DYNAMIC OPTIMIZATION OF MOLECULAR WEIGHT DISTRIBUTION IN BATCH POLYMERIZATION REACTORS

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Abstract: This paper applies the orthogonal collocation on finite elements (OCFE) method and the fixed pivot (FP) technique for the prediction of the molecular weight distribution (MWD) for linear free-radical polymerization systems. It is shown that for linear polymers, the two methods result in similar molecular weight distributions for a bimodal MWD. An optimal operating policy that ensures the satisfaction of desired polymer quality specifications and process economics regulations is derived employing a performance index which penalizes the deviations of the MWD from specific desired values. Finally, the optimal trajectories were applied to a free-radical MMA batch pilot-scale polymerization reactor. *Copyright © 2006 IFAC*

Keywords : optimization problems, optimal trajectory, distributions, finite method numerical algorithm, polymerization, cascade control

1. INTRODUCTION

Commonly employed polymer product quality indicators (e.g., mechanical strength, tear strength, rheological properties and so forth) are directly or indirectly linked with molecular structural properties of the polymer chains (e.g., molecular weight distribution (MWD), long-chain branching (LCD), copolymer composition distribution (CCD), chain sequence length distribution (CSD), and so forth). Hence, the ability of a model to predict accurately the molecular properties of polymers in a polymerization reactor is of profound interest to the polymer industry.

In the past a number of mathematical approaches have been proposed to describe the molecular weight developments in free-radical polymerization reactions. Crowley and Choi, (1997a) and Yoon, (1998), developed a kinetic lumping method in which the quasi steady state approximation (QSSA) for the "live" polymer chains holds true and the polymer chains population is divided into a specified number of "chain lump" domains where the resulting balance equations are solved numerically. Polynomial expansion methods of the MWD require the calculation of high-order moments and may lead to slow convergence (Tobita and Ito, 1993). Discrete weighted Galerkin formulation (Deuflhard and Wulkow, 1989; Wulkow, 1992), even though are computationally demanding, provide a useful tool for the prediction of the MWD in complex polymerization systems. However, the approximation of the infinite summation terms (e.g., resulting from termination by combination reactions), requires special treatment. The use of global orthogonal collocation methods for the prediction of the MWD in free-radical polymerization systems see (Nele et. al., 1999) was

partially successful, because a single interpolation polynomial was employed for the entire domain. As a result, prior knowledge about the type of the approximated distribution is required. Kiparissides et. al., (2002), used the OCFE method assuming that the pseudo-steady-state approximation for "live" polymer chains of length "n" holds true, in order to calculate the MWD.

In operating a batch free-radical polymerization process, a typical task involves manipulation of reactant concentrations, reactor temperature and other variables in order to achieve a desired objective which can usually be expressed in terms of conversion, molecular weight distribution, polymerization time and so forth.

In the past, much attention has been given on control basically of the averages of the MWD (Ponnuswammy et. al., 1987; Kim and Choi, 1991; Kozub and MacGregor, 1992). However, for broad or bimodal distributions, the calculation of the number and weight average molecular weights does not uniquely characterize the MWD of the polymer (Ray, 1972). Crowley and Choi, (1997b), applied a common method of controlling the MWD in batch free-radical polymerization reactors, by predetermining the optimal control variable trajectories, and then attempting to execute these trajectories during the batch. Clarke-Pringle and MacGregor, (1998) developed a batch-to-batch optimization methodology for producing a desired MWD using an approximate model.

In the present study the OCFE and FP methods are used to calculate the MWD for linear polymers. The rate equations for the "live" and "dead" polymer chains of length "n", derived from the mass balances, are solved

at specific discrete points, while no QSSA for the "live" polymer chains is assumed. Additionally the summation terms resulting from termination by combination reactions, are taken into account in both methods. A detailed polymerization model is used in conjunction with the FP and the OCFE methods to determine the MWD. Simulation results of the MWD calculations confirmed the validity and accuracy of both methods.

Finally, a model-based dynamic optimization approach was applied to optimally produce a specific desired MWD, calculated by the OCFE method. The calculation of the optimal trajectory of the reactor temperature set points was handled using sequential quadratic programming (SQP). The resulted model-based optimal set point sequence was subsequently imposed on the experimental pilot-scale reactor system which operates at our laboratory. The mathematical model closely describes the reactor unit, which consists of a well-mixed jacketed vessel. Stirring is provided by a flat-blade turbine, aided by four removable blade baffles. The reaction temperature is controlled by a cascade controller which manipulates the flows of two streams (e.g., a hot and a cold) entering the reactor jacket. The polymerization was highly exothermic and exhibited a strong acceleration in the polymerization rate due to the gel effect (e.g., the termination rate constant decreased with conversion).

