected over dry molecular sieves.⁴ Following the distillation, the purified monomer is transferred to a 500 cc Whitey sample cylinder (under nitrogen) which is then connected to the reactor system. This cylinder serves as the reservoir for the programmable syringe pump (Harvard Instrument, model 55-1144) that is used to inject the purified liquid monomer into the reactor. The pumping rate through the syringe pump may be controlled by a microcomputer through a RS-232 serial connec-

tion. Note that 1-butene, although purified as a gas, is subsequently condensed with dry ice and introduced into the reactor as a liquid.

The catalyst injection system also shown in Figure 1 allows the control of the precontact between the catalyst and the cocatalyst for the Ziegler-Natta catalyst. The three-chamber design makes it possible to control both the aging time as well as the cocatalyst to catalyst ratio. For the production of isotactic polypropylene, cocatalyst and external donor may also be precontacted for a specified time period. The diluent (e.g., heptane or hexane) wash is required in order to further rinse out any possible catalyst residue. For a supported metallocene catalyst, only the nitrogen pressure is needed to inject the catalyst, which is in the form of a dry powder.

In a typical polymerization reaction, the reactor is filled with approximately 160 g of Teflon resin (Grade 9B, E. I. Du Pont, average particle diameter $\approx 650 \mu\text{m}$) as seed bed material. The amount of bed material is selected to insure that good heat conduction through the reactor wall is obtained as well as to guarantee that the dense phase temperature can be measured by a thermocouple. The reactor is then heated to 70°C and kept under vacuum atmosphere for 2 h, followed by a 1 h continuous nitrogen purge. After injecting the catalyst/cocatalyst, the polymerization reaction begins by introducing the reactants into the reactor. The control program in the microcomputer is also started simultaneously. The instan-

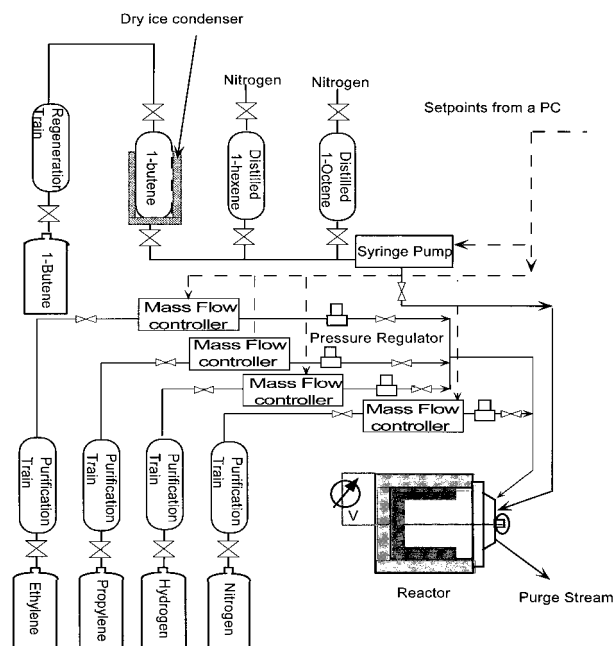


Figure 2 The stirred bed reactor feed system.

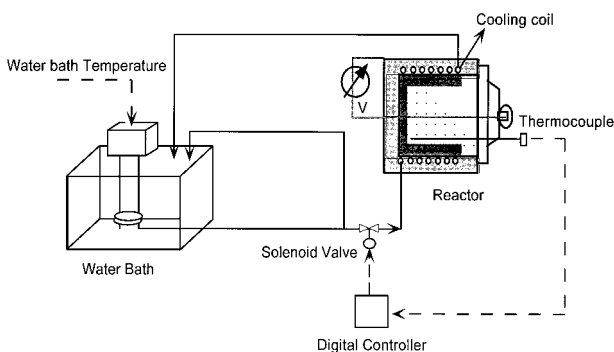
Table I Gas Purification System

Gas Type	Purification Column		
	1st Stage	2nd Stage	3rd Stage
Ethylene	BASF R3-11	Molecular sieves 3A	Activated alumina
Propylene	BASF R3-11	Molecular sieves 3A	Activated alumina
1-Butene	N/A	Molecular sieves 3A	Activated alumina
Nitrogen	RIDOX	Molecular sieves 13X	Activated alumina
Hydrogen	RIDOX	Molecular sieves 4A	Activated alumina

taneous data such as temperature, pressure, as well as inlet and outlet flow rates are all recorded using this control program. After a predefined polymerization time, the reaction is then terminated by shutting off the feed streams, followed by nitrogen purge.

