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A Modelling and Simulation Software for Polymerization with Microscopic Resolution

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ABSTRACT

In the domain of process systems engineering, developing software embedded with advanced computational methods is in great demand to enhance the kinetic comprehension and facilitate industrial applications. Polymer production, characterized by complex reaction mechanisms, represents a particularly intricate process industry. In this work, a scientific software is developed for polymerization modelling and simulation with insight on microscopic resolution. From a software architecture perspective, the software is built on a self-developed process modelling platform that allows flexible user customization. A specific design for polymer species with microscopic chain structure information is conducted. From an algorithm perspective, the software offers high-performance solution strategies for polymerization process modelling by utilizing advanced computation approaches. A Ziegler-Natta copolymerization is presented to demonstrate the software's capability in capturing the microscopic structural information of polymers.

Keywords: Polymerization Process, Modular Modelling, Software Development.

INTRODUCTION

In the domain of process systems engineering, developing process modeling software embedded with advanced computational methods is in great demand to enhance the industrial process simulation, synthesis and optimization.

Industrial systems are often characterized by complex process flowsheets and significant uncertainties, leading to the difficulty in establishing a precise mechanism model. Moreover, the application of these models can be diverse, which may involve the calculation of microscope or macroscope quality indicators, the synthesis of process flowsheets, and the optimization of operating conditions. Due to the complexity of modeling and the diverse applications of the models, some customized modeling software for specific processes has been developed and put into practical industrial applications. In some specific industrial scenarios, these specifically designed software can better meet the diversified and flexible requirements of users.

Polymer production is a particularly intricate process industry. There are many difficulties in developing customized modeling software for the polymerization process. First, a qualified software should model basic reactions involving initiation, propagation, chain transfer and termination, etc., each of which contributes to the overall complexity. Distinct polymerization mechanisms, such as free radical and Ziegler-Natta, add further intricacy. Second, accurate quantification of reaction rate constants, and other kinetic parameters also remains a significant challenge. They are hard to measure experimentally. Estimation of these parameters requires extensive engineering experience and industrial data. Moreover, polymers exhibit a wide variety of molecular structures, such as linear, branched, along with complex molecular weight distributions (MWDs). These microscopic indexes, which significantly influence the product properties, are highly sensitive to reaction conditions, monomer types, and catalysts. Therefore, accurate characterization and prediction of them is crucial and require specialized modeling techniques. Last but not least, polymerization models are inherently nonlinear large-scale equations system[1]. The computational cost of

