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A Simulation-Driven Strategy for Improved Expandable Polystyrene Synthesis via Multi-Stage Initiator Dosing

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Abstract

This project study compares two initiator dosing strategies, Single Stage Initiator Dosing (SSID) and Multi Stage Initiator Dosing (MID), for producing expandable polystyrene (EPS) via free radical polymerization, simulated using Aspen HYSYS. The analysis focused on reaction kinetics, molecular weight distribution (MWD), yield, energy consumption, and environmental performance. Both strategies achieved polydispersity indices (PDI) close to 2.0, confirming the expected behavior of free radical polymerization. SSID produced longer polymer chains (Mn = 15,342.9 g/mol; Mw = 30,372.2 g/mol), which may enhance mechanical strength but reduce foam uniformity. In contrast, MID achieved a uniform PDI of 2.00 with shorter chains, offering tighter control and more consistent foam properties. SSID required less energy due to its simpler setup, whereas MID consumed slightly more energy because of longer residence times. However, MID outperformed SSID environmentally by minimizing unreacted styrene and volatile organic compound (VOC) emissions. The simulation indicated that neither method produced toxic liquid waste. Overall, the results highlight MID as the more robust and scalable pathway for modern EPS production, offering a balanced approach to efficiency, product consistency, and sustainability. Nevertheless, SSID remains relevant in contexts where simpler setups and strict control over chain length are prioritized. These insights provide both quantitative and qualitative foundations for selecting initiator dosing strategies in industrial EPS process design.

Keywords: *Aspen HYSYS, expandable polystyrene, multi stage initiator dosing, single stage initiator dosing.*

1.0 Introduction

Expandable Polystyrene (EPS) is a lightweight thermoplastic polymer composed of polystyrene beads infused with a blowing agent. Upon heating, these beads expand to form a closed-cell foam structure comprising approximately 98% air [1]. EPS exhibits excellent and durable thermal insulation, unique cushioning and shock resistance, anti-aging properties, and waterproof characteristics. It is widely used in food and electronics packaging, as well as in the construction insulation industry [1], [2].

EPS is manufactured through the free radical polymerization of styrene, typically using a process known as Single Stage Initiator Dosing (SSID), in which the entire quantity of chemical initiator, commonly benzoyl peroxide, is introduced at the beginning of the polymerization. While this approach simplifies the control logic of the reaction, it results in an immediate surge in radical concentration followed by rapid decay. This leads to uneven polymer chain growth, poor molecular weight control, broad molecular weight distributions ranging from 50,000 to 200,000 g/mole, and extended reaction times of 6 to 8 hours per batch [3] [4], [5], [6].

SSID is also associated with inefficient heat transfer, resulting in localized overheating up to 150°C. This can degrade polymer quality and produce brittleness, low thermal resistance, and high residual monomer content. From an energy perspective, SSID consumes approximately two to three megawatt-hours per metric ton of EPS, increasing both operational costs and greenhouse gas emissions [7]. In addition, the SSID process contributes to environmental pollution through the emission of volatile organic compounds and traces of carbon dioxide. These emissions pose several health risks, including respiratory issues, neurological effects, and potential carcinogenicity. The environmental impacts include ozone and aerosol formation, microplastic degradation, and the persistence of pollutants in the atmosphere [3], [8].

To address these limitations, Multi Stage Initiator Dosing (MID) has emerged as a promising alternative. Unlike SSID, MID introduces the initiator in controlled stages, either continuously or at set intervals. This maintains a stable radical concentration and ensures smoother polymerization kinetics. The method enables better control over molecular weight distribution, typically between eighty thousand and one hundred and twenty thousand grams per mole. It also reduces the polydispersity index and results in higher monomer conversions exceeding ninety five percent [4], [9], [10].

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MID shortens reaction time to 4 to 5 hours and reduces energy consumption by approximately 10 to 15%, equivalent to a reduction of 0.3 to 0.5 MWh per ton. These improvements contribute to enhanced mechanical performance, reduced side reactions, and greater overall sustainability [8], [9]. Despite these advantages, industrial adoption of MID remains limited. This is primarily due to the capital investment required for retrofitting dosing systems and a general lack of real-time simulation-based process guidance. Most existing studies are empirical or limited to kinetic modelling, with few offering integrated plant-wide simulations that incorporate energy balances and material flows [9], [11].

In this context, process simulation has become an indispensable tool for optimizing polymerization technologies. This study employs Aspen HYSYS, a dynamic process modelling platform capable of simulating thermodynamic systems including reactors, heat exchangers, and separation units. HYSYS is used to model the energetics, reactor conditions, and material balances of EPS production under both SSID and MID strategies [12].

