Effect of Temperature and Pressure on Stability of Metallocene Catalyst with Methyl Aluminoxane

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Abstract

Catalysts are used to increase the rate of reactions. Metallocene catalyst is one such effective catalyst generally used to form polymers. The transition of monomers into metal sites at low pressure and temperature were observed in earlier work. Methyl aluminoxane (MAO) used as a catalyst for polymerization and propylene along with varying temperature and pressure. Optimized values of temperature and pressure are worked upon in this work through particle swarm optimization (PSO). Overall process consists of monomer initialization. This phase is termed as forming population for polymerization. Next phase includes population selection. This phase extract monomers based upon the crossover values. Multiple monomers are combined to generate new offspring that is used within next iteration. Metaheuristic approach includes multiple parameters tuning including temperature and pressure with each iteration. By varying the temperature and pressure new polymers are obtained that are stable in nature.

Keywords: Particle Swarm Optimization, Metallocene catalyst, Temperature, Pressure.

1. Introduction

Metallocene catalyst used to generate polymers that may or may not be stable. Temperature and pressure impact the formation of metal polymers[1]. Through ZeiglerNatta Catalyst, metal polymers were formed but at low temperature. The polymer breaks down as the temperature and pressure increases and hence stability is an issue with this catalyst[2]. For the high-pressure polymerization, MAO catalyst is used for combining monomers for stable polymers. The issue includes the breakage of molecules at high temperature and pressure[3]. To stabilize polymer structure, metallocene catalyst is mixed with polyolefin nanocomposites. The temperature and pressure are varied with the metaheuristic approach and stability of the formed polymers is examined.

Figure 1 Polymerization mechanism

Overall process of polymerization can be impacted by the increasing or decreasing the pressure[4]. The pressure will directly impact the mechanical properties of the metallocene catalyst[5]. As the pressure increase the molecular weight of the Propylene-based polymerization[6]. It also causes storage modulus and reduced melting temperature[7]. It is almost critical to analyze the impact of pressure and temperature on the metallocene catalyst[8].

Synthesis of magnesiumsupported Ziegler Natta catalyst with pressure is given within figure 2.

Figure 2 Impact of pressure on Ziegler Natta catalyst

Next section describes methods and material used for achieving the desired objective.

2. Materials and Methods

The material for the desired operation includes MAO and Propylene. Other material required includes titanium chloride and magnesium chloride[9]. All of these are used along with MAO with varying temperature and pressure. The simulation-based environment is used for achieving the result. The simulation is conducted within MATLAB[10]. The simulator requires initialization with fixed value of temperature and pressure. At each different iteration this value is varied to observe the impact on polymer structure[11]. The Copolymers (PW) formed during the process of polymerization are stable through the proposed approach. The used data for the polymerization in the proposed work is given within table 1.

Table 1 Polymerization material with first 10 iteration

Iterations	MAO	Etheline	Temp($^{\circ}$ C)	Pressure	PW
1	71.3	5	25	1	162356
2	71.3	5	25	2	161233
3	140.23	5	25	3	163656
4	140.23	5	50	1	165878
5	142.6	10	50	2	166587
6	142.6	10	50	3	166989
7	143.6	10	70	1	165878
8	143.6	10	70	2	167548
9	145.6	10	70	3	165878
10	145.6	10	75	1	166525

3. Result and Discussion

The obtained result indicates that as the temperature and pressure increases, the stability of polymers decreases[12]. To enforce stability, pressure can be decreased in the upcoming iterations. The effect of temperature and pressure on PW is analyzed in this section. The result for the same is given in the figure 3. Number of iteration considered for evaluation are 50 with time 30 minutes. Result corresponding to storage modulus (MP) is described in figure 3.

Figure 3 Storage modulus corresponding to polymer formation with different iterations

The increase in polymerization pressure thus causes the termination of polymerization reaction. This will happen if temperature is not adjusted. The converse is also true in this case. This means that if temperature is increased and pressure is not adjusted, reaction still terminates[13].

Propylene polymerization model is applied to solution phase polymerization of propylene with metallocene catalyst /MAO system and kinetic parameters are obtained[14]. Kinetic parameters for Me₂ Si [Ind]₂ZrCl₂ / MAO catalyst system are estimated by simulating the model with experimental data at 25 oC and 75 oC with Al/ Hf molar ratio of 500[15]. Experimental data for Al/Hf ratio of 2000 are used to validate the model at both temperatures.

Table 2 Me₂Si[Ind]₂ZrCl₂ / MAO catalyst at varying temperature from iteration 1 to 50.ss

T ° C	25	75
$k_{in} \times 10^3$ (M ⁻¹ .s ⁻¹)	7.870525	15.74105
$k_p \times 10^{-4}$ (M ⁻¹ .s ⁻¹)	4.172725	8.34545
$k_d \times 10^4$ (s ⁻¹)	3.029002	6.058004
K_{tM} (M ⁻¹ .s ⁻¹)	4.003503	8.007006
$K_{tr} \times 10^6$ (s ⁻¹)	2.525051	5.050102
$K \times 10^{-2}$ (M ⁻¹ .s ⁻¹)	3.631215	7.26243
$k_s \times 10^7$ (M ⁻¹ .s ⁻¹)	3.434840	6.86968
$k \times 10^4$ (M ⁻¹ .s ⁻¹)	1.712346	3.424692
K_{sM} (M ⁻¹ .s ⁻¹)	7.908342	15.816684
$K_{t, Al}$ (M ⁻¹ .s ⁻¹)	5.838210	11.67642
$K_{tr, Al}$ (M ⁻¹ .s ⁻¹)	1.155187	2.310374
$F(k)$ (-)	1000	-

The result corresponding to table 2 is given within figure 4. The analysis indicates that with increased temperature stability is affected but by adjusting pressure stable polymers can be formed.

Figure 4 Effect of Al/Hf mole ratio on propylene rate catalyst=10uM, T=25 C to T=75 deg C, P=3 psi

4. Conclusion

The proposed approach uses the particle swarm optimization procedure for determining the optimal pressure and temperature values for obtaining stable polymers. As the temperature increases the stability of the polymers are at stakes. This means they will be unstable and at higher values of temperature, molecules structure breaks down. With propylene and MAO catalyst, keeping pressure constant at 3 Psi gives the stable metal polymers but temperature range must be within 25 to 700C. Also with experiment analysis it was concluded the molecular weight of metallocene catalyst decreases causing easy decoupling of molecules.

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