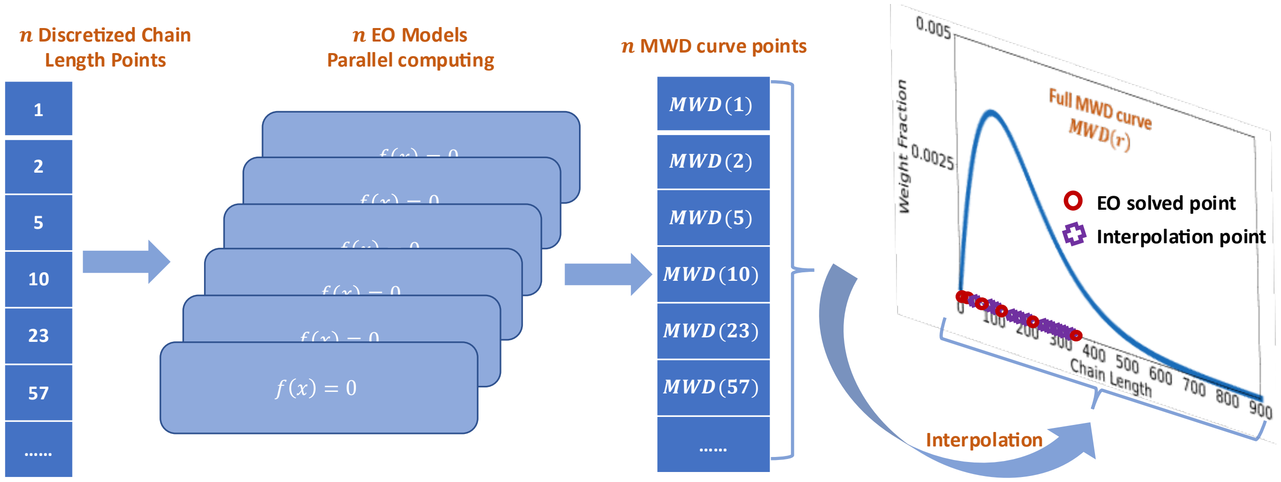


Figure 1: A graphic illustration of the solution process for the cumulative MWD is provided. The computation of the full MWD curve is decomposed into *n* sparse systems of linear equations, each with identical topology. These systems are solved to obtain the values of *n* discretized points along the MWD. Using these discretized points, interpolation is applied to reconstruct the full MWD curve. The final MWD curve is constructed from both the discretized points obtained through the solution process and the interpolated points.

solving such models is high. The numerical stability and convergence are also challenging. In light of this, a scientific software is developed for polymerization modelling and simulation with insight on microscopic resolution.

SOFTWARE ARCHITECTURE

The software is built on a self-developed process modelling platform that allows flexible user customization. It is modularly designed, and each module supports external libraries and secondary development. Pivotal modules, including reaction components, reaction kinetics, process units, process streams and solution strategies, are meticulously constructed and seamlessly integrated.

Components

The software enables users to define various types of components, including conventional, site-based and polymers. Due to their distinct macroscopic and microscopic representation methods, the corresponding data structures of components in the software are also designed differently. Taking polymer components as an example, their macroscopic properties, such as moments of chain length distribution (CLD) and average molecular weight, as well as microscopic properties, including CLD, molecular weight distribution (MWD), branch structure and monomer composition, are modelled.

Meanwhile, each type of component introduces unique variables that must be solved in the model. Specifically, for all streams, the model needs to solve the flowrate of conventional components, the flowrates of potential, vacant and dead sites of site-based components and moments of polymer distribution.

Streams

Streams serve as intermediaries between different process units, facilitating the transfer of data structures and solution results of all components. They can also conveniently store various local information that users may wish to retain.

Units

The software designed a standard unit module for process modelling, which are interconnected through streams. Various unit types and their corresponding functions can be customized, such as continuous stirred tank reactors (CSTR), mixers, and others.

Kinetics

The designed kinetics module allows for the definition of individual reactions, including the specification of reactants, products, and parameters associated with reaction rates. The defined reaction kinetics can be assigned to reactors and utilized to solve the model. The Arrhenius equation, as shown in Equation 1, is used to calculate the reaction rate K, requiring values of the pre-exponential factor A, activation energy E_a, and reference temperature T_0. R is the universal gas constant and T is the temperature.

$$K = Ae^{-\frac{E_a}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)} \quad (1)$$

A standard Ziegler Natta reactions library has been developed in this module. The provided polymerization reactions templates, including different kinds of activation, initiation, propagation, chain transfer and deactivation, can be easily called by users. Besides these reactions, users can also customize various reaction templates.

Macroscopic process solution strategies

At the flowsheet level, the software provides both an equation-oriented and a sequential-module approach to solve for macroscopic information. The Method of Moment (MoM) is employed to characterize the polymer components throughout the process [2]. As a result, the equation-oriented model will incorporate the balance equations derived from the moment model.

Microscopic quality indexes solution strategies

The software provides users with both deterministic and stochastic algorithms to predict microscopic quality indexes, particularly the molecular weight distribution. To evaluate cumulative polymer on the stream level, the equation-oriented method is utilized to enable the calculation of cumulative MWD for each stream. For example, in a CSTR with one feed stream and one output stream, the cumulative MWD of the polymer in the output stream is modelled as a weighted sum of the cumulative MWD in the feed stream and the MWD of the newly produced polymer within the CSTR. When solving for the cumulative polymer's MWD of every stream, such equality relationships are systematically established and solved across the entire flowsheet. As shown in Figure 1, efficient solution strategies are adopted during this process. First, the whole MWD curve is discretized into n discrete points. Next, for each discrete point the balance equations model of the whole process is solved. Thus, the dimension of the equations is reduced by a factor of n and we solve n equation models with the exact same topology.

ALGORITHMS

The software provides users with both deterministic and stochastic algorithms to complete the simulation and computation.

