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Dynamics and stability analysis of gas-phase bulk polymerization of propylene

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HIGHLIGHTS

- A detailed propylene polymerization model is conducted based on the industrial data.
- A significant reaction parameter fluctuation in operation is reported and a Hopf singularity point is also found on the lower branch of the bifurcation diagram of the open-loop system.
- PI control is introduced to enhance the stability of the process. But without proper controlling parameter settings potential threats still exists.
- The stable region one the plane of controller parameter is pointed out to guide a safer and more productive industrial process.

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ABSTRACT

As one of the most important downstream products of propylene, polypropylene (PP) plays a key role in industrial production and our daily life. In this paper, a detailed mechanism model is built which is derived from practical data and bifurcation diagrams are also obtained to assess an open-loop stability analysis of the reactor, finding out the existence of Hopf point which leads to instability of the open-loop system. Since temperature runaway and oscillations resulted from unstable operation and Hopf point could pose a threat to the safety, productivity and quality of the production process, PI controller is introduced to the system and forms a closed-loop system to improve the stability and controllability of the system. Further calculation shows that, in the case of PI control, the Hopf point, which is the dividing point of the stable and unstable region on the parameter plane, not vanishes but moves to another position with higher catalyst feed rate and the risk of instability still remains. In this situation, appropriate controller parameters can be helpful to avoid unstable operation and expand the range of stable region. Additionally, in the latter part of our work, different closed-loop dynamic simulations are also conducted to show how stability index and the imaginary part of eigenvalues affect the dynamic behaviors of the closed-loop system. In general, this work mainly focuses on the relationship between the process stability and controller parameters and the outcomes are expected to be a guide for industrial operation and design of control system.

1. Introduction

Polypropylene is one of the five general synthetic resins. According to relative positions of branch chains, it can be classified into three types: atactic, isotactic and syndiotactic structure. The common polypropylene products are mixtures of 90–95% isotactic PP and little atactic PP. Because of features such as low density, non-toxic, low production cost, flexural resistance and electrical insulation, PP is widely used in industrial production and daily life. According to statistical data, from 2000 to 2007, the average annual growth rate of global polypropylene demand is 5.7%, while this number will keep at 5.1% from 2011 to 2016 (Li and Wu, 2013).

From some experiments and industrial data, it is reported significant fluctuations of reaction parameters such as temperature and pressure are observed in steady state operation, which increases the control difficulty of production process (Ho and Shamiri, 2012; Jesus et al., 2011; Shamiri and Hussain, 2013). In fact, many literatures have revealed the existence of rich nonlinear phenomenon in some highly exothermic polymerization process and this should be considered to be a root cause of these fluctuation problems. In general, polymerization is carried out by two classes of mechanism: additional polymerization and condensation polymerization. But compared to the condensation

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mechanism, additional polymerization reactions including the homopolymerization of propylene may result in unstable steady states and complicated dynamic behaviors because of its highly exothermic characteristic (Ray and Villa, 2000). Thermal parameters for additional polymerization of some common monomers are listed in Table 1, what needs to be noted is that the data is just for reference and it will be depending on reaction state, temperature, pressure and other factors in practice. The table indicates that, for pure propylene, the adiabatic temperature rise could be as high as 850 °C. Without careful reactor design, the occurrence of thermal runaway may lead to serious melting of polymer and even other safety and production problems.

In existing work, the mechanism and kinetics of homo- and copolymerization reaction of propylene have already been analyzed (Liu, 2009). The stability and dynamic characteristic results of temperature and monomer concentration in Liu's model also provide a guidance for a rational operation. Tong and Luo build a steady-state model based on a bulk polymerization process, indicating that the polymerization of propylene, which is a nonlinear and strong exothermic process, is open-loop unstable. Conventional heat-removing strategies such as jacket heat exchanger may be deficient in the bulk polymerization process. Open-loop operations around unsteady stable state is sensitive as well as vulnerable to disturbances which might result in thermal runaway (Tong and Luo, 2004). Gorbach uses different type models to describe the horizontal stirred bed reactor applied in polymerization of olefins and figures out the bifurcation diagrams with Hopf point. Different disturbances are also added to study the dynamics and oscillation behaviors of steady states around the Hopf point (Gorbach et al., 2000). But the reactor model in this work is quite simple which just focuses on the chain propagation reaction and is unavailable for in-depth study.

