

## Simulation and Analysis of Propylene Coordination Polymerization Process Based on Aspen (polymer) plus

<sup>1</sup>Jinjin Wang, <sup>1</sup>Wangbin Chen, <sup>2</sup>Manlin Zhang, <sup>2</sup>Bin Pan\*, <sup>1,3</sup>Xiaorong Wang\*, <sup>1</sup>Bin Wang

<sup>1</sup>College of Chemistry, Chemical Engineering and Environmental Engineering, Liaoning Shihua University, Fushun, Liaoning 113001, China.

<sup>2</sup>College of Science, Liaoning Shihua University, Fushun, Liaoning 113001, China.

<sup>3</sup>Chinese Academy of Sciences, Beijing 100190, P. R. China.

wangxiaorong@lnpu.edu.cn\*

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**Summary:** Based on the industrial conditions of coordination polymerization of polypropylene, Polymer plus was used to simulate and analyze the coordination process of propylene. The effects of the amount of propane, main catalyst (TiCl<sub>4</sub>), chain transfer agent (hydrogen), shielding gas (nitrogen), and monomer (propylene) on the number average degree of polymerization (DPN), the weight average degree of polymerization (DPW), the number average molecular weight (MWN), the weight average molecular weight (MWW), the polydispersity index (PDI), and the throughput of polypropylene were explored to guide actual production in this paper. Through analysis, the polymerization degree and molecular weight of polypropylene could be adjusted by hydrogen in actual production. The monomer (propylene) should be purified as much as possible to reduce the feed amount of propane. The increase of the propylene contributed to the molecular weight and polymerization degree of the product. The increase in the nitrogen feed amount had no effect on the product performance index. The feed amount of nitrogen could be adjusted as needed according to the actual equipment specifications. The catalyst has the greatest influence on the comprehensive performance index of the product, thus the amount of main catalyst TiCl<sub>4</sub> must be strictly controlled.

**Keywords:** Aspen (Polymer) Plus; Simulation; Propylene; Polymerization; Feed amount.

### Introduction

In recent years, with the continuous optimization of chemical process simulation software, its practicality in the chemical design process is increasing. With the chemical process simulation software—Aspen (Polymer) Plus, you can accurately simulate the polymer production process. Usually, the mechanism analysis modeling method is used in the polymerization reaction. The skeleton of mechanism model is derived from the reaction mechanism and the simplified assumption, and then the parameters are determined by experimental data. The simulation operation results are very close to the actual production results, which has great guiding significance and saves a great deal of exploration time and economic cost for actual production [1, 2].

Polypropylene, one of the four general-purpose plastics, has outstanding advantages such as heat resistance, corrosion resistance, low density, and high transparency. It has a wide range of applications in daily life [3, 4]. The use of

Zeigler-Natta catalyst for coordinated bulk liquid phase polymerization is currently the most stable and advanced process for polypropylene. However, the modeling based on this mechanism and the amount of each feed (H<sub>2</sub>/N<sub>2</sub>/catalyst/C<sub>3</sub>H<sub>8</sub>/C<sub>3</sub>H<sub>6</sub>) on the molecular weight, polydispersity, and product output of polypropylene polymerization has not been reported.

The chemical process simulation software—Aspen (Polymer) Plus was used in this paper to simulate the production process of polypropylene. By changing the feed amount of each type of feed, product polymerization degree, number average molecular weight, weight average molecular weight, polydispersity index and polypropylene output (rate) of polypropylene were simulated. According to the comparison, the appropriate law is obtained. This work is of great significance for the study of the best production process for propylene polymerization.

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\*To whom all correspondence should be addressed.