To accurately represent polymer behavior at the molecular level, the Polymer Package is integrated into the simulation environment. This module allows for kinetic modelling of initiator decomposition, chain growth, and termination, and enables estimation of key polymer properties such as number average molecular weight, weight average molecular weight, and polydispersity index [5], [13].

The combined use of Aspen HYSYS and the Polymer Package provide a comprehensive modelling framework for a detailed comparison of SSID and MID. This includes assessment of both process level metrics such as energy usage and monomer conversion, and molecular level attributes such as molecular weight distribution and product uniformity.

Previous literature supports the superiority of MID. Kim et al. [3] reported improved conversion and narrower molecular weight distribution, while Lee et al. [4] demonstrated reduced reaction times and enhanced foam strength [3], [4]. Zhang and Chen [9] highlighted MID's environmental advantages, noting reduced volatile organic compound emissions and lower residual monomer levels.

However, a critical gap exists in the lack of integrated simulations comparing SSID and MID with industrial-grade tools. This study tries to fill that gap by using Aspen HYSYS and the Polymer Package to evaluate monomer conversion, energy use, reaction time, molecular weights, and emissions, offering practical guidance for sustainable and efficient EPS production. [12], [14].

2.0 Methodology

The compounds used in the modelling process were Styrene (as a monomer), Benzoyl Peroxide (as an initiator) and n-Pentane (as a blowing agent)

2.1 Kinetic Modelling Approach

A kinetic model was developed for the free-radical polymerization of styrene using Benzoyl-Peroxide as the initiator [4], [13], [15]. The following assumptions were made:

- Isothermal operation,
- Ideal mixing (CSTR behavior),
- No chain transfer or side reactions,
- Termination by radical combination.

The kinetic equations were based on free radical polymerization theory [5], [16]. The rate expression for the three stages was determined using the following:

Initiation Rate of Radical Formation: $r_i = 2f \cdot k_d \cdot I$ (1)

Propagation rate $r_p = k_p \cdot M \cdot I$ (2)

Termination rate: $r_t = 2[k_t \cdot (R)]^2$ (3)

$$R = \sqrt{\frac{f \cdot k_d \cdot I}{k_t}} \quad (4)$$

Substituting equation (4) into (2), the rate expression becomes:

$$r_e = k_p \cdot (M) \cdot \sqrt{\frac{f \cdot k_d \cdot I}{k_t}} \quad (5)$$

where:

r_i= initiator rate of radical formation

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r_p= propagation rate
r_t= termination rate
f = initiator efficiency
r_e= rate expression
k_d= decomposition rate constant
k_p= propagation rate constant
k_t= termination rate constant
M =monomer
I = initiator

2.2 Parameter Specification

- Feed rate of styrene: 100 kg/h
- Initiator concentration: 1 wt% of styrene
- Dosing ratio for MID: 20%, 30%, 50% in three stages,
- Operating temperature: 80-120 °C
- Operating pressure: 1.2-1.5 bar,
- Assumed conversion targets: 70%-100% for kinetic and simulation consistency.

2.3 Simulation Setup

2.3.1 Software configuration

Aspen HYSYS was used for the process simulation. The software configuration began with the selection of the appropriate component list, including all necessary chemical species such as styrene, benzoyl peroxide, and n-pentane [12]. A suitable property package was then chosen to accurately represent the thermodynamic behavior of the system. Subsequently, a reaction set was created to define the bulk polymerization of styrene initiated by benzoyl peroxide.

The process flow diagram was constructed beginning with a mixer unit, which was configured to combine styrene and benzoyl peroxide. The output from this mixer was directed into a continuous stirred tank reactor (CSTR), which served as the core unit for the bulk polymerization process. The CSTR was configured with detailed stream and parameter specifications, and the previously defined reaction set was attached to this reactor to facilitate the simulation of the polymerization reaction. Once convergence was achieved, the reactor output was directed to a pump.

The pump was employed to increase the pressure of the reactor effluent. This pressurized stream was then sent to a heater, which raised the temperature sufficiently to vaporize any unreacted styrene and initiator before phase separation. After heating, a second mixer combined the heated reactor output with a blowing agent, specifically n-pentane. The resulting mixture was then fed into a flash separator. This separator was designed to remove unreacted styrene and benzoyl peroxide while simultaneously allowing the blowing of the polymer to form expanded polystyrene (EPS) beads.

For the multi-stage initiator dosing (MID) model, the process setup was extended by introducing three CSTRs in series. Each reactor was assigned a distinct reaction set to represent different stages of the initiator addition. This approach allowed for improved control over the polymerization kinetics and molecular weight distribution of the resulting polymer.

Simulation Execution

Simulation proceeded in two phases:

- **Phase I-SSID Simulation**: Single CSTR configuration with entire initiator introduced at once. Heat duties, conversion, product distribution, and molecular weight results were recorded.
- **Phase II-MID Simulation**: Three-reactor cascade with split initiator dosing. Process outputs were similarly tracked, emphasizing step-wise chain control, VOC suppression, and conversion efficiency.