REACTOR TEMPERATURE CONTROL

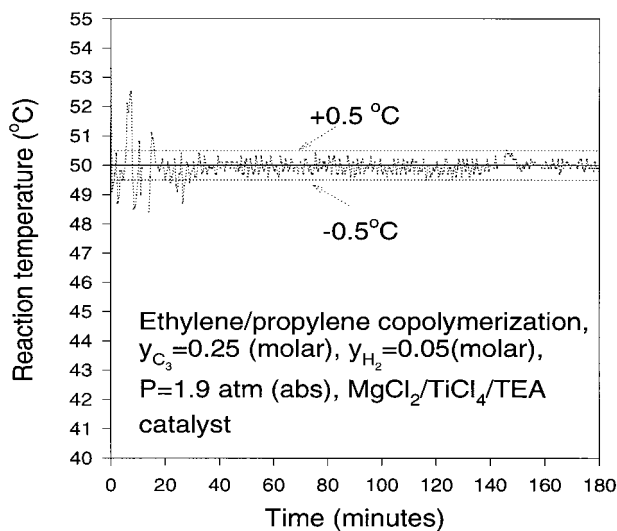
The reactor temperature is controlled by a combination of heating and cooling. An electrical heating jacket custom-made by GLAS-COL is used to provide a constant heating source. Cooling is achieved using both ambient air and external cooling water, which is pumped from an isothermal bath through copper coils soldered to the outside of the reactor. Although the desired reactor temperature is maintained by the balance between the voltage supply to the heating jacket and the temperature setpoint for the water bath, the manipulated variable in the reactor temperature control loop is the on/off switch of the external cooling water. A simple schematic diagram of this arrangement is shown in Figure 3. Note that the energy balance also depends on the polymerization rate as well as the temperature difference between the reactor temperature and the ambient temperature. With a careful balance, the desired

**Figure 3** The temperature control system.

reaction temperature can be maintained to within $\pm 0.5^\circ\text{C}$ for most of the duration of the reaction. However, as is shown in Figure 4, a slightly larger temperature oscillation may exist for a few minutes during the initial stages of the reaction.

REACTOR PRESSURE CONTROL

When the reaction is operated under no-purge mode (usually in the case of homopolymerization), reactor pressure is maintained by opening the monomer flow controller fully in order for the gas to flow as needed to maintain a constant pressure. When the gas composition in the reactor needs to be monitored and controlled, a continuous gas purge is necessary. Under this condition, a back pressure regulator (Tescom Corp.) is used. As indicated in Figure 5, part of the purge stream is fed to the gas composition analyzer. A typical reactor pressure readout during a copolymerization experiment is presented in Figure 6.

**Figure 4** Example of reactor temperature control.

ON-LINE GAS COMPOSITION CONTROL

Heterogeneous transition metal catalysts can be used to produce a wide variety of polyolefins. These range from homopolymers (polypropylene, polyethylene) to copolymers (high-density polyethylene, HDPE; linear low-density polyethylene, LLDPE; polypropylene copolymers; ethylene propylene rubber, EPR; etc.), and from single-layer polymers to multilayer polymers (impact polypropylene). Consequently, for purposes of kinetic studies, the control of the composition of the gas mixture becomes quite important.

The gas compositions commonly used in olefin polymerization reactions can be quite broad depending on the product. Some typical components and their approximate compositional ranges are listed in Table II.

The fundamental basis for selecting the appropriate measurement technology is the difference in physical properties between the constituents in the gas mixture. Some other important considerations come from the fact that, since it is used as

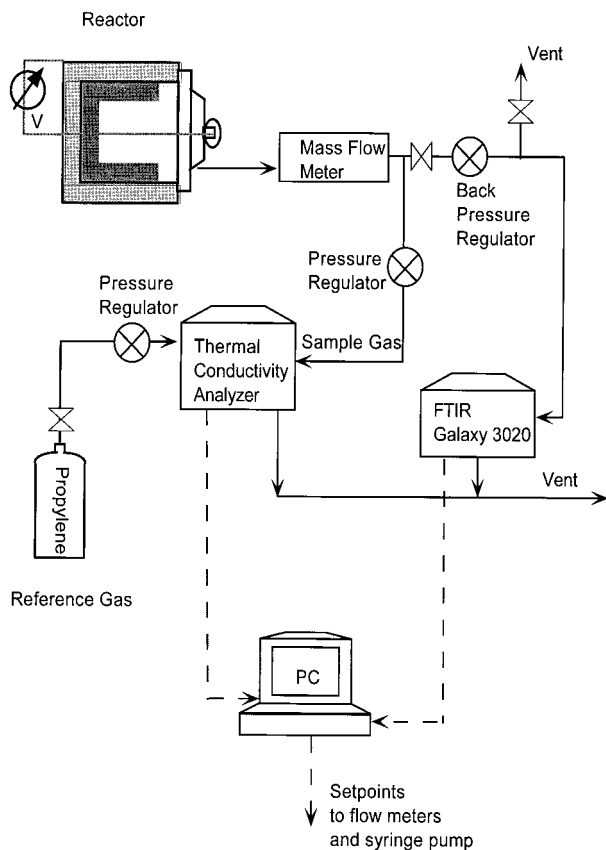


Figure 5 Schematic diagram of the stirred bed reactor system: exit system and on-line gas composition measurement.

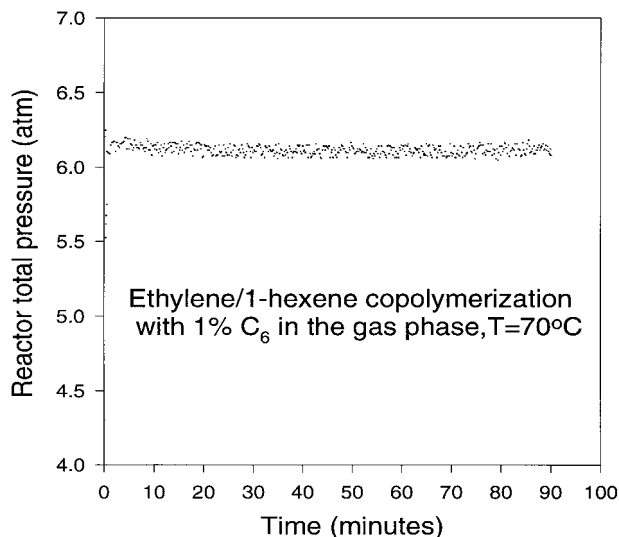


Figure 6 Example of reactor pressure control.

an on-line sensor, the selected composition measurement method must be amenable to continuous sampling, exhibit rapid response, and allow for easy integration into an automatic data acquisition system using a microcomputer.