Stochastic Methods

The SSMC algorithm proposed by our group is used for the modelling and simulation of steady-state polymerization process with complex mechanisms [3]. As illustrated in Figure 2, by utilizing "buffer pool", it decomposed the complex polymerization process into several steps for modelling.

This SSMC algorithm enables the prediction of detailed microscopic structure of polymer. Customized data structures are designed for elaborate polymer chain modeling. Through tracking the formation of every simulated chain, it not only provides MWD information but also offers more detailed insights, such as the number and position of branching in each polymer chain when there involves chain transfer to polymer reaction.

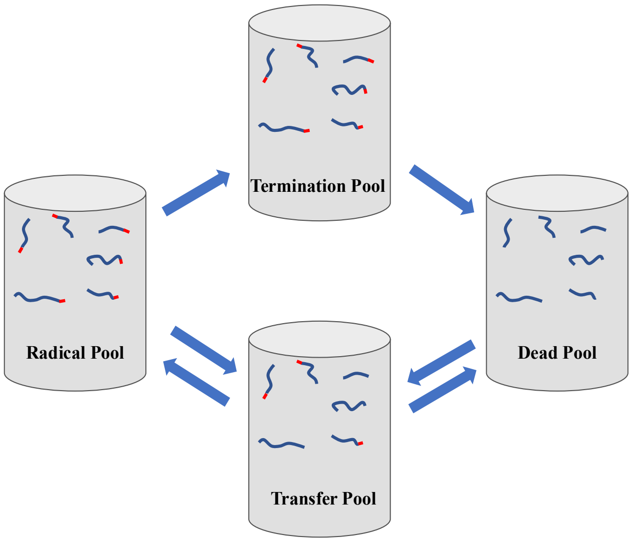


Figure 2. Buffer pools and the multistep polymerization model in the SSMC algorithm.

The scheme of this method is shown in Figure 3. It is a general method as long as the moment model can be established and solved by the software. When this algorithm is called in the software, the results from the moment model and the reaction rates from the mechanisms are required, and the microscopic structural information of the polymer is returned as output.

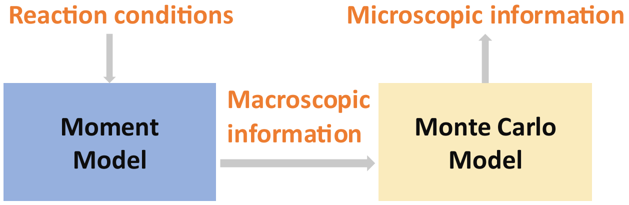


Figure 3. Scheme of applying the SSMC algorithm.

Moreover, this SSMC algorithm have an advantage in efficiency compared with traditional Monte Carlo simulation methods which inherently suffer from significant time and computational resource consumption. When the algorithm is implemented in this software as Python code, a modern high-performance code compiler Numba is employed to accelerate Monte Carlo simulations [4]. Numba generates optimized machine code directly from Python code, ensuring improved computational efficiency without compromising the accuracy of the results.

Deterministic Methods

An orthogonal collocation method with model reformulation strategies for mathematical operations caused by various reactions is involved in the solution algorithms of the software [1]. Theoretically, the number of equilibrium equations of polymer can be infinite if the MWD curve is also inserted in them. This algorithm allows for the discretization of CLD curve in time and chain length dimensions, thus it significantly decreases the number of equations. It is also applicable for the steady-state considering only chain length dimension.

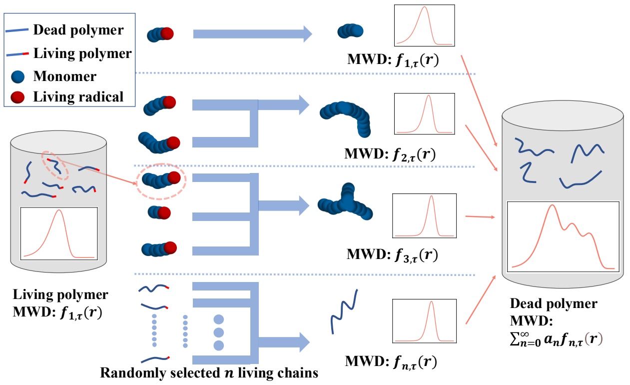


Figure 4. Scheme of applying analytical expressions for MWD derivation in the software.