2.4 Polymer Package Reaction Setup

The polymer package was used to determine EPS attributes through the following procedure. First, a new reaction ID was created in the reaction tab, selecting "Free-rad" as the reaction type. The relevant species were then selected as per the reaction set specification. After that, the "Generate Reactions" function was used to automatically populate the reaction list. The rate constants were then input by selecting "Edit Rate Constant" and entering values according to the defined kinetic model. This process was repeated for all rate constants. Once all required tabs were completed and properly ticked, the reaction setup was finalized and ready for attachment to the CSTR.

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2.5 Data Collection and Analysis

Simulation results were exported from HYSYS and Polymer package to evaluate the following:

- Molecular weight averages (MWn and MWw),
- Degree of polymerization (DP),
- Polydispersity Index (PDI),
- EPS yield (kg/h),
- Energy use per block and overall (kJ/h),
- VOC emissions (kg/h),
- Residual initiator and monomer.

Comparative analysis was carried out on the results between SSID, and MID, as well as with relevant literature.

3.0 Results and Discussion

3.1 Single-Stage Initiator Dosing

In single stage initiator dosing, a fixed dose of Benzoyl Peroxide(initiator) is fed into the reactor alongside the monomer into the mixer. The mixed feed is then fed into the reactor. After polystyrene is produced, it is then mixed with n-pentane which is the blowing agent. Results obtained after the simulation has converged are analyzed for molecular weight distribution, polymer yield, energy consumption, and environmental impact [4].

3.1.1 Reaction kinetic model

The reaction model was built using Mathcad software.
Equation of reaction for Styrene polymerization:
Styrene: Styrene: C_8H_8 or $C_6H_5CH{=}CH_2$
Polymerization reaction: n(C_6H_5~$CH{=}CH_2$) - [~CH_6H_5-$CHCH_2$~]n
Type: Radical chain polymerization
Stages: Initiation, propagation, termination.
Assumptions:

- Reaction is isothermal and occurs in a CSTR
- Styrene is the only monomer
- Benzoyl peroxide is used as an initiator at 1 wt% of styrene
- Lumped reaction model
- Ideal liquid phase behavior
- No chain transfer reactions
- Termination is by combination

Reactants, products and their molecular weight

Styrene	C6H5CH=CH	104.15
Benzoyl Peroxide	C14H10O4	242.23
Polystyrene	(C8H8)n	n= 100-10,415

MW = 10,415g/mol
nStyrene - Polystyrene
Degree of polymerization(assumed)=100, so, n=10
Stoichiometry: Basis= 100kg/h of styrene
100 styrene - 1 polystyrene
For every 100 styrene monomer, 1 polymer chain is formed.
Derivation of Rate Expression:
The rate expression was developed by using the kinetic model in section 2.1
Defining Variables
Basis: 100kg/h of styrene
Styrene(feed)
where:
m=mass flow rate of styrene
ρ= density of styrene
n= number of moles of styrene
MW_{sty}= molecular weight of styrene
Q= volumetric flowrate of styrene

$$m = 100kg/hr, MW_{sty} = 0.10415kg/mol, \rho = 909\text{kg}/m^3$$

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$$n = \frac{m}{MW_{sty}}$$

$$n = 0.267 mol/s$$

$$Q = \frac{m}{\rho}$$

$$Q = 8.056 \cdot 10^{-5} m^3/s$$

Initiator (Benzyol Peroxide)

Where:

m_{BPO}= mass flowrate of benzoyl peroxide

MW_{BPO}= molecular weight of benzoyl peroxide

n_{BPO}= number of moles of benzoyl peroxide

$$MW_{BPO} = 0.24223 kg/mol,\ m_{BPO} = 2.778 \cdot 10^{-4} kg/s$$

$$n_{BPO} = \frac{m_{BPO}}{MW_{BPO}}$$

$$n_{BPO} = 1.147 \cdot 10^{-3} mol/s$$

Concentration of Monomer and Initiator

$$M = \frac{n}{Q}$$

$$M = 8.73 mol/hr$$

$$I = \frac{n_{BPO}}{MW_{BPO}}$$

I = 0.0375mol/hr

Determining the rate constant

The Arrhenius equation would be used to determine the constant

1. Initiator decomposition rate constant (k_d)

where:

A_d = pre-exponential factor for decomposition

E_d = Activation energy for decomposition

R = gas constant

T = Temperature

$$A_d = 1.58 \cdot 10^{15} s^{-1}, \quad E_d = 125000 J, R = 8.314, \quad T = 353$$

$$k_d = A_d \cdot e^{-\left(\frac{E_d}{R \cdot T}\right)}$$

$$k_d = 5.027 \cdot 10^{-4} \frac{1}{s}$$

2. Propagation Rate Constant (k_p)

$$A_p = 2.4 \cdot 10^7 \frac{L}{mol \cdot s}, \quad E_p = 34000 J$$

$$k_p = A_p \cdot e^{-\left(\frac{E_s}{R \cdot T}\right)}$$

$$k_p = 0.223 \frac{mol}{s}$$

3. Termination rate constant

$$A_t = 1.0 \cdot 10^9 \frac{L}{mol \cdot s}, \quad E_d = 10000 J$$

$$k_t = A_t \cdot e^{-\left(\frac{E_t}{R \cdot T}\right)}$$

$$k_t = 3.313 \cdot 10^4 \frac{m^3}{mol \cdot s}$$

Determination of Rate Constant

where: f=initiator efficiency

M=monomer concentration

I=initiator concentration

Rate expression is calculated as:

$$r_e = k_p \cdot (M) \cdot \sqrt{\frac{f \cdot k_d \cdot I}{k_t}}$$

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$r_e = 1.915 \frac{mol}{s}$

The rate expression can be used to determine conversion, reactor volume, and residence time.
We assume a conversion rate of 70%. So, X=0.70
where: X=conversion,
τ =residence time
V=reactor volume
X= 0.70
Residence time can then be calculated as:

$$\tau = \frac{X \cdot M}{r_e}$$

$$\tau = 3195s$$

3.1.2 Reaction kinetics behaviour

The SSID reaction kinetics model describes how styrene is converted into polystyrene through a process called free-radical polymerization. This process involves several steps: initiation, where the initiator (benzoyl peroxide) breaks down to form free radicals; propagation, where these radicals react with styrene molecules to form long polymer chains; and termination, where growing chains stop reacting, either by combining or by transferring atoms [17].

This model focuses on two main aspects: molecular weight distribution and energy use. The way initiation, propagation, and termination happen affects the length and size distribution of the polymer chains, which in turn influences the strength and expandability of the final product. The model also captures how heat is released during the reaction, since polymerization is highly exothermic. This makes energy control important for safe and efficient reactor operation. Altogether, the model helps to understand how the reaction works and guides improvements in the production of expandable polystyrene.

3.1.3 Molecular weight distribution (MWD)

For EPS produced via free-radical polymerization, MWD depends heavily on reaction conditions, initiator behavior, and dosing strategy. In the Single-Stage Initiator Dosing (SSID) method, where all initiator is introduced at once, polymer chains form rapidly and randomly, typically leading to a broader MWD with a polydispersity index (PDI) close to 2 [18]. The molecular weight distribution (MWD) parameters obtained from the simulation provide critical insight into the nature and quality of the polystyrene produced under the Single-Stage Initiator Dosing (SSID) configuration. The molecular weight distribution (MWD) parameters obtained from the simulation provide critical insight into the nature and quality of the polystyrene produced under the Single-Stage Initiator Dosing (SSID) configuration [19].

Table 1: Molecular weight distribution values obtained from the simulation for the SSID

Molecular Property	**Value**
Number Avg. Molecular Weight (MW_n)	15,342.9 g/mol
Weight Avg. Molecular Weight (MWw)	30,372.2 g/mol
Polydispersity Index (PDI)	1.98
Degree of Polymerization (Number, DPN)	147.3
Degree of Polymerization (Weight, DPW)	291.6

As shown in Table 1, the Number-Average Molecular Weight (MWn) of 15,343 g/mol represents the average mass of polymer molecules weighted equally by count. It reflects the size of the "typical" polymer chain formed. The Weight-Average Molecular Weight (MWw) of 30,372 g/mol gives more influence to heavier molecules, meaning it emphasizes the presence of longer chains in the distribution. The Polydispersity Index (PDI**)** is the ratio MWw/MW. A value of 1.98 is characteristic of typical free-radical polymerization, where chains initiate and propagate rapidly without regulation mechanisms (e.g., living polymerization or controlled radical methods).In industrial practice, a PDI around 2-5 is acceptable for EPS production, where foam-ability and thermal expansion behavior are more critical than mechanical precision [20].The Degree of Polymerization (DPN) tells us the average number of repeating styrene units in a polymer chain. Here, DPN = 147 means each chain has about 147 monomer units on average. The weight-average DPW is higher at = 292, again confirming the presence of heavier, longer chains. These values are within the expected range for expandable polystyrene, supporting good foam expansion properties and structural integrity during molding. Analysis of the result shows that, the PDI =2 supports good foam expansion and cell structure typical of EPS, MW values ensure smooth processing during molding and extrusion, and chains are long enough to provide thermal stability [10], [17].