Comonomer Composition Measurement

A Fourier transform infrared spectrometer (Galaxy 3020, Mattson Instrument) is used to measure the composition ratio of comonomer to major monomer. Although gas chromatography (GC) is usually used for gas composition detection in continuous commercial operation,^{2,5} the elution time for hydrocarbons such as 1-hexene and 1-octene is on the order of many minutes.⁶ This limits the quality of feedback composition control. For the purpose of composition control in a lab-scale semi-batch reactor, FTIR is extraordinarily advantageous because of its speed; it can provide a composition measurement within 15 s. In order to obtain good composition control, particularly for experiments having run times ranging from a few minutes to several hours, this short response time has proven to be very important.

To measure the gas composition, a beam forming gas cell (TGC-B5, Harrick Scientific Corp.) with KBr lenses is used. This gas cell, which is temperature controllable, has a path length of 5 cm and a volume of 4 cc to maintain a short gas residence time. The detection of hydrocarbons using FTIR is based on the fact that each constituent of the mixture has specific absorption bands. Using Beer's law,⁷ concentrations of the constituents in the sample may be determined

Table II Summary of Major Constituents in Olefin Polymerization Experiments

Species	Roles in Reaction	Composition Range (mol %)
Ethylene	Monomer in HDPE/LLDPE	85–100
	Monomer in EPR	40–60
Propylene	Monomer in EPR	40–60
	Comonomer in HDPE/LLDPE	0–15
1-Butene	Comonomer in HDPE/LLDPE	0–10
1-Hexene	Comonomer in HDPE/LLDPE	0–10
Other higher α -olefins	Comonomer in LLDPE	0–10
Hydrogen	Chain transfer agent	0–50
Nitrogen	Inert	0–50

from the intensities of the absorption bands. Figure 7 shows clearly the change of peak areas for an ethylene–propylene mixture as the compositions of the components vary. Although FTIR does not have selective absorption for diatomic molecules such as H_2 and N_2 , the total concentration of FTIR inert species can be back-calculated from the calibration equation. Note that in this study, the gas mixtures of known compositions used to calibrate the FTIR spectrometer were prepared through both static (premixed reference gas) and

dynamic (on-line mixing of metered gas samples) methods.⁸

Hydrogen Concentration Measurement

Gas-phase hydrogen concentration is measured with a thermal conductivity analyzer (Model 50-150, GOW-MAC Instrument Co). This is justified on the grounds that hydrogen has an extremely high thermal conductivity (Table III) relative to the other species of interest in this study.

In the thermal conductivity analyzer (TCA), the sample gas is passed through a cell containing filaments within a metallic block. The filaments are heated electrically and arranged in a balanced Wheatstone bridge. The loss of this heat depends on cell geometry (fixed) as well as gas properties; in particular, the thermal conductivity. Therefore, a change in composition of the sample generates an imbalance in

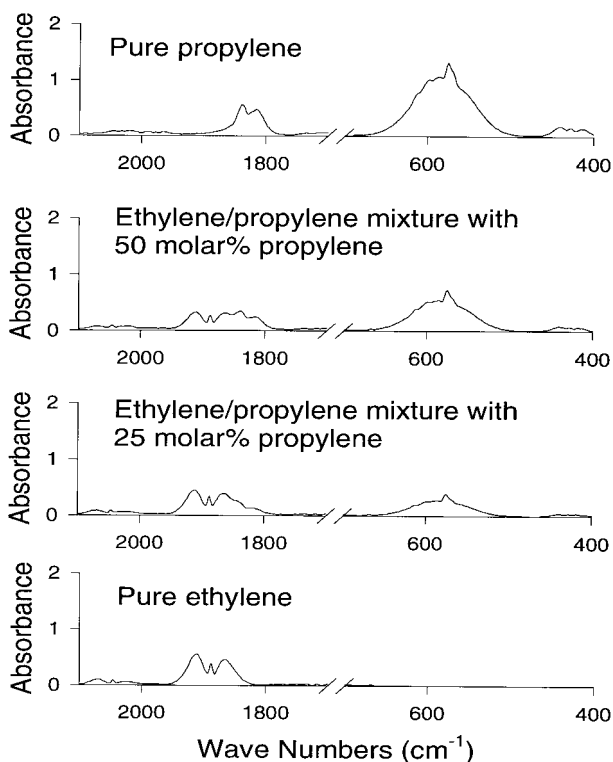


Figure 7 Infrared spectrum for ethylene–propylene mixture.

Table III Thermal Conductivities of Possible Constituents in Olefin Polymerization

Species	Thermal Conductivity (Relative to N_2)	
	27°C	127°C
Ethylene	0.79	1.07
Propylene	0.68	0.90
1-Butene	0.60	0.79
1-Hexene	N/A	0.72
1-Octene	N/A	0.64
Hydrogen	7.2	7.1
Nitrogen	1.0	1.0

From D. R. Lide, Ed., *CRC Handbook of Chemistry and Physics*, CRC Press, Boca Raton, FL, 1991. Used with permission.

the Wheatstone bridge. The signal resulting from this imbalance (proportional to the change in gas composition) can thus be measured and used to infer the gas composition. Figure 5 shows the connection of the TCA to the reactor system. Propylene is used as a reference gas.