Besides the equation-oriented methods, analytical expressions are derived for the MWDs associated with specific mechanisms. Represented by the Flory distribution, these expressions provide a straightforward way to calculate the MWD. In this method, the classical Flory distribution is extended to a more general form to handle more complex mechanisms, including bi-molecular termination, chain transfer to polymer and reversible reactions. As shown in figure 4, this method defines a general form of probability density functions (PDFs) and basically analyses all the reactions that producing dead polymer and derives the corresponding MWDs. The PDFs is shown in Equation 2, where n and τ are parameters associated with reaction mechanisms and r is the variable.

$$f_{n,\tau}(r) = \frac{\tau^{n+1} r^n}{n!} e^{-\tau r} \tag{2}$$

The total MWD of all dead polymer is determined as a weighted combination of these MWDs. When this algorithm is called within the software, it requires the mechanisms and results from the moment model as input, and returns the polymer's MWD as output.

INDUSTRIAL APPLICATION

The software has designed standard functions for defining and solving polymerization models. The core modeling functions are designed for specifying individual modules of the model, including components, streams, units, and kinetics. These functions make the modelling process of each module convenient and efficient. The modelling and simulation steps of this software are illustrated in Figure 5.

An industrial application is next demonstrated by using the software. It is a Ziegler-Natta copolymerization produced by two CSTRs as shown in Figure 6. This case focuses on polymerization kinetics and the microscopic structure of the polymer.

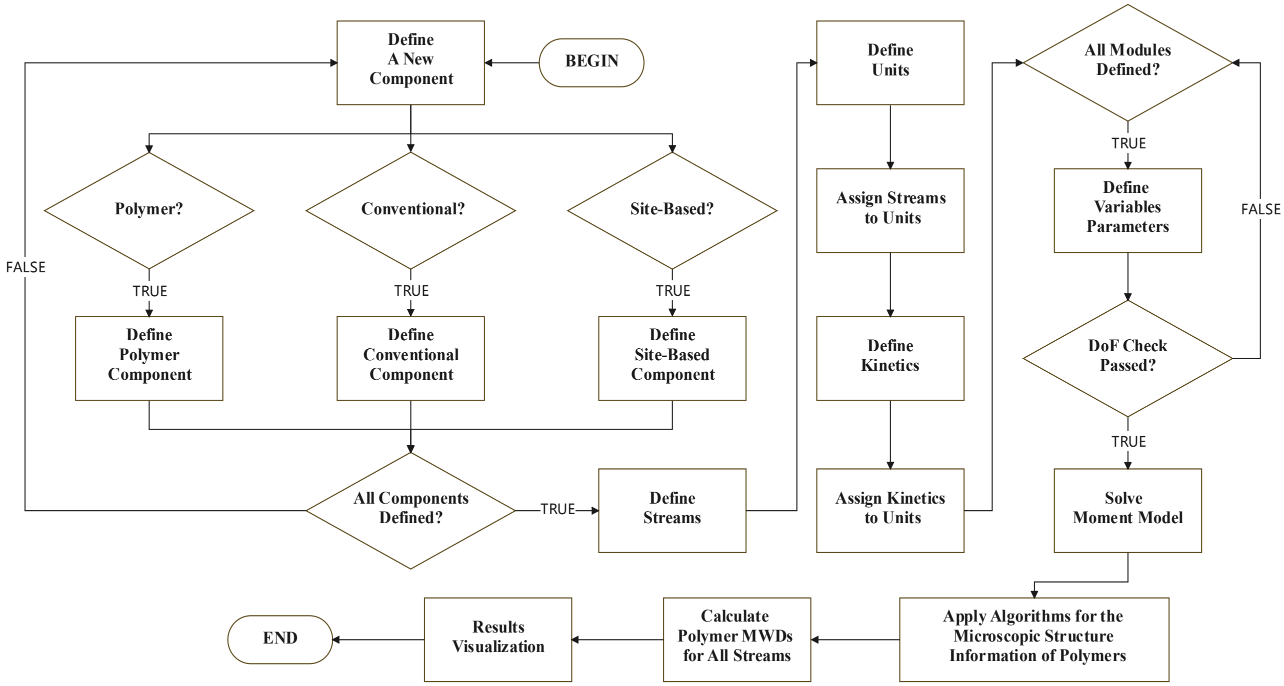


Figure 5: The flowchart for the modeling and simulation steps of the software, outlining the sequential process from model definition to simulation execution.