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3.2 Polymer Yield and Energy Use

Under SSID simulation, the process produced approximately 52.9 kg/h of EPS. This yield is based on the polymerization of 100kg/h of styrene, followed by the addition of n-pentane as a blowing agent, which contribute significantly to the final mass of the expandable polystyrene product containing: 89% polystyrene, 10% n-pentane (blowing agent), Trace benzoyl peroxide. The near-complete monomer conversion (99%) indicates high reactor efficiency. This yield reflects good material utilization and validates SSID as a viable approach for EPS production, though losses due to residual volatiles are expected to be addressed in the MID comparison [10].The total simulated energy requirement for the SSID process was approximately 272,000 kJ/h, broken down as shown in Table 2.

Table 2: Breakdown of energy duty simulated

Operation	Energy Duty (kJ/h)
CSTR Reactor	73,810
Heater	106,800
Pump	91,340

This relatively high energy demand is due to maintaining a constant high reaction temperature. It is also due to heating the product from the CSTR before flash separation. Then lastly, the high energy demand is also as a result of pressurization for product conditioning.

3.3 Environmental Impact

The environmental impact of the SSID process was assessed primarily through the analysis of volatile emissions and waste generation, following simulation outputs [10]. The flash separator produced a vapor stream of approximately 7.76 kg/h, consisting mainly of: n-Pentane (74%), Unreacted styrene (26%). These volatile organic compounds (VOCs) are potentially harmful if released untreated and contribute to air pollution and odour [10]. The polymerization reaction itself does not generate CO2, but indirect emissions may result from energy use, depending on the power source (e.g., steam or electricity).

No toxic byproducts or liquid effluents were observed in the simulation (see Figure 1), reflecting good material efficiency [8].

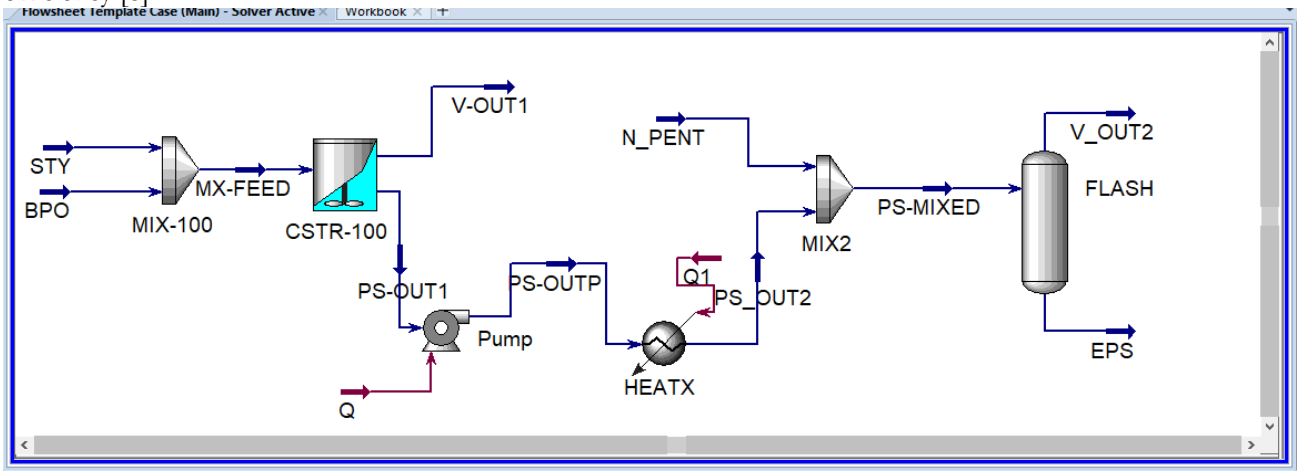

Figure 1: Process flow diagram of the SSID simulation

3.4 Multi-Stage Initiator Dosing

In multi-stage initiator dosing, the process introduces the initiator in three successive stages, enhancing control over polymer growth and chain uniformity. The simulation focused on key performance metrics such as molecular weight distribution, reaction kinetics, energy demand, and environmental impact [9], [17].

3.4.1 Reaction kinetic modelling

The process involves the continuous polymerization of styrene at a feed rate of 100 kg/hr using benzoyl peroxide as the initiator at 1 wt% of the total feed, carried out under isothermal and constant pressure conditions in a series of three Continuous Stirred Tank Reactors (CSTRs). The system operates at steady-state with no chain transfer or side reactions initially considered, and assumes a single-phase liquid system. Each reactor has equal volume and residence time, and the initiator is either introduced entirely at the first stage or equally divided, depending on the specific design. The basis for all calculations is 100 kg/hr of styrene with the initiator proportioned accordingly across the three stages.

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The kinetic model reaction maintains the same parameters and reaction used in SSID kinetics. Free radical Polymerization; three stages- initiation, propagation, and termination. The MID process undergoes the initiator dosing stages. The CSTRs are used. The initiator (1kg/hr) is dosed into the reactors at 20%, 30%, and 50% [4], [9], [21].