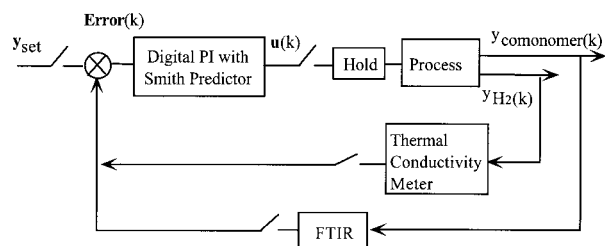
During calibration, the sample gas composition is calculated from the gas flow meter installed on each gas stream. For a binary system such as ethylene and hydrogen, the voltage output from the TCA depends only on the hydrogen composition. However, for a tertiary system such as ethylene, propylene, and hydrogen, the voltage output depends largely on hydrogen composition, but must be compensated for the relative monomer composition. This compensation term can be especially significant when hydrogen occupies less than 10 mol % of the total sample. Therefore, in our calibration, an equation derived from a simple mixing rule based on mole fractions is used:

$$V_{\text{output}} = \frac{m_1 + m_2 \text{ Ratio}}{1 + \text{Ratio}} + \frac{m_3 + m_4 \text{ Ratio}}{1 + \text{Ratio}} y_{H_2} \quad (1)$$

$$\text{where Ratio} = \frac{y_{C_3}}{y_{C_2}}.$$

Feedback Composition Controller Design

A simple block diagram of the control system is presented in Figure 8. A digital PI controller with Smith predictor has been applied as a re-



where:

$$y_{\text{set}} = [y_{\text{set}}(\text{comonomer}), y_{\text{set}}(\text{hydrogen})]^T$$

$$\text{Error}(k) = [\text{Error}_{\text{comonomer}}(k), \text{Error}_{\text{hydrogen}}(k)]^T$$

$$u(k) = [u_{\text{comonomer}}(k), u_{\text{hydrogen}}(k)]^T$$

Figure 8 Block diagram of the composition control system.

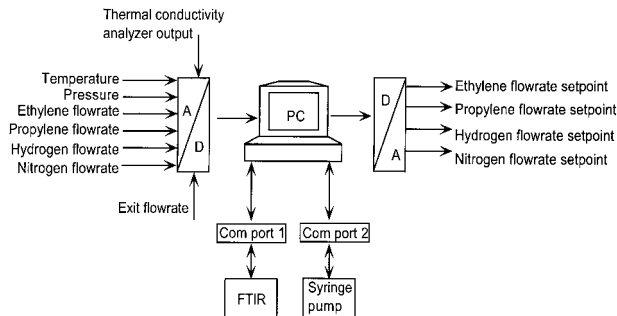


Figure 9 Microcomputer-based data communication system.

sult of the dynamic characteristic of this system. Modeling studies coupled with system identification reveal that the copolymerization reaction system in this study can be modeled as a first-order system with time delay. The time-domain realization of the controller is given by equations of the form:⁹

$$u(k) = \left(\frac{\tau_r}{\tau_r + \Delta t} \right) u(k-1) + \left(\frac{\Delta t}{\tau_r + \Delta t} \right) u(k-D) + \left[\frac{\tau + \Delta t}{K(\tau_r + \Delta t)} \right] \varepsilon(k) - \left[\frac{\tau}{K(\tau_r + \Delta t)} \right] \varepsilon(k-1) \quad (2)$$

where $u(k)$ represents control variables such as reactor feedrates and ε is deviations from desired composition. Here τ and K are the time constant and system gain, respectively, of the first-order system model, τ_r is the designed rise time for the closed-loop response, Δt is the sampling interval, and D is the integer delay. Using this control strategy, the appropriate control parameters are determined through system identification and further fine tuned on-line. The data communication system is implemented as shown in Figure 9.

KINETIC STUDY EXAMPLES

In this section, three examples are given to illustrate the various kinetic studies that can be con-

ducted using this reactor system. These examples were selected only to demonstrate the potential possibilities presented by the system. Other comprehensive studies can also be conducted; for example, two-stage impact polypropylene production.

Ethylene Homopolymerization with Hydrogen as the Chain Transfer Agent

For conventional Ziegler–Natta catalysts, hydrogen is often used as the chain-regulating agent. It is generally accepted that the average molecular weight obeys the following relationship when hydrogen is used:^{10,11}

$$1/\overline{M}_n = a + b[H_2]^n \quad (3)$$

where $n = 0.5$. Even so, in spite of various research efforts,^{12–15} no general conclusion appears to have been made regarding the kinetic effect of hydrogen. In most of the lab-scale investigations studying the hydrogen effect, the reactor was usu-