## 2. FREE-RADICAL POLYMERIZATION MODEL

The kinetic scheme for the free-radical suspension polymerization of methyl methacrylate (MMA) is shown in Table 1. In this scheme the termination reactions include the combination and the disproportionation mechanisms.

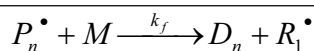Table 1: Kinetic mechanism for free-radical MMA polymerization.
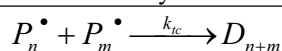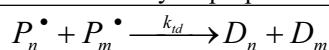
Initiation:
$$I \xrightarrow{k_d} 2PR^\bullet$$
$$PR^\bullet + M \xrightarrow{k_I} P_1^\bullet$$
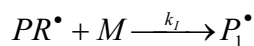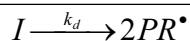
Propagation:
$$P_n^\bullet + M \xrightarrow{k_p} P_{n+1}^\bullet$$
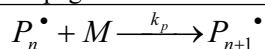
Chain transfer to monomer:
$$P_n^\bullet + M \xrightarrow{k_f} D_n + R_1^\bullet$$

Termination by combination:
$$P_n^\bullet + P_m^\bullet \xrightarrow{k_{tc}} D_{n+m}$$

Termination by disproportionation
$$P_n^\bullet + P_m^\bullet \xrightarrow{k_{td}} D_n + D_m$$

To account for the effect of the diffusion-controlled phenomenon on the termination and propagation rate constants, the model of Chiu et. al. (1983), was employed. Given the above detailed kinetic mechanism, the following balances for the "live" and "dead" polymer chains of chain length "n" ($n \in [1, 660000]$) are obtained:

$$\frac{dP_n}{dt} = 2 f_i k_d IV \delta(n-1) + kf\, M \sum_{m=1}^{\infty} P_m \delta(n-1) + k_p P_{n-1} M$$
$$- k_p M P_n - kf\, M P_n - k_{td} P_n \sum_{m=1}^{\infty} P_m \left(\frac{1}{V}\right) - k_{tc} P_n \sum_{m=1}^{\infty} P_m \left(\frac{1}{V}\right) \quad (1)$$

$$\frac{dD_n}{dt} = kf\, M P_n + k_{td} P_n \sum_{m=1}^{\infty} P_m \left(\frac{1}{V}\right) + \frac{1}{2} k_{tc} \sum_{m=1}^{n-1} P_{n-m} P_m \left(\frac{1}{V}\right) \quad (2)$$

3. METHOD OF MOMENTS

The method of moments is based on the statistical representation of the average molecular properties of the polymer (e.g., number average, Mn, and weight average, Mw, molecular weights) in terms of the leading moments of the number chain length distributions (NCLDs) of "live" and "dead" polymer chains, defined by the following equations:

$$\lambda_k = \sum_{n=1}^{\infty} n^k R_n, \qquad \mu_k = \sum_{n=1}^{\infty} n^k P_n \quad , \quad k = 0, 1, 2 \quad (3)$$

The relevant rate functions for the moments of the NCLDs of the "live" and "dead" polymer chains can be obtained by multiplying each term of eqs (1)-(2) by n^k and summing up the resulting expressions over the total degree of polymerization, N∞. The resulting rate equations for the leading moments are see (Pladis et al., 1998):

$$\frac{d\lambda_k}{dt} = k_I [R^\bullet][M] + k_{fm}[M] \lambda_0 + k_p [M] \sum_{i=0}^{k} \binom{k}{i} \lambda_i$$
$$- k_p [M] \lambda_k - k_{fm}[M] \lambda_k - k_t \lambda_0 \lambda_k \quad (4)$$

$$\frac{d\mu_k}{dt} = k_{fm}[M] \lambda_k + \frac{1}{2} k_{tc} \sum_{i=0}^{k} \binom{k}{i} \lambda_i \lambda_{k-i} + k_{td} \lambda_0 \lambda_k \quad (5)$$

where $[R^\bullet]$ and $[M]$ denote concentrations of the radicals and monomer, respectively. Usually, one needs to know the leading moments (i.e., λ_0, λ_1, λ_2 and μ_0, μ_1, μ_2) of the NCLDs of "live" and "dead" polymer chains to calculate the values of M_n and M_w.