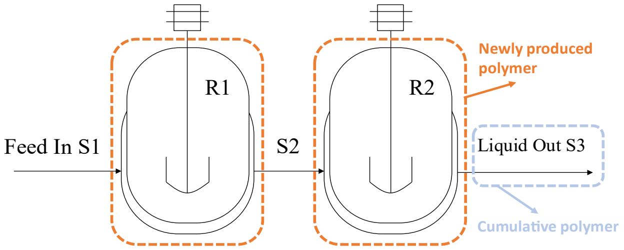


Figure 6. The simplified flowsheet of the Ziegler-Natta copolymerization case.

First, we define the components involved in this application. Ethylene and 1-butene are defined as monomers, triethyl aluminum as the cocatalyst, n-hexane as the solvent, and hydrogen as a controlling agent. The site-based component, titanium tetrachloride, is defined as the catalyst, with the potential, vacant, and dead sites being tracked. The number of active sites is set to five. For the olefin polymer, the moments, MWD, and other structure properties are studied.

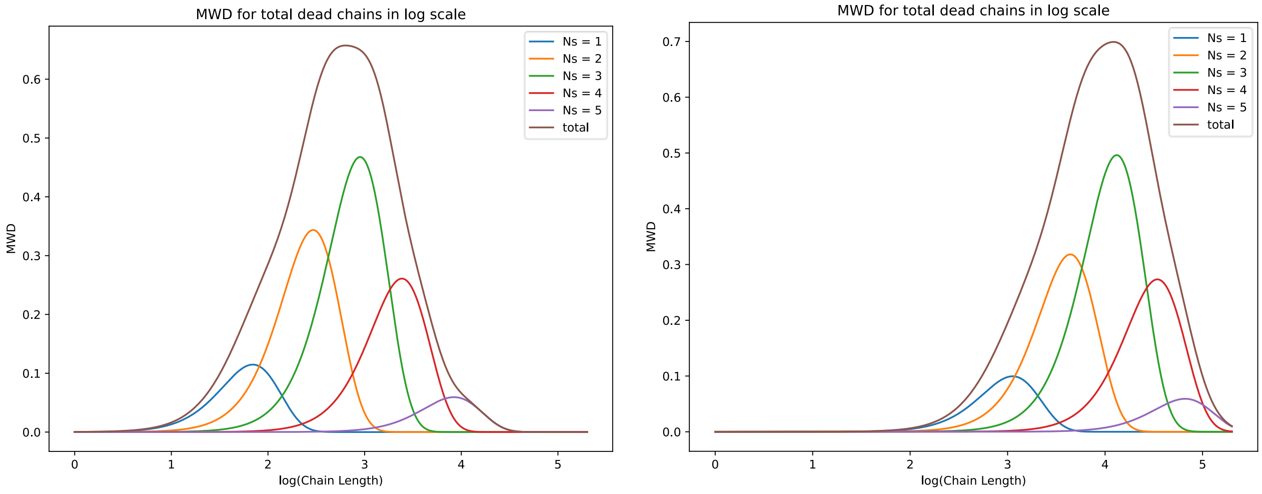
The CSTRs operate under fixed conditions with a constant liquid phase volume. Next, we define the Ziegler-Natta kinetics with reactions occurring on five active sites. The reactions involved in this kinetic model are listed in Table 1. $P_r^*[M]$ denotes living polymer with chain length r and the end monomer M. D_r denotes dead polymer with chain length r. Values of the pre-exponential factor A, activation energy E_a, and reference temperature T_0 are specified to calculate the corresponding reaction rates. The defined kinetics are then assigned to the two CSTRs.

Eventually, the moment model is established and solved. The results obtained include the concentrations of conventional components, the concentrations of potential, vacant, and dead sites, as well as the moments of the polymer CLD within the two CSTRs. The self-developed algorithms are applied to derive the MWD of newly produced polymer in R1 and R2. The results are plotted in Figure 7, the MWD curves of five activate sites are derived, respectively.