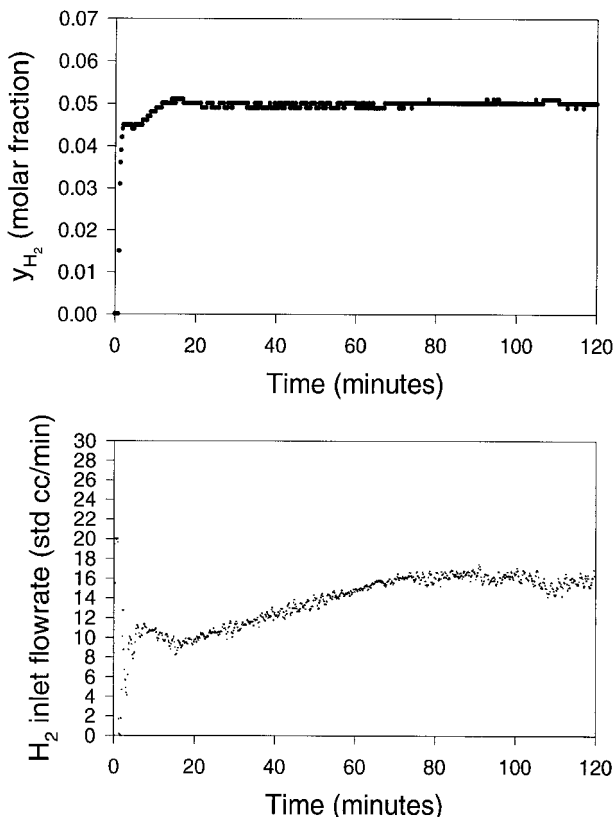


Figure 10 Hydrogen gas phase composition control during an ethylene homopolymerization reaction using supported $MgCl_2/TiCl_4/TEA$ catalyst. Top: y_{H_2} ; bottom: manipulated variable ($T = 50^\circ C$, $Al/Ti = 85.5$).

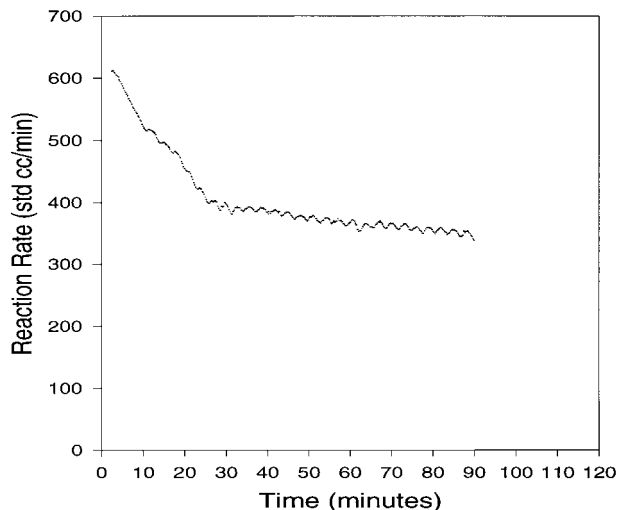


Figure 11 Polymerization reaction rate of ethylene as a function of reaction time ($T = 50^\circ C$, $Al/Ti = 85.5$).

ally operated in a batch mode with varying hydrogen partial pressure,¹⁶ yielding inconclusive results. However, in our reactor system, the on-line composition control of hydrogen has been implemented, and this makes it possible to systematically investigate this hydrogen effect. Shown in Figure 10 is the hydrogen mole fraction in the reactor during an ethylene homopolymerization reaction using high-activity $MgCl_2$ supported $TiCl_4$ catalyst with $Al(Et)_3$ as the cocatalyst. The desired hydrogen composition y_{H_2} is 5% (molar). Also depicted is the manipulated variable (inlet hydrogen flowrate). Since the total gas inlet flowrate is fixed, the exit flowrate changes if the reaction rate varies with time. For this catalyst system, a typical reaction rate curve for ethylene polymerization at $50^\circ C$ (Fig. 11) can be described as an immediate attainment of maximum activity, followed by a decay which eventually tails off to a stable value. Therefore, the hydrogen inlet flowrate in Figure 10 exhibits an increase and gradual leveling-off in order to compensate for the change in the exit flowrate.

Another advantage of employing the gas-phase reactor for kinetic studies is the ease of changing operating conditions during a single run.¹⁴ Such studies are important in analyzing the reversibility of effects arising from changing operating parameters.¹⁷ For this reactor system, not only can both the reaction temperature and pressure be varied, but with the on-line gas composition control, it is also possible to change the gas-phase composition during the polymerization. Figure 12 shows one such example where the influence of the hydrogen composition on the kinetic behavior

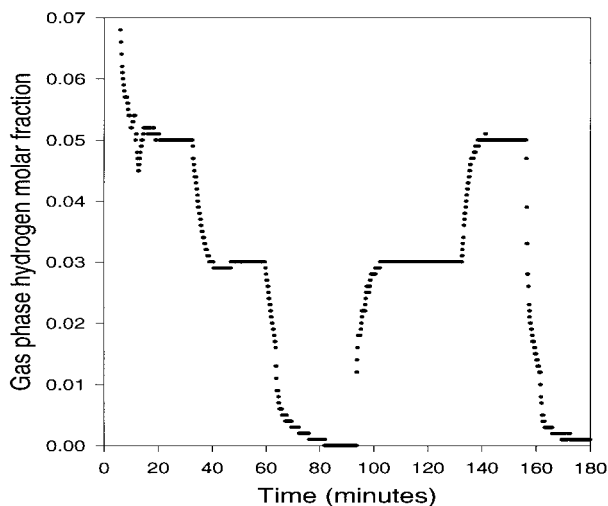


Figure 12 Change of gas-phase hydrogen composition during ethylene polymerization reaction in order to study the reversibility of its kinetic effect ($T = 70^{\circ}\text{C}$, $\text{TiCl}_4/\text{MgCl}_2/\text{Al}(\text{Et})_3$, $\text{Al}/\text{Ti} = 85.5$).

of ethylene homopolymerization is investigated. It is clear that once the set point is changed, the hydrogen composition settles down to the desired value within a reasonable time period.