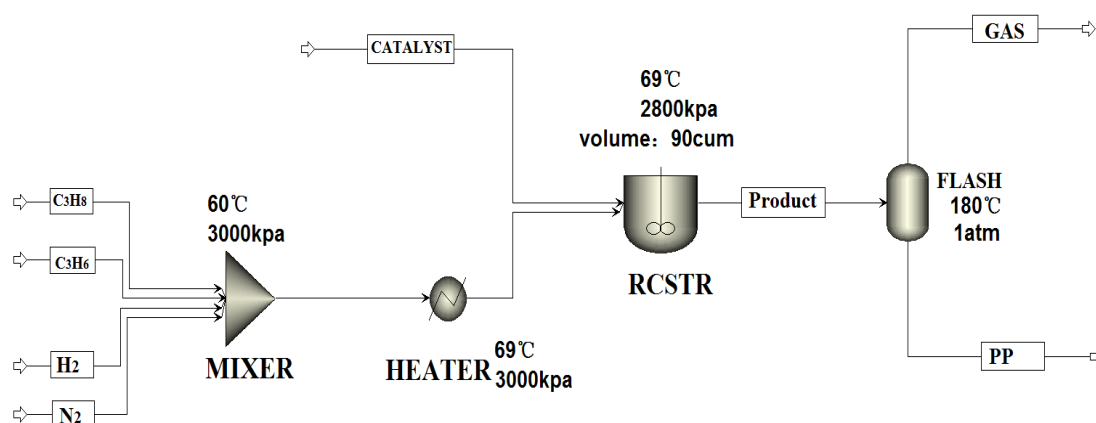


Fig. 1: Polymerization process.

## Experimental

### Modeling

As shown in Fig. 1, a continuous stirred tank reactor (RCSTR) was established. An inlet was connected to the catalytic system (CATALAT) feed stream, the polymerization feedstock feed stream (propylene, propane, nitrogen and hydrogen) was mixed in the MIXER and preliminarily heated in a heat exchanger (HEATER). The outlet for the product was connected to the FLASH, and the mixture of polypropylene and other products flowing out of the reactor was separated and purified. The product (polypropylene) was from the bottom of the flasher, and the process proceeded to a post-treatment process such as granulation, drying, and packaging; The gas was discharged from the top of the flasher and could be recycled and reused (no cycle was set here).

### Definitions of the reaction equation

This simulation was based on the liquid phase bulk process of polypropylene, with titanium tetrachloride ( $\text{TiCl}_4$ ) as the main catalyst, triethyl aluminum (TEA) as the cocatalyst, and hydrogen as the chain transfer agent. The liquid phase bulk polymerization was carried out in the reactor. Due to the four active sites of  $\text{TiCl}_4$  and 8 elemental reactions (Act-Spon was a catalyst self-activation reaction; Chain-Ini was a chain-initiated reaction; propagation was a chain-growth reaction; Chat-Mon was a monomer-chain transfer; Chat-Cocat was a cocatalyst chain transfer reaction; Chat- $\text{H}_2$  was  $\text{H}_2$  chain transfer reaction; Deact-Spon was a catalyst

self-inactivation reaction; And Atact-Prop was an irregular chain transfer reaction). There were a total of 32 reaction equations (Table-2) [5, 6].

Table-1: List of the definitions of reactions ((1-4) indicate four active sites).

Reaction	Reaction	Products
1) Act-Spon (1-4)	$\text{Cps}[\text{TiCl}_4]$	$\rightarrow$ Po
2) Chain-Ini (1-4)	Po	$\rightarrow$ $\text{P1}[\text{C}_3\text{H}_6\text{-R}]$
3) Propagation (1-4)	$\text{Pn}[\text{C}_3\text{H}_6\text{-R}] + \text{C}_3\text{H}_6$	$\rightarrow$ $\text{Pn+1}[\text{C}_3\text{H}_6\text{-R}]$
4) Chat-Mon (1-4)	$\text{Pn}[\text{C}_3\text{H}_6\text{-R}] + \text{C}_3\text{H}_6$	$\rightarrow$ $\text{Dn} + \text{P1}[\text{C}_3\text{H}_6\text{-R}]$
5) Chat-Cocat (1-4)	$\text{Pn}[\text{C}_3\text{H}_6\text{-R}] + \text{Tea}$	$\rightarrow$ $\text{Dn} + \text{Po}$
6) Chat- $\text{H}_2$ (1-4)	$\text{Pn}[\text{C}_3\text{H}_6\text{-R}] + \text{H}_2$	$\rightarrow$ $\text{Dn} + \text{Po}$
7) Deact-Spon (1-4)	Po/Pn	$\rightarrow$ Csd(+ Dn)
8) Atact-Prop (1-4)	$\text{Pn}[\text{C}_3\text{H}_6\text{-R}] + \text{C}_3\text{H}_6$	$\rightarrow$ $\text{Pn+1}[\text{C}_3\text{H}_6\text{-R}]$

Initial parameter values under simulated process conditions

## Results and Discussion

### Results of the operation

Based on the above conditions and simulated operation, the simulated results of chain size and molecular weight distribution are shown in Fig. 2. The five curves are the results of each active site participating in the polymerization (site 1, site 2, site 3, site 4), and the average fitted result (composite).