Because of the strong nonlinear characteristics of additional polymerization process, control measures are necessary to maintain the stability of the system. In former work, Ray (1986) has already analyzed the control measures for different polymerization processes and point out the existing problems as well as some solutions. Besides, Chang and Chen provides us a theoretical basis for PID control design (Chang and Chen, 1984) and Zavala-Tejeda et al. (2006) applies PID control measures into a polyurethane continuous stirred tank reactor to achieve a stable production, but theoretical controller parameter tuning method is not given. There are lots of references focusing on the control of polymerization process of ethylene and other monomers but just a few are on propylene. Table 2 shows a summary of control studies on propylene polymerization. Most of these studies just place emphasis on the modeling and analysis of the dynamic behaviors of open- or closed-loop system, but the reason why these oscillation happens and the controller parameter setting methods that could be taken to avoid these undesired problems are still unknown in these papers.

In other fields such as machinery and fermentation, there are also studies focusing on parameter oscillation and process stability which give us a deeper insight into this kind of problem (Mease et al., 2003; Ouyang, 2010; Wang et al., 2013a, 2013b, 2014). For example, in a *Zymomonas mobilils* continuous fermentation process producing ethanol, undesired Hopf singularity points are found to be harmful to the stable productivity operation. Wang takes an analysis on this case, calculating the distribution of Hopf points and take measures to enhance the stability of the process (Wang et al., 2013a). He has also proposed a process design framework for considering the stability of operating points and Hopf singularity points (Wang et al., 2013b), it will contribute to high productivity, product quality and stability in dynamic processes. And some of his idea such as the Homotopy algorithm and the stability index will be adopted in this paper.

In our work, based on the industrial data, a detailed mechanism model is built in accordance with the process of gas-phase bulk polymerization of propylene. Then a stability analysis is conducted to find out the root cause of the oscillations. Finally, PI controller is introduced to achieve a stable closed-loop system. The dynamic behaviors as well as the relationship between the controller parameters and stability are both analyzed, and the region of controller parameters for stable production is also given out, aiming to provide a guidance for industrial operation.

2. Innovene process

The polypropylene production process can be divided into solution method, slurry method, bulk polymerization method, gas phase method and bulk-gas phase method by reaction state, among which the gas phase method and bulk-gas phase method are relatively advanced production processes. In recent years, with the rapid increase in the number of production plants, gas phase method is trend to replace the most widely used Spheripol process. As one of the gas phase method, Innovene process, which is also named BP-Amoco process, uses continuous stirred bed reactors to produce polymer products with very good rigidity and impact resistance. Fig. 1 shows a schematic of a continuous stirred reactor of Innovene process according to descriptions in some paper (Gorbach et al., 2000; Khare et al., 2004). Each reactor can be divided into several reaction regions which can be regarded as CSTRs along the axis and named R-1–R-5 in latter part of the work, while the distribution of reactor's residence time is similar to PFRs. This arrangement of reaction region series avoids short circuits of catalyst and unnecessary colloid. The gas and liquid propylene feed steams are also divided into different streams and flow into the reaction region from top and bottom correspondingly. There are two gas outlets on the top of the reactor which are designed to get rid of excess gas and take control of the concentration of propylene, propane and H_2. The

Table 1
Thermal parameters for some additional polymerization (Ray and Villa, 2000).

Monomer	Heat poly (kcal/mol)	Pure mon conc (mol/L)	Adiab. temp rise (°C)	Heat removal duty (kcal/kg)
Propylene	20.1	12.3	850	477
Ethylene	25.9	14.2	1609	922
1-Butene	19.9	10.6	647	355
Isobutylene	11.5	10.6	395	204

Table 2
Control studies in propylene polymerization.

Reactor type	Model	Control algorithm	Variables controlled	Reference
Continues stirred bed polypropylene	CSTR (well mixed)	PID	Temperature bed level pressure	(Choi and Ray, 1985)
Fluidized bed polypropylene and polyethylene	two phase	PI	Temperature	(Choi and Ray, 1988)
Slurry polypropylene	CSTR (well mixed)	NMPC	Melt flow index amount of unreacted monomer	(Bolsoni et al., 2000)
Hollow shaft liquid-pool polypropylene	CSTR (well mixed)	GMC	Melt index monomer conversion	(Ali et al., 2007)
Fluidized bed gas phase propylene	Two phase	FLC+ANFIS	Temperature	(Shamiri et al.,2015)