4. FIXED PIVOT TECHNIQUE

The inherent limitations of the numerical solutions resulting from the discretization of the chain length, can be avoided in the more general formulations (i.e., fixed and moving pivot techniques) of Kumar and Ramkrishna (1996) and (1997). The last methods guarantee the correct calculation of any two moments of the distribution and are applicable to any type of discretization of the chain length.

The fixed pivot technique is a very efficient method for the calculation of the weight chain length distribution (WCLD). It assumes that the overall polymer chain population can be assigned to selected discrete lengths. Specific reaction steps (i.e., termination and propagation) leading to the formation of polymer chains other than the representative ones, are incorporated in the set of discrete equations in such a way that selected properties of the WCLD (i.e., total number, mass, etc.) corresponding to any two moments of the WCLD, are exactly preserved.

For the preservation of the zero and first moments of the WCLD, the assigned polymer chain fractions to the discrete lengths n_I and n_I+1 will be given by the following equation:

$$n_t = \begin{cases} \dfrac{n_{i+1} - n}{n_{i+1} - n_i} & n_i \leq n \leq n_{i+1} \\[2mm] \dfrac{n - n_{i-1}}{n_i - n_{i-1}} & n_{i-1} \leq n \leq n_i \end{cases} \tag{6}$$

5. ORTHOGONAL COLLOCATION ON FINITE ELEMENTS

A key characteristic of the OCFE method is the treatment of the discrete polymer chain length domain as a continuous one. Hence, the concentrations of "live" and "dead" polymer chains are handled as continuous variables. Accordingly, the chain length domain is divided into a number of finite elements, NE, with element boundaries at the points: $\zeta_0 = 1$, ζ_1, ζ_2,..., ζ_{NE-1}, $\zeta_{NE} = S_f$, where S_f is the final degree of polymerization [$S_f = 660000$]. For each element a number of n interior collocation points, [s1, s2,..., sn] are specified. The concentrations of the "live" and "dead" polymer chains are then approximated by continuous low-order polynomial functions within each finite element. In the present study, Lagrange interpolation polynomials were used to approximate the concentrations of the "live" and "dead" polymer chains:

$$\widetilde{R}(s) = \sum_{i=0}^{n} W_{i,j}^{R}(s)\widetilde{R}(s_{i,j}) \qquad \zeta_{j-1} \leq s \leq \zeta_j \quad j = 1,...,NE \tag{7}$$

$$\widetilde{P}(s) = \sum_{i=1}^{n} W_{i,j}^{P}(s)\widetilde{P}(s_{i,j}) \qquad \zeta_{j-1} \leq s \leq \zeta_j \quad j = 1,...,NE \tag{8}$$

The tilde denotes approximation variables. The functions, $W_{i,j}^{R}(s)$ and $W_{i,j}^{P}(s)$ are Lagrange interpolation polynomials of order n+1 and n, respectively, given by the expressions:

$$W_{i,j}^{R}(s) = \prod_{\substack{k=0 \\ k \neq i}}^{n} \frac{s - s_{k,j}}{s_{i,j} - s_{k,j}} \quad \zeta_{j-1} \leq s \leq \zeta_j \tag{9}$$
$$i = 0,...,n \quad j = 1,...,NE$$

$$W_{i,j}^{P}(s) = \prod_{\substack{k=1 \\ k \neq i}}^{n} \frac{s - s_{k,j}}{s_{i,j} - s_{k,j}} \quad \zeta_{j-1} \leq s \leq \zeta_j \tag{10}$$
$$i = 1,...,n \quad j = 1,...,NE$$

The Lagrange polynomials $W_{i,j}^{R}(s)$ and $W_{i,j}^{P}(s)$ are equal to zero at the collocation points $s_{I,j}$, for $k \neq i$ and equal to unity for $k=i$. To take into account the concentration of "live" polymer chains at chain length x=1, the left boundary point of the first element was included as an interpolation point.

A set of residual equations was then derived, by substituting eqs (7)-(8) into the material balance equations. The main requirement of the OCFE formulation forces the residual balances to vanish at the selected collocation points, $s_{i,j}$.