It can be seen that the polymerization at the third active site (site 3) produces the highest degree of polymerization, and accounts for the highest proportion in the overall polymerization reaction. The active sites reduced in turn are the first active site (site 1), the fourth active site (site 4), and the second active site (site 2).

Table-2: Initial conditions of fluid feed.

	Temperature ( °C )	Pressure ( kpa )	Mass-Flow/Component/Value ( kg/hr )					
			TiCl <sub>4</sub>	TEA	C <sub>3</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	H <sub>2</sub>	N <sub>2</sub>
Catalytic system	30	3000	3	10				100
Non-catalytic system	60	3000			820000	160000	4000	5000

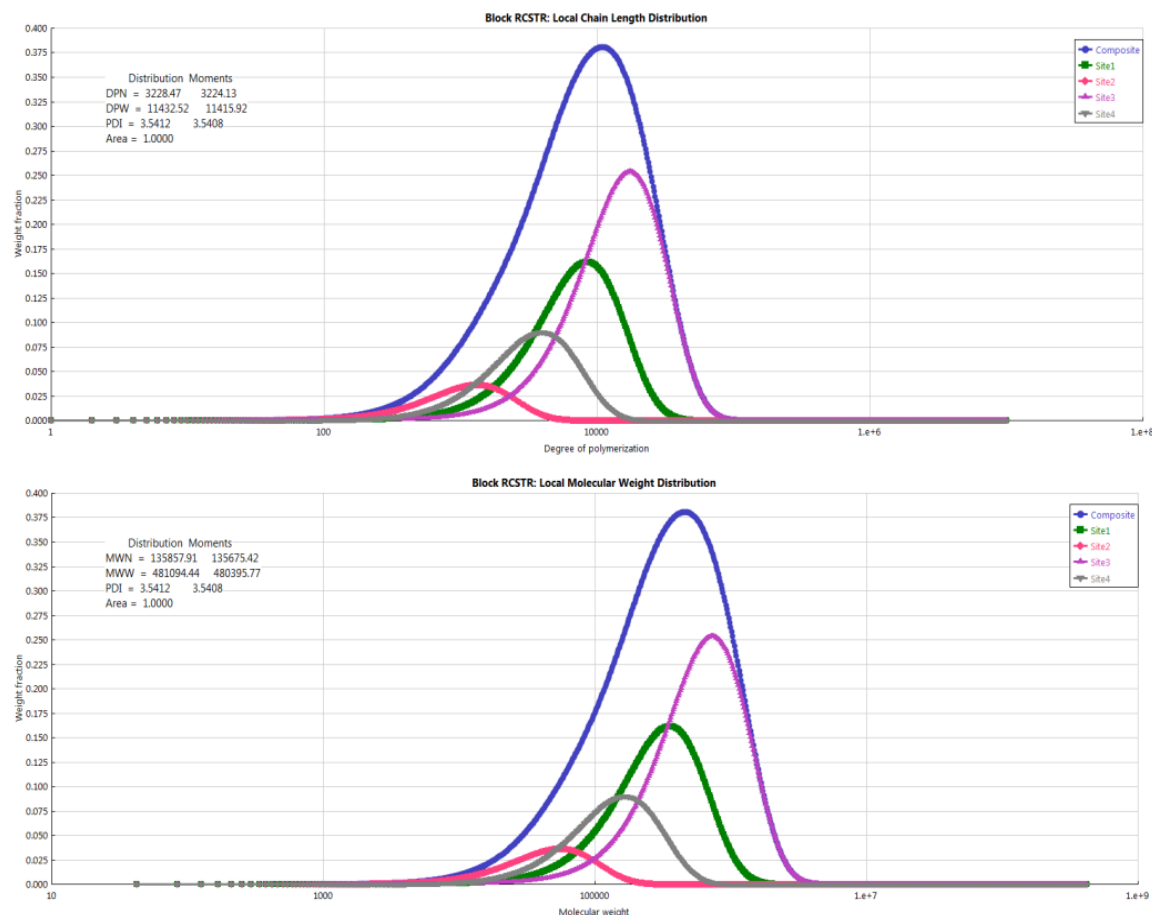


Fig. 2: Distribution curve for chain sizes (top) and molecular weights (bottom)

The average fitting results of polypropylene under these conditions showed that the number-average degree of polymerization (DPN) was 3228; the weight-average degree of polymerization (DPW) was 11433; the polydispersity index (PDI) of the polymer was 3.54; the number-average molecular weight (MWN) was 135858; and the weight-average molecular weight (MWW) was 481094.