Linear Low-Density Polyethylene with 1-Hexene as the Comonomer

In the production of LLDPE, comonomers such as propylene, 1-butene, 1-hexene and 1-octene are used. The amount of comonomer incorporated into

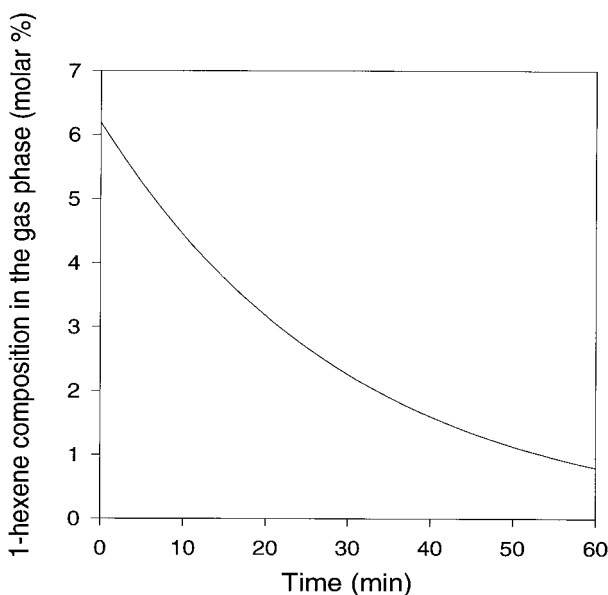


Figure 13 Simulation of 1-hexene gas-phase composition change if comonomer is only charged initially.

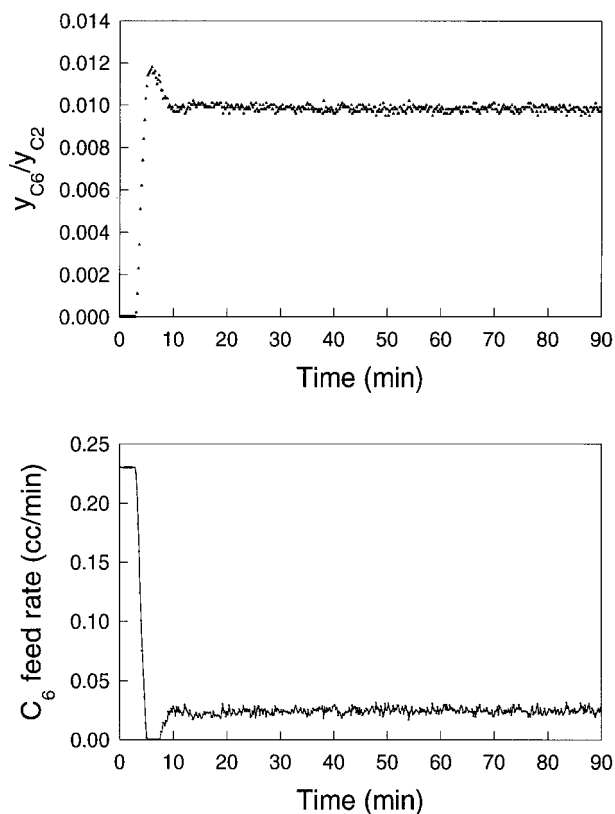


Figure 14 1-Hexene gas-phase composition control during an ethylene–1-hexene copolymerization reaction. Top: y_{C_6}/y_{C_2} ; bottom: manipulated variable ($T = 70^{\circ}\text{C}$).

the polymer is directly linked to polymer properties such as density, melting temperature, and crystallinity. Furthermore, when comonomer is present in the system, it has been observed that the reaction rate of ethylene increases dramatically.¹⁸ This so-called comonomer effect has generated significant attention. However, a complete understanding of this rate enhancement effect is still lacking. In studying this effect, the usual practice is to operate the reactor in a no-purge mode, and then to inject the comonomer either at the beginning of the run or periodically during the run.¹⁸ Both methods invariably lead to significant drift of the comonomer composition during the course of the reaction.

In order to further illustrate the possibility of composition drift, a simple calculation is carried out assuming a 2-L reactor with initial charge of 3 cc 1-hexene. The catalyst load is about 125 mg, ethylene partial pressure is 75 psi, and temperature is 70°C . It is assumed that both ethylene and 1-hexene follow the ideal gas law, and no sorption