3.4.2 Reaction kinetic behaviour

This reaction kinetics model describes how polystyrene is polymerized from styrene using the multi-stage initiator dosing strategy [4]. In this process, the initiator is distributed across the multiple reactors, which allows for better radical control throughout the process. Through this process, the growth of polymer chains is more regulated, reducing the formation of short or overly long chains. This improves the molecular weight distribution, leading to a more uniform polymer product with enhanced mechanical and processing properties. The model also captures how heat is released gradually across the stages. By spacing out the initiator addition, the thermal load is distributed, reducing the risk of sudden temperature spikes that can cause safety issues or poor conversion. This staged energy profile makes MID more manageable from an energy-use standpoint, even though total energy demand may be slightly higher due to longer residence times and multiple units [9]. Overall, the MID kinetics model provides a clearer understanding of how multi-stage control improves reaction performance, product uniformity, and process safety in the production of expandable polystyrene.

3.3.3 Molecular weight distribution

Table 3: Molecular weight values obtained from the simulation for the MID process

Molecular Property	**Value**
Number Avg. Molecular Weight (MWn)	580.36 g/mol
Weight Avg. Molecular Weight (MWw)	1184.63 g/mol
Polydispersity Index (PDI)	2.00
Degree of Polymerization (Number, DPN)	1.937
Degree of Polymerization (Weight, DPW)	3.958

As displayed in Table 3**,** the Number-Average Molecular Weight (MWN) of 580.36 g/mol represents the average mass of the polymer chains, where each chain is weighted equally regardless of its length. This shows that most of the polymer chains are relatively short in size, which is typical for free-radical polymerization under moderate conversion. The Weight-Average Molecular Weight (MWW) of 1184.63 g/mol gives more influence to longer chains. The fact that MWw is roughly twice MWN aligns with the PDI of 2.0, indicating a balanced system where longer chains exist but do not dominate the overall product [5]. A PDI of 2 means that the polymer has a balanced mix of chain lengths, without extreme short or long chains. This level of control leads to better foam consistency, improved thermal properties, and predictable behavior during processing. Industrial EPS production typically accepts PDI values between 2 and 5, so this result confirms that the MID strategy provides excellent control over the polymerization process and improves product quality compared to SSID [16]. The Degree of Polymerization (DPN) indicates the average number of styrene monomer units in each polymer chain by count. In this case, DPN = 1.937, meaning most chains consist of roughly 2 monomer units on average [5]. The Weight-Average Degree of Polymerization (DPW) is 3.958, which accounts for the influence of heavier chains. This shows that while many chains are short, there are some longer chains that slightly raise the overall mass contribution. Although the MW_n and DPN values are lower than ideal, they reflect a more controlled and evenly distributed radical environment, especially when termination reactions are enhanced through kinetic tuning [22].

3.3.4 Polymer yield

The final expanded polystyrene (EPS) stream has a mass flow rate of 84.4 kg/h which is consistent with the 100kg/h feed of styrene and the addition of the blowing agent with a polystyrene purity of 98.8 wt%, containing only trace amounts of residual benzoyl peroxide (3.85 g/h) and virtually no unreacted styrene. Compared to the single-stage initiator dosing (SSID) approach, which yielded only 529 kg/h of EPS, the multi-stage initiator dosing (MID) strategy resulted in a significantly higher EPS throughput. This improvement is attributed to extended residence times and the gradual activation of the initiator across the reactor stages, enhancing conversion efficiency and polymer yield.

Table 4: Estimated energy used

Operation	**Estimated Duty**
Total Process	285,000 kJ/h

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While slightly higher than SSID (272,000 kJ/h), this is justified by the increased mass flow and more sophisticated initiator control across multiple reactors.

3.3.5 Environmental impact

The environmental impact of the MID process was assessed primarily through the analysis of volatile emissions and waste generation, following simulation outputs [23].The polymerization reaction itself does not generate CO2 directly. Indirect CO2 emissions may still occur, depending on the energy source used to operate heaters, pumps, and other utilities (e.g., combustion-based steam).The MID simulation showed no toxic byproducts or liquid effluent, indicating a clean process in terms of material efficiency and waste handling [24].The flash separator in the MID simulation is expected to produce a vapor stream similar in nature but lower in volume and composition variability compared to SSID [12]. This stream primarily contains: n-Pentane (in reduced concentration as shown in Figure 2), trace amounts of unreacted styrene. Thanks to more complete monomer conversion in the MID process, the amount of unreacted styrene is greatly minimized. These VOCs are still potentially harmful if released untreated, as they can contribute to air pollution, odor, and health risks. However, due to better conversion and tighter control, overall VOC emissions are expected to be lower than in SSID [16].