Table-3: Main performance parameters of the simulation results.

DPN	DPW	MWN	MWW	PDI	PP Mass Flow (kg/hr)
3228	11433	135858	481094	3.54	9905

#### *Influence of hydrogen feed amount*

The flow rate of melt is the main basis for dividing the grade of polypropylene, which is closely related to the molecular weight of polymer. In the polymerization process, the chain transfer agent (H<sub>2</sub>) plays a key role in regulating the molecular weight of polypropylene. At the same time, it also increases the initial polymerization rate of propylene, and works on the activity decay of the catalyst. In the model below, the effects of changes in hydrogenation on polymer were analyzed with no change of other parameters.

As shown in Fig. 3, the amount of hydrogen feed increased, the DPN/DPW (A), MWN/MWW (B), and output (D) of the polypropylene were gradually reducing, and the PDI (C) was gradually increasing.

For example, if the feed amount of  $H_2$  was increased to 37.5% of the initial value (4000→5500 kg/h), the discharge flow rate of the obtained polypropylene was 9280 kg/h. Compared with before (9905 kg/h), the flow rate was reduced by ~6.31%; the DPN (2725) and MWN(114661) were decreased by ~15.48%; the DPW (10033) and MWW (422207) were reduced by ~12.11% too; the PDI was 3.68, which was increased by ~3.95%.

When the feed amount of  $H_2$  was reduced to 37.5% of the initial value (4000→2500kg/h), the discharge flow rate of the obtained polypropylene was 10651kg/h, which was increased by ~7.53%; the DPN (4014) and MWN (168,897) were increased by ~24.50%; the DPW (13418) and MWW (564,627) were also added by ~17.54%; the PDI was 3.34, which was reduced by ~5.65%.

It can be seen that when the feed amount of  $H_2$  is increased, the flow rate of the discharged product by one reactor will decrease to a certain extent, the degree of polymerization will decrease greatly, and the polydispersity will increase to some extent.

#### Effect of nitrogen feed amount

As the amount of  $N_2$  was increased, DPN /DPW (A) and MWN/MWW (B) of polypropylene were gradually increasing, while the PDI (C) and the output amount (D) were gradually increased.

If the feed amount of  $N_2$  was increased to 30% of the initial value (5000→6500 kg/h), the discharge flow rate of the obtained polypropylene was 9856 kg/h, which was reduced by ~0.49%; the DPN (3228) and MWN (135838) were increased by ~0.12%; the DPW (11425) and MWW (480786) were added by ~0.08%; the PDI was 3.54, which was reduced by ~0.06%.

When the feed amount of  $N_2$  was further reduced to 30% of the initial value (5000→3500 kg/h), the discharge flow rate of the obtained polypropylene was 9954 kg/h which was increased by ~0.50%; the DPN (3220) and MWN (135507) were reduced by ~0.13%; the DPW (11406) and MWW (479,987) were increased by ~0.08%; the PDI was 3.54, which was reduced by ~0.03%.

It can be seen from Fig. 4 that, the variation on the flow rate, degree of polymerization, and polydispersity of the product obtained through one reactor are very small by changing the amount of  $N_2$ .