The selection of the finite element boundaries controls the density of the collocation points in the overall chain length domain. Thus a high density of collocation points is usually required in chain length regions, where steep changes in the concentrations of "live" and "dead" polymer chains are foreseen. Therefore, the domain partition into finite elements can be performed either based on previous knowledge about the shape and characteristics of the weight chain length distribution (e.g., steep fronts and flat profiles in the WCLD) or based on the satisfaction of a certain error criterion (e.g., equidistribution of error throughout the domain). Extensive simulations showed that low-order interpolation polynomials predict the overall WCLD more accurately, compared to high-order polynomials for the same total number of collocation points. This was attributed to the oscillatory behavior of the high-order Langrange polynomials.

6. DYNAMIC OPTIMIZATION OF THE MWD

For the dynamic optimization of the molecular weight distribution of the free-radical MMA polymerization, the reactor temperature was chosen as manipulated variable, because it is a key process condition that has the greatest direct impact on the MWD. The optimal reactor temperature sequence can be used as temperature set points in order to control the MWD. A cascade control system was employed to drive the actual reactor temperature as close as possible to the optimal set point trajectory. The objective is to minimize the time required to produce a polymer with desired molecular properties. Thus, the objective function to be minimized, can be defined in terms of the final MWD and polymerization time:

$$\min J(T) = \sum_{i=1}^{N_d} w_i \left(\frac{MWD_i - MWD_{di}}{MWD_{di}} \right)^2 + w_{Nd+1} \, t_f \tag{11}$$

subject to single bound constraints : $\quad l < T_i < u$

where, MWD_{di} are the desired values of the MWD, N_d is the number of the desired values of the MWD, t_f is the final polymerization time and w_i are appropriate weights. l and u represent the lower and upper single bound constraints. The desired values of the MWD lie within a feasible domain of MWDs accounting for the capabilities of both the reactor control and heating systems. T stands for the vector of the sequence of the reactor temperature during the polymerization. Each element of the vector T represents a constant manipulated control variable during a specific time interval. The number of the elements j of the vector T is equal to the ratio of the final polymerization time over the number of time intervals selected by the user. All the time intervals have equal length. The objective function is minimized using NPSOL. The method of NPSOL is a sequential quadratic programming (SQP) method.

7. RESULTS

The predictive capabilities of the OCFE method and the FP technique on the MWD of linear polymers were

tested by direct comparison of the two methods for different values of monomer conversion see (Fig. 1). In the reported runs, the initiator (AIBN), monomer and water initial masses were 4 gr, 1.070 kg and 4.8 kg respectively. The reactor temperature was kept constant at 335 K during the whole polymerization horizon (isothermal operation). The continuous lines represent the simulation results derived from the application of the OCFE method while the discrete points represent the results from the FP technique. It is apparent that an excellent agreement between the two methods exists along the whole range of monomer conversion. Notice that both methods are capable to predict bimodal distributions.
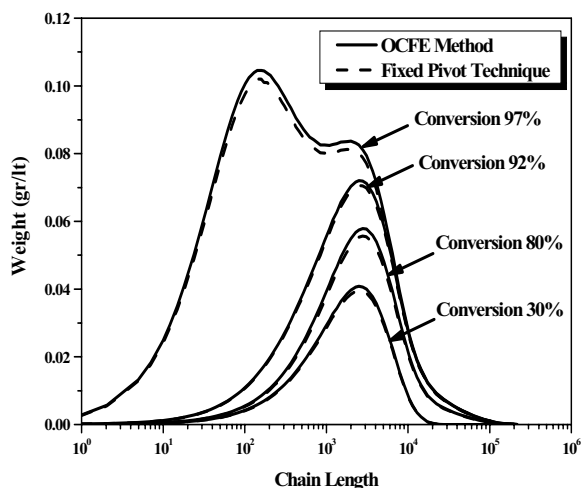
Fig. 1. Comparison of OCFE method and FP technique on the MWD at different monomer conversions

The reliability of the results derived from the application of the OCFE method and the FP technique was further tested by a direct comparison of the zero, first and second moments of the "live" and "dead" polymer chains derived from the predicted MWDs with the analogous ones derived from the application of the method of moments (Figures 2 and 3). Apparently, there is an excellent agreement among the predictions from all these methods.
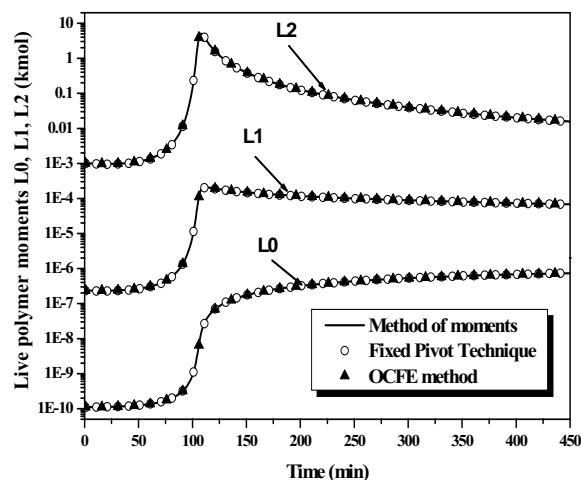