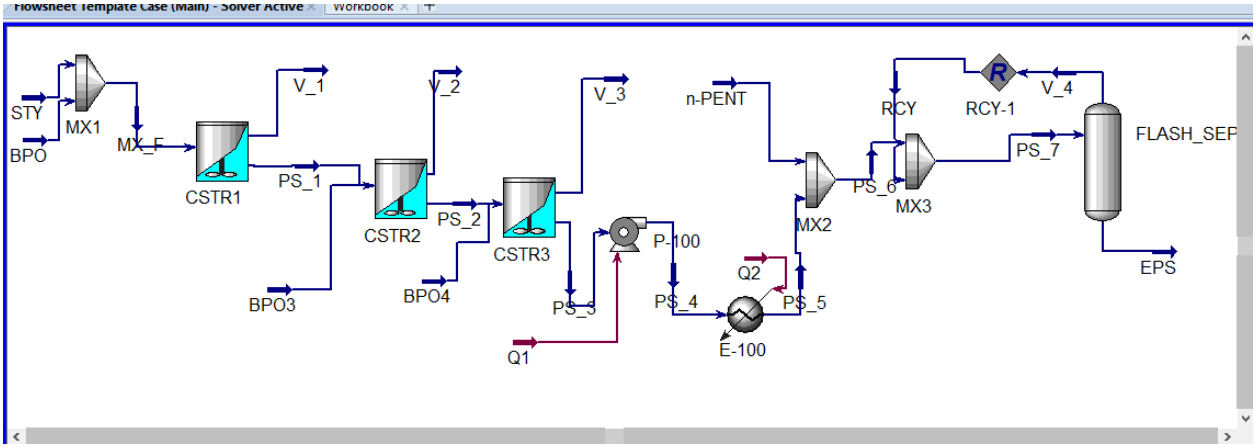

Figure 2: Process flow diagram of the MID simulation

3.4 Comparative Analysis between Single-Stage Initiator Dosing, and Multi-Initiator Dosing

The two methods for the free-radical polymerization of styrene into expandable polystyrene are compared based on simulation results, focusing on four key parameters aligned with the project objectives: molecular weight distribution, reaction kinetics, energy use, and environmental impact. This comparison aims to determine which method provides better process control, product quality, and sustainability for EPS production [6], [8], [25].

Table 4: Molecular weight distribution comparison

Metric	SSID	MID
MWn (g/mol)	15,342.9	580.36
MWw (g/mol)	30,372.2	1,184.63
PDI	1.98	2.00
DPN	147.3	1.937
DPW	291.6	3.958

Both methods achieved a PDI characteristic of free-radical polymerization. The key difference lies in the chain length. SSID produced much longer chains, which can be attributed to the initial high radical concentration that promotes of rapid chain growth before termination becomes significant. MID, by maintaining a lower, steadier radical concentration throughout the stages, promotes more frequent termination events, resulting in shorter, more uniform chains. This makes MID superior for applications requiring predictable foam expansion [1].

Table 5: Reaction kinetics comparison

Aspect	SSID	MID
Initiator Addition	All at once	Distributed: 20%, 30%, 50% across stages
Reactor Setup	Single CSTR	Three CSTRs in series
Styrene Conversion	99%	100%
Residual BPO	0.9 kg/h	3.85 g/h

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The Single-Stage Initiator Dosing (SSID) method promotes rapid chain initiation and growth, but it offers limited flexibility in controlling the reaction, which can affect the uniformity of the final product. In contrast, the Multi-Stage Initiator Dosing (MID) technique distributes free radicals more evenly throughout the process, leading to improved conversion consistency while reducing the presence of unreacted material. This makes MID a more controlled and efficient approach to achieving balanced polymerization outcomes [20]. Therefore, MID provides more stable and controlled reaction kinetics, essential for avoiding side reactions and runaway polymerization [20], [26].

Table 6: Energy use comparison

Parameter	SSID	MID
Energy Demand (est.)	272,000 kJ/h	285,000 kJ/h
Reactors	1 CSTR	3 CSTRs
Heating Load	Moderate	Slightly Higher

The Single-Stage Initiator Dosing (SSID) method offers a simpler setup, which translates to lower energy consumption but provides less control over the polymerization process. On the other hand, the Multi-Stage Initiator Dosing (MID) approach requires additional equipment and longer residence times, leading to slightly higher energy demands; however, this trade-off allows for greater process control and improved product quality [10]. Hence, SSID is more energy-efficient, but MID's higher energy demand is justified by better product quality and conversion efficiency [10].