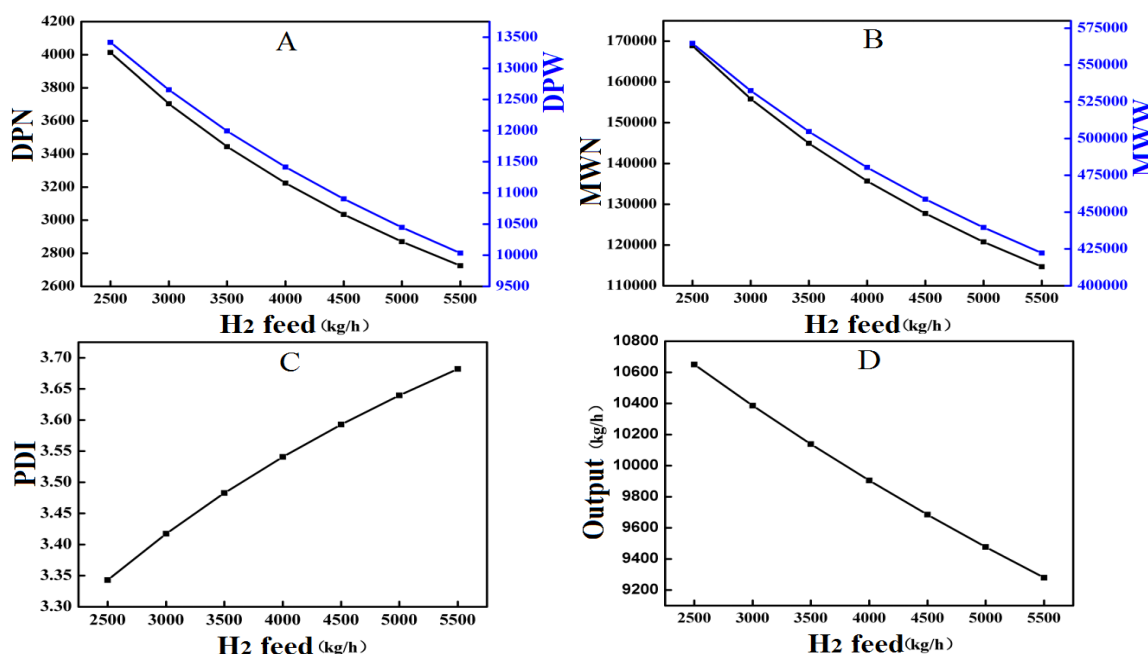


Fig. 3: Effect of hydrogenation on polypropylene polymerization (A), molecular weight (B), polydispersity (C) and polypropylene yield (D).

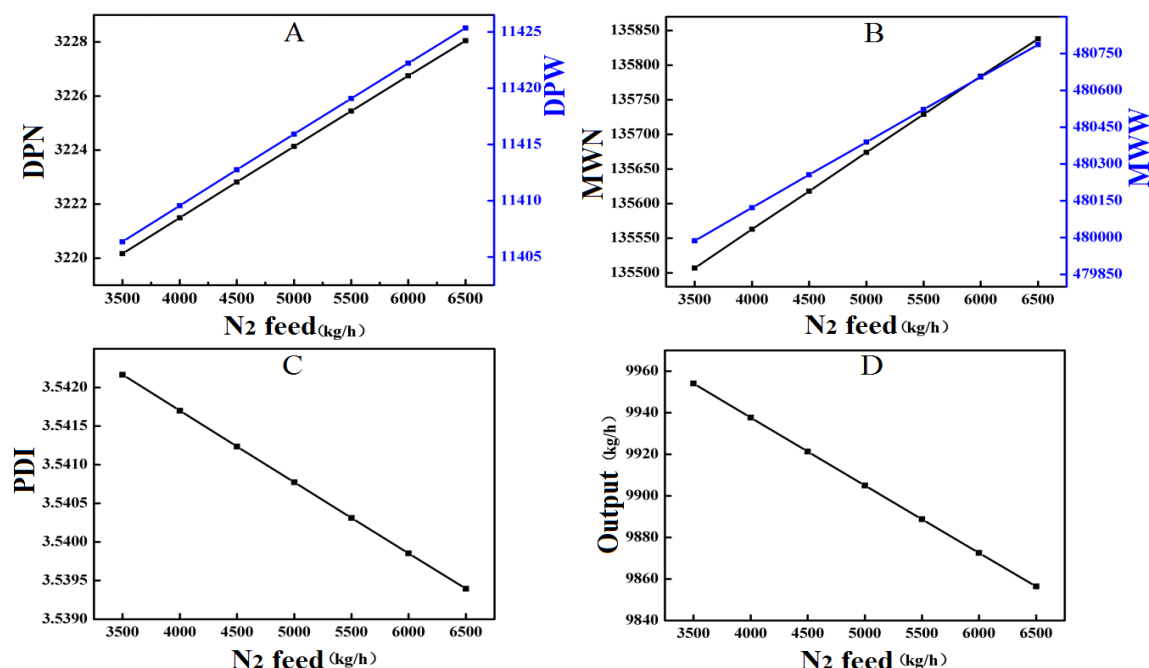


Fig. 4: Effect of nitrogen feed on polypropylene polymerization (A), molecular weight (B), polydispersity (C) and polypropylene yield (D).

#### Effect of propane

With the increase of propane content, the DPN /DPW (A), MWN/MWW (B) and output (D) of polypropylene were gradually decreasing, and the PDI (C) was gradually increasing according to Fig. 5.

If the content of propane was increased to 37.5% of the initial value (160000  $\rightarrow$  220000 kg/h), the discharge flow rate of the obtained polypropylene would be 9538 kg/h. Compared with the previous product of 9905 kg/h, the flow rate was reduced by  $\sim 3.71\%$ ; the DPN (3201) and MWN (134691) were decreased by  $\sim 0.71\%$ ; the DPW (11348) and MWW (477529) were reduced by  $\sim 0.60\%$ ; the PDI was 3.55, which was increased by  $\sim 0.11\%$ .