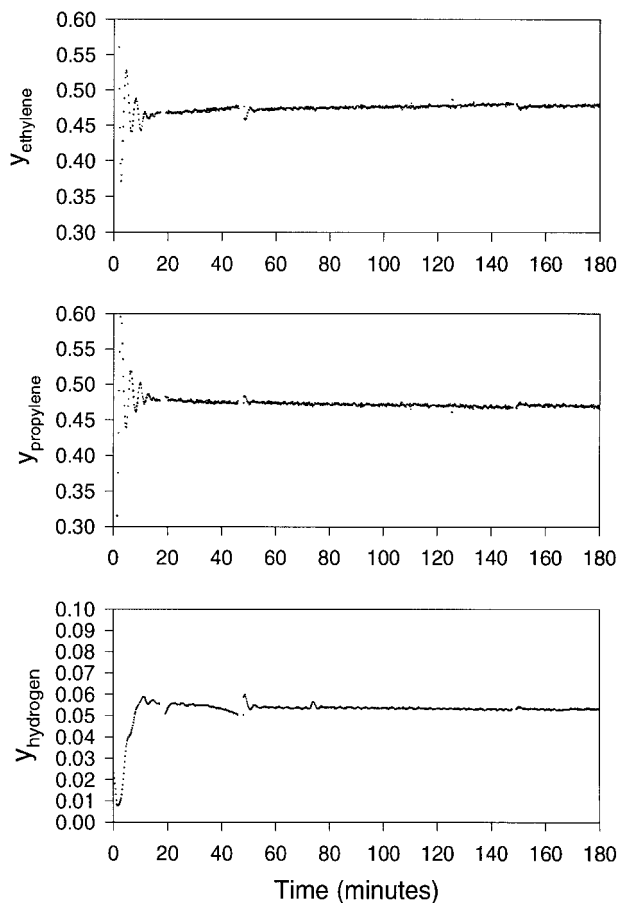


Figure 15 Monomer and hydrogen gas-phase composition control during an ethylene–propylene copolymerization reaction with hydrogen as the chain transfer agent. Catalyst system: $\text{TiCl}_4/\text{MgCl}_2/\text{Al}(\text{Et})_3$, $T = 50^\circ\text{C}$. Top: y_{C_2} ; middle: y_{C_3} ; bottom: y_{H_2} .

of 1-hexene into seed bed material is included. For the 1-hexene consumption rate, a typical value of 100 g C_6 per gram of catalyst per hour per 1 atm C_6 is used. Figure 13 shows the resulting 1-hexene gas phase composition drift during the reaction. This would produce a very broad copolymer composition distribution and greatly distort the reaction rate profile.

By contrast, with our reactor using the on-line composition control scheme, Figure 14 shows much-improved gas-phase 1-hexene composition control during the reaction. Also presented in the same figure is the manipulated variable (1-hexene feed rate through the syringe pump). This figure indicates quite clearly that a constant comonomer concentration is maintained by the controller essentially over the entire duration of the reaction.

Ethylene–Propylene Copolymerization with Hydrogen as the Chain Transfer Agent

In ethylene–propylene copolymerization with hydrogen as the chain-transfer agent, both the comonomer composition and the hydrogen composition need to be maintained constant. An illustrative result obtained from such a study is presented in Figure 15. In this case, during a 3-h copolymerization reaction using high-activity MgCl_2 supported TiCl_4 catalyst, the gas compositions of both monomers and hydrogen are the controlled variables. If a mass balance is performed across the reactor inlet and outlet, the instantaneous reaction rate of each monomer can be obtained (Fig. 16). It should be emphasized that only with this quality of on-line composition control is it possible to obtain reaction rate information for both monomers. An estimate of the monomer reaction rate in turn enables the calculation of the comonomer incorporation rate as a function of time (Fig. 17). The instantaneous comonomer composition of the polymer is fundamental

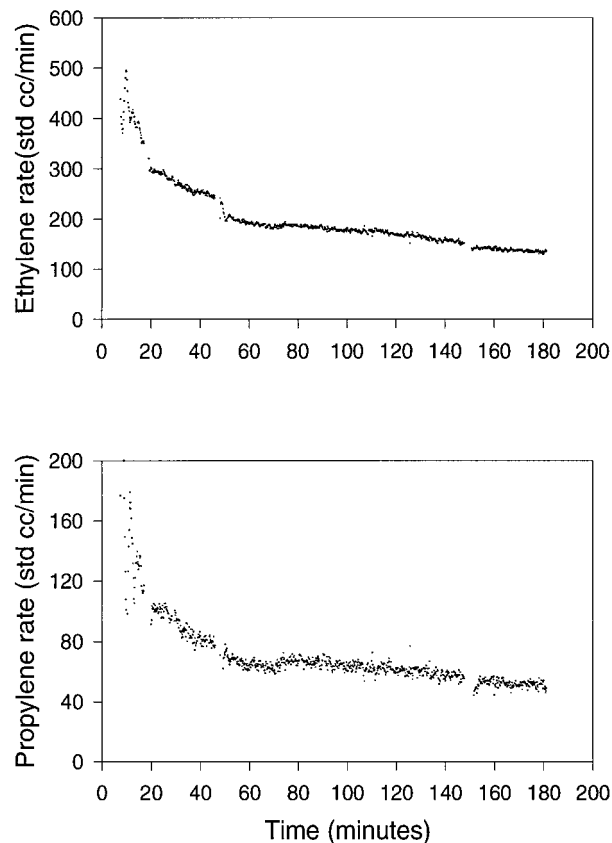


Figure 16 Consumption rates of ethylene and propylene as a function of time. Catalyst system: $\text{TiCl}_4/\text{MgCl}_2/\text{Al}(\text{Et})_3$, $T = 50^\circ\text{C}$. Top: ethylene rate; bottom: propylene rate.