Fig. 2.Comparison of "live" polymer moments between the FP technique, the OCFE method and the method of moments
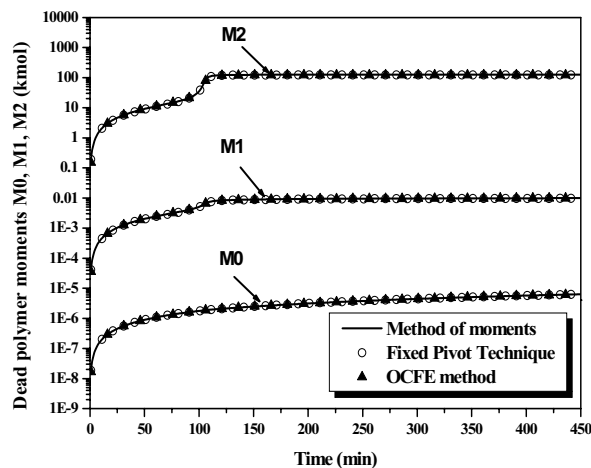

Fig 3.Comparison of "dead" polymer moments between the FP technique, the OCFE method and the method of moments

A model-based study of the optimization problem of a minimum-time production of polymer with a desired MWD is presented next, employing the OCFE method as a representative and reliable method for the MWD calculations. A bimodal MWD (i.e., $PD \approx 5$) was selected as desired profile to be optimaly produced. An optimization policy, where the time domain was discretised into five intervals was selected. The optimization problem was solved for various initial guesses of the temperature set point profile. All these profiles exhibited a single step change in the area of the gel-effect phenomenon. The optimal results obtained by the different optimization runs were slightly different in terms of the time minimization and the shape of the final MWD, indicating low sensitivity on the initially guessed temperature set point profile.

The validity of the model was further tested by direct implementation of the model produced optimal temperature trajectory to a cascade control system of the pilot-scale batch polymerization reactor. The cascade control system consists of a primary proportional-integral-derivative (PID) and two secondary PI controllers.
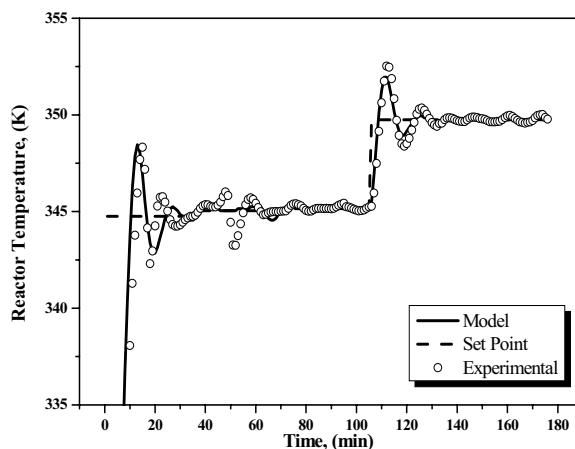

Fig. 4. Comparison between model predictions and experimental results on the reactor temperature (I_0=2 gr/kg of MMA).

Figure 4 depicts a comparison between model predictions and experimental results on the reactor temperature produced from the implementation of the optimal temperature trajectory as set points to the reactor's cascade control system. The optimal MWD in comparison with the desired MWD is shown in Figure 5. As can be seen from Figures 4 and 5, the optimizer, after the heat-up period, forces a low temperature in the reactor to restrain the polymerization, facilitating simultaneously the production of long polymer chains. At the onset of the gel effect and onwards a kick of the reactor temperature is necessary leading to the production of short polymer chains that result in the formation of a second peak in the MWD.
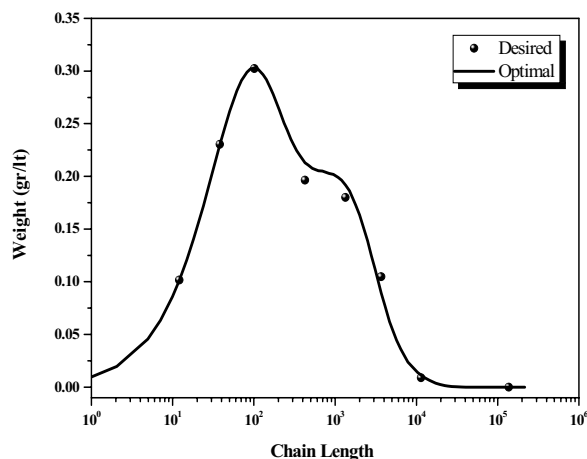