When the content of propane was reduced to 37.5% of the initial value (160000  $\rightarrow$  60000 kg/h), the discharge flow rate of the obtained polypropylene would be 10306 kg/h, as opposed to that of the previous polypropylene of 9905 kg/h. The feed rate was increased by  $\sim 4.04\%$ ; the DPN (3249) and MWN (136550) reduction were increased by  $\sim 0.78\%$ ; the DPW (11488) and MWW (483438) were increased by  $\sim 0.63\%$ ; the PDI was 3.54, which was reduced by  $\sim 0.14\%$  compared with the polypropylene parameter obtained before the reduction.

#### Effect of catalyst

In the process of increasing the feed amount of  $\text{TiCl}_4$  from 1.5 kg/h to 4.5 kg/h, the DPN, DPW, MWN, and MWW of polypropylene increased at first and then decreased. The DPI and output maintained a growing trend (Fig. 6).

When the feed amount of  $\text{TiCl}_4$  was 2.5 kg/h, the DPN and MWN reached the maximum value of 3224, 135688 respectively. When the feed amount of  $\text{TiCl}_4$  was 3.5 kg/h, the DPW and MWW reached the maximum of 11417, 480,422 respectively.

When the feed amount of the main catalyst  $\text{TiCl}_4$  was increased to 50% of the initial value (3.0  $\rightarrow$  4.5 kg/h), the discharge flow rate of the obtained polypropylene was 14242 kg/h, which was increased by  $\sim 43.78\%$ ; the PDI was 3.54, which was reduced by  $\sim 0.06\%$  compared with before.

When the feed amount of  $\text{TiCl}_4$  was reduced to 50% of the initial value (3.0  $\rightarrow$  1.5 kg/h), the discharged flow rate of the polypropylene was 5198 kg/h, which was reduced by  $\sim 47.52\%$ ; the PDI was 3.53, which was reduced by  $\sim 0.25\%$ .

The increase of  $\text{TiCl}_4$  feed was beneficial to the output of polypropylene, along with slightly decreasing PDI. Considering the distribution of degree of polymerization and molecular weight, the

optimal value of  $\text{TiCl}_4$  feed should be controlled at 2.5~3.0 kg/h.