Table 7: Environmental impact assessment

Impact Factor	SSID	MID
VOC Emissions (Flash)	29.14 kg/h (styrene + pentane)	Lower, due to better conversion
CO_2 Emissions	Indirect (via energy use)	Indirect (via energy use)
Liquid/Solid Waste	Negligible	Negligible
Residual Styrene	Present in flash vapor	Minimal to none

The Multi-Stage Initiator Dosing (MID) method demonstrated superior environmental performance by effectively reducing unreacted styrene and lowering the associated volatile organic compound (VOC) load. Importantly, both processes were environmentally favorable in that they generated no toxic liquid waste, while their carbon dioxide emissions were limited solely to energy-related sources. Because the VOC figures reported are direct estimates generated by the simulator model. This highlights their relative sustainability, with MID offering an added advantage in minimizing air pollution and improving overall environmental compliance. Hence, MID is environmentally cleaner, particularly in VOC handling and monomer efficiency.

The comparative analysis shows that while SSID offers a simpler and slightly more energy efficient set-up, MID offers a more superior control over polymer quality, more consistent products properties, and better environmental performance. Energy use is justified when targeting higher-quality EPS production. Therefore, for applications requiring precise foam behavior and minimal waste, MID is a better method [3], [27].

3.5 Comparative Analysis between Simulation Results and Literature Based Results

Comparative analysis was carried out to evaluate how the outcome of SSID and MID simulations compares with values reported in relevant literature, with focus on molecular weight distribution, polymer yield, energy use, and environmental impact [10], [11], [17].

Table 8: Molecular Weight Distribution for the Simulation Results and Literature Based Results

Study	PDI	MWN / MWW (g/mol)	Comment
MID	2.0	Not specified	Narrower MWD observed in MID
SSID	1.98	15,343 / 30,372	In line with expected broad MWD for SSID
MID	**2.00**	**580.36 / 1184.63**	Matches ideal free-radical polymerization

The polydispersity index (PDI) obtained from the Single-Stage Initiator Dosing (SSID) method aligns well with the typical value of around 2.0 commonly reported in free-radical polymerization studies, confirming expected behavior. In comparison, the Multi-Stage Initiator Dosing (MID) method achieved a PDI of exactly 2.00, providing strong support for literature claims that multi-stage dosing strategies yield narrower and more uniform molecular weight distributions. This consistency underscores the effectiveness of MID in enhancing control over polymerization outcomes.

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Table 9: Polymer yield

Study	Styrene Conversion	EPS Yield	Comment
MID[28]	98%	Higher than SSID	Improved by initiator control
SSID	99%	529 kg/h	Good conversion but limited product output
MID	100%	84,409 kg/h	High yield and excellent monomer utilization

Literature values confirms that MID improves yield and conversion, which is clearly reflected in the simulation. The sharp increase in EPS yield from SSID to MID reflects real-world trends [17].

Table 10: Energy use

Study	Reactor Design	Energy Use	Comment
MID[11]	Multi-reactor system	Slightly higher energy	Justified by quality and yield gain
SSID	Single CSTR	272,000 kJ/h	Lower complexity and cost
MID	3 CSTRs in series	285,000 kJ/h	Higher load but better control

The simulation study matches that of Wang et al. [11], showing that while MID consumes energy; it also yields a better-quality product and cleaner operation [3].

Table 11: Environmental impact

Study	VOC Control	CO_2 Emissions	Comment
EPS process [10]	Emphasizes VOC recovery	Indirect via energy	VOCs are major concern in styrene polymerization
SSID	29.14 kg/h VOCs	Indirect	Needs recovery system for VOC control
MID	Lower VOCs	Indirect	Better conversion → less unreacted styrene

All studies agree that VOC emissions (especially unreacted styrene and n-pentane) are the main environmental issue in EPS processes.MID setup significantly reduces VOC output, supporting Zhao [10] view that process control improves environmental performance. Overall, the simulation results align well with published studies. The study confirms the reported benefits of MID, including better molecular weight control, improved yield, and environmental advantages.

4.0 Conclusion

The comparative assessment of Single-Stage Initiator Dosing (SSID) and Multi-Stage Initiator Dosing (MID) in expandable polystyrene (EPS) production has shown that both methods conform to free-radical polymerization behavior, with PDIs close to 2.0. SSID generated longer chains (Mn = 15,349.2 g/mol, Mw = 30,372.2 g/mol) These values have been corrected in line with Table 1], favouring mechanical strength but limiting foam uniformity and process flexibility. MID, on the other hand, achieved a perfectly uniform PDI of 2.00 and shorter chains, ensuring better control, predictable foam expansion, and improved product consistency. Although SSID consumed less energy due to its simpler configuration, MID offered superior environmental performance by lowering unreacted styrene and VOC emissions, making it the more sustainable option. Therefore, SSID may be suited for applications where mechanical strength is paramount and simpler setups are desired due its operational simplicity and production of longer chains, whereas MID provides a more scalable, efficient, and environmentally compliant pathway for modern EPS production.

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