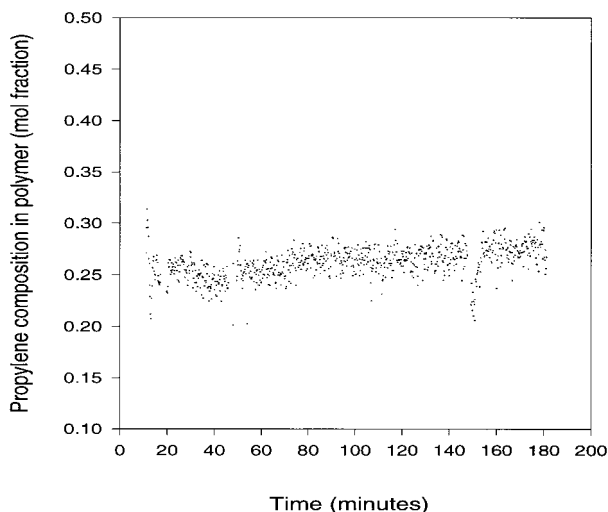


Figure 17 Propylene incorporation as a function of time. Catalyst system: $\text{TiCl}_4/\text{MgCl}_2/\text{Al}(\text{Et})_3$, $T = 50^\circ\text{C}$.

to any study related to kinetic aspects such as the stability of the active sites as well as the characterization of site transformations which result in different comonomer incorporation rates.

CONCLUSIONS

In this study, the design and operation of a lab-scale stirred bed gas-phase reactor system for investigating the kinetic behavior of olefin copolymerization reactions using heterogeneous catalysis has been presented.

Through experimental studies using this reactor system, it has been demonstrated that reliable temperature, pressure, and composition control is achievable. A key component of the system is the on-line gas composition control system, which provides close control of comonomer composition as well as hydrogen composition during the entire reaction period. Consequently, the system as described makes it possible to carry out fundamental studies of catalyst kinetic behavior. In addition to the illustrative examples presented here, comprehensive kinetic studies of several catalyst systems are currently in progress and these will be the subject of future publications.^{3,19}

The authors are indebted to the National Science Foundation and the industrial sponsors of the University of Wisconsin Polymerization Reaction Engineering Laboratory (UWPREL) for support of this research. We are grateful to Jitka Rosendorfova and Clovis Chiu for their assistance in the control system development, to Tom Palionis for his help in the design and implementation

of the FTIR measurement system, and to Mr. Masashi Hamba for his help with the illustrative examples.

REFERENCES

1. K. Y. Choi and W. H. Ray, *J. Appl. Polym. Sci.*, **30**, 1065 (1985).
2. C. M. Chen, Ph.D. thesis, Department of Chemical Engineering, University of Wisconsin-Madison, 1993.
3. J. A. Debling, Ph.D. thesis, Department of Chemical Engineering, University of Wisconsin-Madison, 1994.
4. Isam A. Jaber and W. H. Ray, *J. Appl. Polym. Sci.*, **49**, 1695 (1993).
5. S. J. Rhee, E. C. Baker, D. N. Edwards, K. H. Lee, J. H. Moorhouse, L. S. Scarola, and F. J. Karol, Process for Producing Sticky Polymers. U. S. Pat. 5,106,927 (1993) (to Union Carbide Corp.).
6. P. G. Jeffery and P. J. Kipping, *Gas Analysis by Gas Chromatography*, Pergamon Press, Oxford, 1972.
7. O. P. Bochkova and E. Ya. Shreyder, *Spectroscopic Analysis of Gas Mixtures*, Academic Press, New York, 1965.
8. D. W. Hill and T. Powell, *Non-Dispersive Infra-Red Gas Analysis in Science, Medicine and Industry*, Plenum Press, New York, 1968.
9. N. A. Ogunnaike and W. H. Ray, *Process Dynamics, Modeling and Control*, Oxford University Press, New York, 1994.
10. G. Guastalla and U. Giannini, *Makromol. Chem. Rapid Commun.*, **4**, 519 (1983).
11. T. Keii, *The Kinetics of Ziegler-Natta Polymerization*, Kodansha, Tokyo, 1972.
12. N. Kashiwa and M. Kioka, in *Proceedings on the American Chemical Society, Division of Polymeric Materials: Science and Engineering*, Spring Meeting 1991, Vol. 64, 43-44.
13. T. Keii, in *Transition Metal Catalyzed Polymerization: Ziegler-Natta and Metathesis Polymerization*, R. P. Quirk, Ed., Cambridge University Press, New York, 1988, 84.
14. Y. V. Kissin, *J. Mol. Catal.*, **56**, 220 (1989).
15. P. R. Srinivasan, Shashikant, and S. Sivaram, in *Hydrogen Effect in Olefin Polymerization Catalysts*, H. Heinemann, Ed., Marcel Dekker, New York, 1988, 723.
16. M. M. V. Marques, Clemente Pedro Nunes, P. J. T. Tait, and Alberto Romao Dias, *J. Polym. Sci. Part A: Polym. Chem.*, **31**, 209 (1993).
17. V. Pasquet and R. Spitz, *Makromol. Chem.*, **94**, 451 (1993).
18. D. C. Calabro and F. Y. Lo, in *Transition Metal Catalyzed Polymerization: Ziegler-Natta and Metathesis Polymerization*, R. P. Quirk, Ed., Cambridge University Press, New York, 1988, 729-739.
19. G. C. Han-Adebekun, PhD Thesis, Department of Chemical Engineering, University of Wisconsin-Madison, 1996.