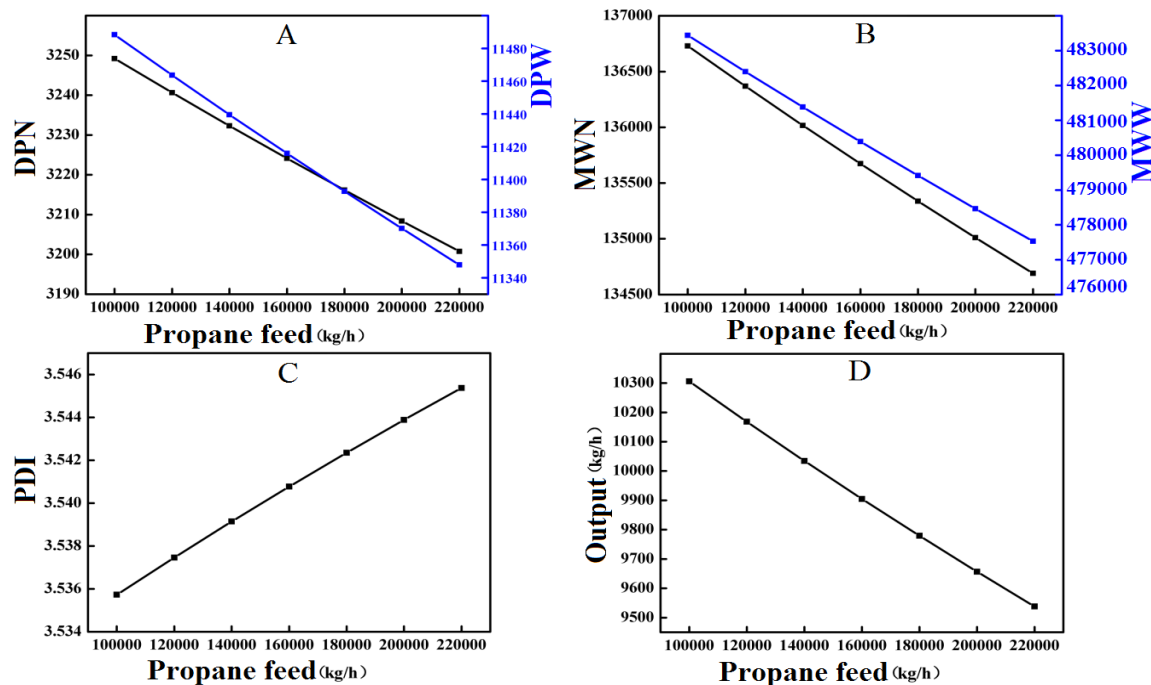


Fig. 5: Effect of propane content on polypropylene polymerization degree (A), molecular weight (B), polydispersity (C) and polypropylene yield (D).

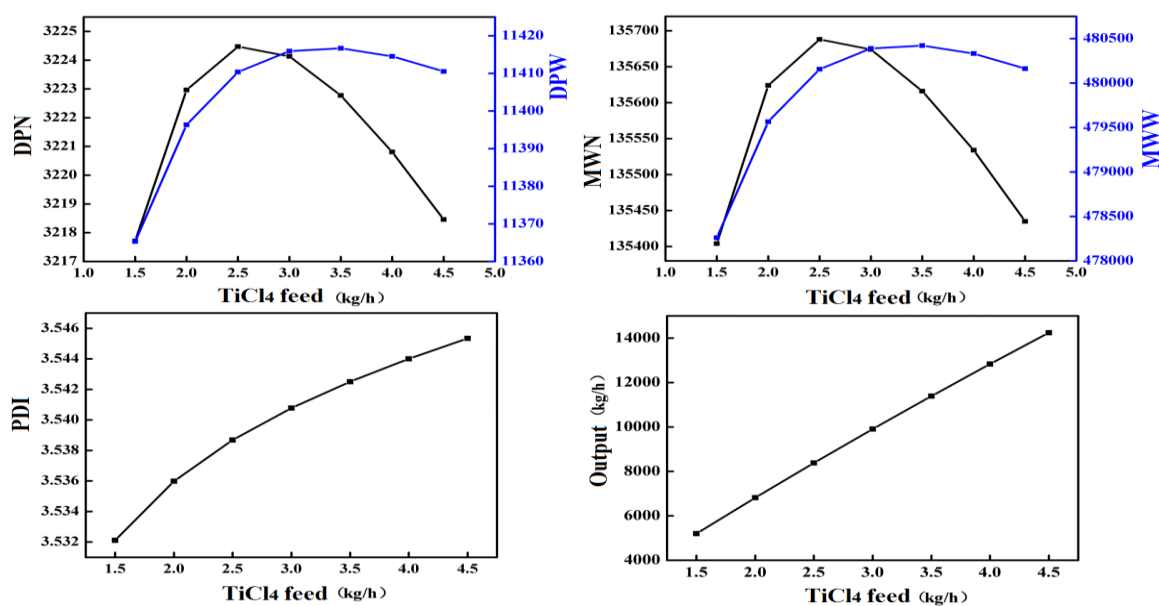


Fig. 6: Effect of catalyst feed on polypropylene polymerization (A), molecular weight (B), polydispersity (C) and polypropylene yield (D).