Fig. 5. Desired and optimal bimodal MWD using the OCFE method (I_0=2 g/kg of MMA).

Finally, in Figures 6, 7 and 8, model predictions on monomer conversion, average molecular weights and hot and cold water flowrates are compared with experimental data produced from the optimal temperature profiles depicted in Figure 4. It is apparent that a satisfactory agreement exists between model predictions and experimental results, proving the reliability of the proposed model to produce desired MWDs.
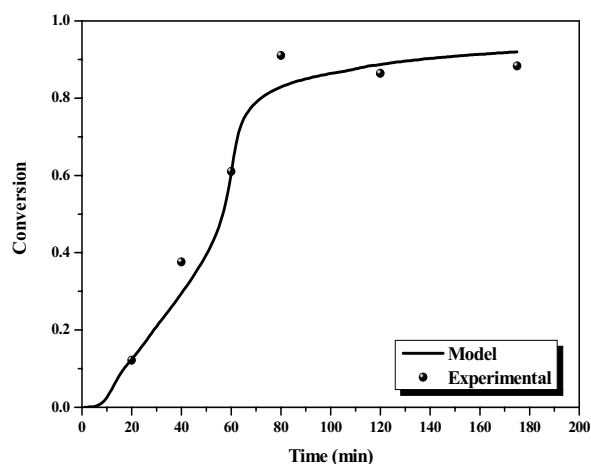

Fig. 6. Comparison of model predicted and experimental monomer conversion produced from the optimal temperature profile (I_0=2 g/kg of MMA).

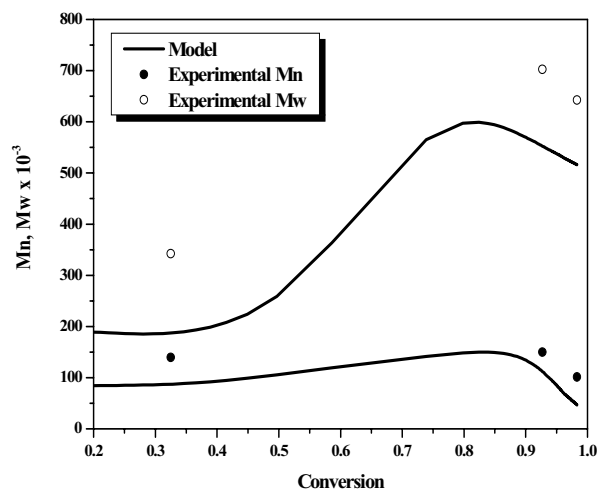
Fig. 7. Comparison of model predicted and experimental average molecular weights produced from the optimal temperature profile (I_0=2 g/kg of MMA).
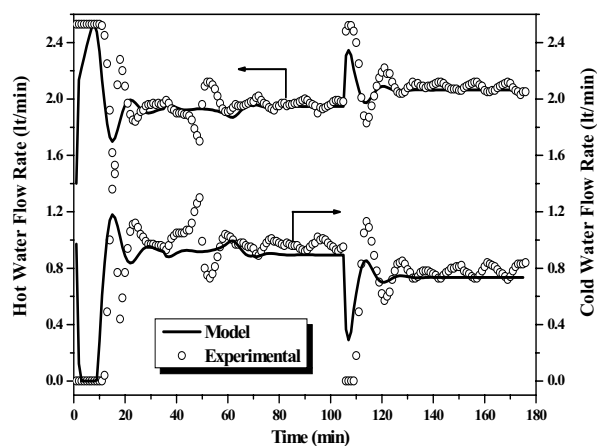

Fig. 8. Comparison of model predicted and experimental measurements on hot and cold water flowrates produced from the optimal temperature profile (I_0=2 g/kg of MMA).

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