Table 1: Reactions involved in the Ziegler-Natta kinetic.

Description	**Chemical Equation**
Initiation	$P_0^* + C_2H_4 \rightarrow P_1^*[C_2H_4]$
	$P_0^* + C_4H_8 \rightarrow P_1^*[C_4H_8]$
Propagation	$P_r^*[C_2H_4] + C_2H_4 \rightarrow P_{r+1}^*[C_2H_4]$
	$P_r^*[C_2H_4] + C_4H_8 \rightarrow P_{r+1}^*[C_4H_8]$
	$P_r^*[C_4H_8] + C_4H_8 \rightarrow P_{r+1}^*[C_4H_8]$
	$P_r^*[C_4H_8] + C_2H_4 \rightarrow P_{r+1}^*[C_2H_4]$
Transfer to monomer	$P_r^*[C_2H_4] + C_2H_4 \rightarrow D_r + P_1^*[C_2H_4]$
	$P_r^*[C_2H_4] + C_4H_8 \rightarrow D_r + P_1^*[C_4H_8]$
	$P_r^*[C_4H_8] + C_4H_8 \rightarrow D_r + P_1^*[C_4H_8]$
	$P_r^*[C_4H_8] + C_2H_4 \rightarrow D_r + P_1^*[C_2H_4]$
Transfer to hydrogen	$P_r^*[C_2H_4] + H_2 \rightarrow D_r + P_0^*$
	$P_r^*[C_4H_8] + H_2 \rightarrow D_r + P_0^*$
Transfer to cocatalyst	$P_r^*[C_2H_4] + Al \rightarrow D_r + P_0^*$
	$P_r^*[C_4H_8] + Al \rightarrow D_r + P_0^*$
Transfer	$P_r^*[C_2H_4] \rightarrow D_r + P_0^*$
	$P_r^*[C_4H_8] \rightarrow D_r + P_0^*$
Deactivation	$P_r^*[C_2H_4] \rightarrow D_r$
	$P_r^*[C_4H_8] \rightarrow D_r$
	$P_0^* \rightarrow D_0$

Last but not least, the microscopic information of cumulative dead polymer in streams S2 and S3 can also be determined. Mathematically, the MWD curve of the final product is a weighted sum of the MWDs of the



(a) CSTR1 (b) CSTR2

Figure 7: The MWD results of the dead polymer in R1 and R2 are presented. Each subfigure displays the MWD curves of dead polymer at five sites, along with the MWD curve of the total dead polymer. All curves are plotted on a logarithmic scale.

products from both R1 and R2, as shown in Figure 8.

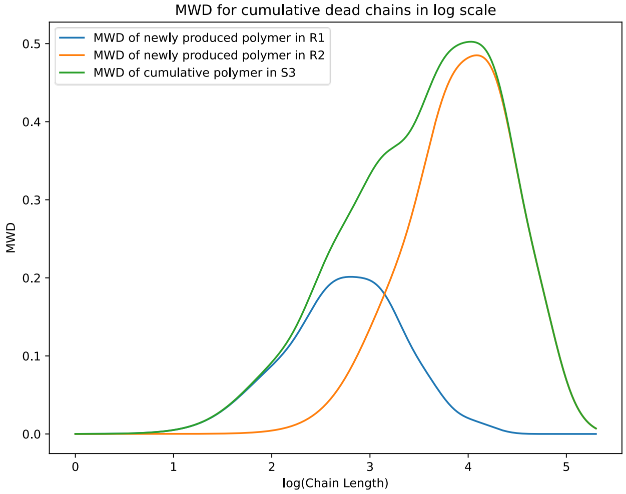


Figure 8. The MWD result of the cumulative dead polymer in S3 is shown. The blue and orange lines represent the weighted MWD curves of the newly produced polymer inside R1 and R2, respectively.

CONCLUSION

A modelling and simulation software for polymerization with microscopic resolution is proposed in this study. The module architecture and self-developed efficient algorithms of this software are introduced in detail. To demonstrate the software's capability in capturing the microscopic structural information of polymers, a Ziegler-Natta polymerization is applied. The insights gained from this work open up opportunities for process analysis and optimization of polymerizations.

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