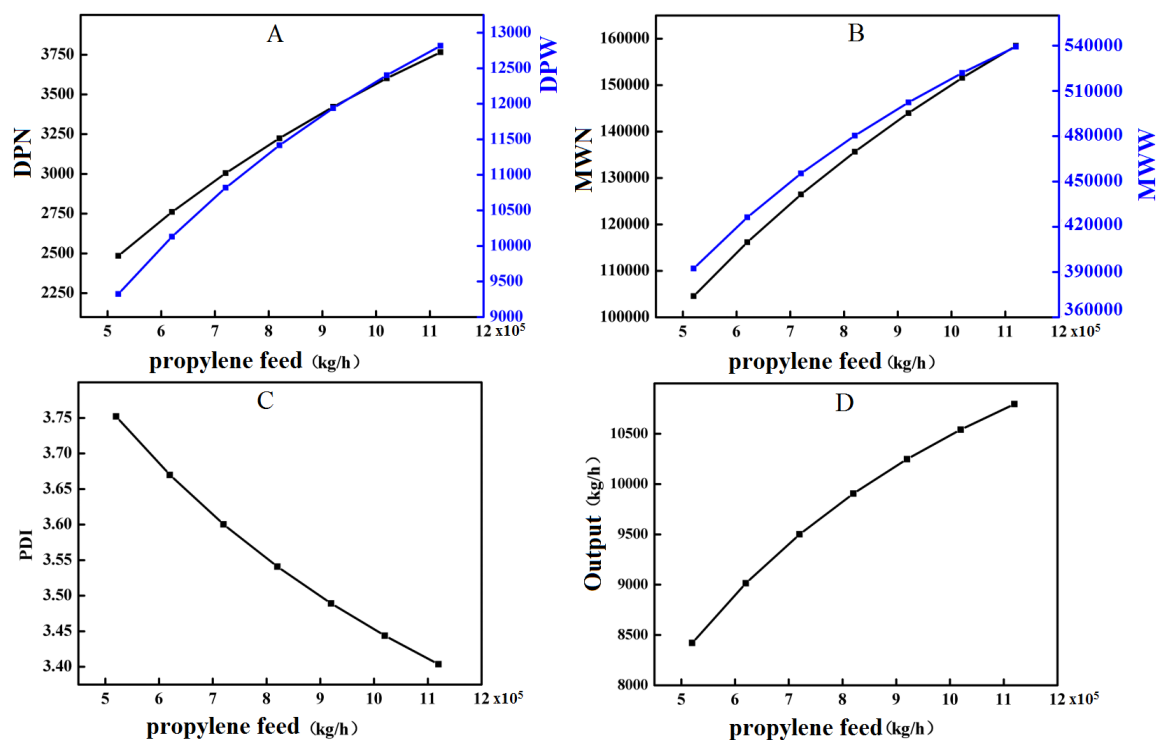


Fig. 7: Effect of propylene feed on polypropylene polymerization (A), molecular weight (B), polydispersity (C) and polypropylene yield (D).

#### Effect of propylene feed

As the amount of monomer (propylene) was increasing, the DPN /DPW(A), MWN /MWW (B), and output (D) of polypropylene were gradually increasing, and the PDI was gradually decreasing (C).

As shown in Fig. 7, if the feed amount of propylene was increased to 36.7% (820000 → 1120000 kg/h) of the initial value, the discharge flow rate of the obtained polypropylene was 10795 kg/h, which was increased by ~8.99%; the DPN (3765) and MWN (158,453) were increased by ~16.78%; the DPW (12816) and MWW (539,315) were increased by ~12.26%; the PDI was 3.40, which was increased by ~3.87%.

When the feed amount of propylene was further reduced by ~36.7% (820000→600000kg/h) of the initial value, the flow rate of the obtained polypropylene was 8420kg/h, which was reduced by ~14.99%; the DPN (2485) and MWN (104579) were reduced by ~22.92%; the DPW (9325) and MWW (392,385) were reduced by ~18.32%; the PDI was

3.75, which was reduced by ~5.96%.

It can be seen that with the increase of the feed of propylene, the flow rate of product obtained through one reactor can be increased to a certain extent; the degree of polymerization is greatly increased, and the polydispersity is reduced to some extent.

#### Conclusion

From the above research, some concrete conclusions could be obtained:

1. H<sub>2</sub> acted as a chain transfer agent in the polymerization of propylene, participated in the polymerization reaction, and could adjust the degree of polymerization, molecular weight, yield and polydispersity index of the polypropylene (Increasing the amount of hydrogen introduced, the degree of polymerization, molecular weight and output of polypropylene had a significant downward trend, and the polydispersity index had a clear upward trend.)

2. N<sub>2</sub> created an inert environment for the reaction. The role of the N<sub>2</sub> in the catalytic system was to press the catalyst into the reactor. The fluctuation of the nitrogen flux in the actual production process had no effect on the performance index of the polypropylene. (The increase of nitrogen feed amount had no significant effect on the performance indexes of polypropylene)
3. The increase of propane in propylene would decrease the polymerization degree, polydispersity index and output of polypropylene, and increase the polydispersity index, which had a negative impact on the production index of polypropylene, so the content of propane in raw materials should be minimized in actual production.
4. The polymerization degree, molecular weight, dispersion index and output of polypropylene were sensitive to the amount of main catalyst TiCl<sub>4</sub>, so the amount of TiCl<sub>4</sub> should be strictly adjusted (controlled) to achieve the best performance index of polypropylene.
5. The increase in feed amount of monomer (propylene) helped increase the polymerization degree, molecular weight and output of polypropylene, reduced the polydispersity index, and improved the performance index of the polypropylene.

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