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Numerical prediction of kinetic model for enzymatic hydrolysis of cellulose using DAE-QMOM approach

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Abstract. Bioethanol production from lignocellulosic biomass consists of three fundamental processes; pre-treatment, enzymatic hydrolysis, and fermentation. In enzymatic hydrolysis phase, the enzymes break the cellulose chains into sugar in the form of cellobiose or glucose. A currently proposed kinetic model for enzymatic hydrolysis of cellulose that uses population balance equation (PBE) mechanism was studied. The complexity of the model due to integrodifferential equations makes it difficult to find the analytical solution. Therefore, we solved the full model of PBE numerically by using DAE-QMOM approach. The computation was carried out using MATLAB software. The numerical results were compared to the asymptotic solution developed in the author's previous paper and the results of Griggs et al. Besides confirming the findings were consistent with those references, some significant characteristics were also captured. The PBE model for enzymatic hydrolysis process can be solved using DAE-QMOM method. Also, an improved understanding of the physical insights of the model was achieved.

1. Introduction

In [1], Mohd Jamil introduced a mathematical analysis for two separate models for enzymatic hydrolysis of cellulose. It was observed that the number of cellulose chains in both models increased over time due to the effect of enzymes in breaking the cellulose chains into smaller chains; hence more cellulose particles were generated. The limitation of mathematical analysis in measuring one of the enzyme activities is that it would miss the effect of other types of enzymes. Studies by Srisodsuk et al. [2] have shown the importance of synergism between both enzymes, i.e. the simultaneous action of endoglucanase and exoglucanase cellulose during cellulosic hydrolysis. Therefore, an aggregate solution of kinetic model that incorporates the synergism between both enzymes is required. Due to the complexity of the kinetic model proposed by [3] and determining its analytical solution is almost impossible, we have to resort to numerical methods.

Therefore, in this paper, a full PBE model as in [3] is solved numerically by using DAE-QMOM approach. This choice is supported by making a brief comparison between DAE-QMOM approach and asymptotic solution of Model I developed in [1]. In order to evaluate the physical insights of the



model, a comparison with the results of Griggs et al. [3] is carried out. Besides confirming the findings are consistent with Griggs, our aim is to further shape the dimensions for developing concepts and relevant implications to integrate hydrodynamic effect within the system.

Structurally, this paper consists of four thematic sections with relevant subsections. In the first section, the paper is introduced. Next, the issues of numerical methods for population balance modelling are addressed. Also, the verification of DAE-QMOM result with the solution of Model I in [1] is presented. In the third section, the solution of the full model using DAE-QMOM is solved and discussed. Finally, a conclusion of this paper is provided.

2. Numerical methods for PBE

The kinetic model for enzymatic hydrolysis of cellulose proposed by [3] is in the form of population balance equation (PBE). To date, various methods have been developed and introduced to solve the PBE problems [4] [5] [6] [7]. Generally, they can be classified into four main categories; moment method, class method (CM), weighted residuals method, and stochastic method. Recently, attention has been given to moment-based method to avoid the computational cost inherent in the integrodifferential equations. The moment-based method mainly includes method of moments (MOM), quadrature method of moments (QMOM) [5], and direct quadrature method of moments (DQMOM) [6].

Method of moments (MOM) was originally derived by [8]. The major issue of MOM is that it suffers from closure problem. An alternative way to overcome the closure problem is by using QMOM, which was first proposed by [5] to study size-dependent growth in aerosols. QMOM is based on the approximation of unclosed terms by using a quadrature formula. Rather than an exact PBE, QMOM gives a series of N weights and N abscissas that can be converted into $2N$ moments. A major advantage of QMOM is, it has fewer variables involved in terms of number of moments.

The quadrature weights, ω_k and abscissas, ξ_k which are required in QMOM could be determined through a product-difference (PD) algorithm developed by Gordon [9]. The algorithm needs $2N$ first moments ($m_0, m_1, \dots, m_{2N-1}$) of the distribution as an input to produce N weights and abscissas. In the algorithm, a tridiagonal matrix is constructed recursively from the moments; and the weights and abscissas are obtained from the eigenvalues and eigenvectors of this matrix. This technique has been validated in many cases of PBE including simultaneous breakage and aggregation, growth, and nucleation [10]. However, PD-QMOM might lead to an ill-conditioned problem for certain cases [11]. An alternative solution for QMOM method without using PD algorithm in solving the PBE has been proposed by Gimbut et al. [12] which is known as DAE-QMOM. In this research, the DAE-QMOM is implemented to solve the kinetic model for enzymatic hydrolysis of cellulose.

2.1. Verification of DAE-QMOM for Model I

An asymptotic solution for Model I as presented in [1] was developed. Model I is a reduced model from the full model of enzymatic hydrolysis of cellulose that only considers EG which breaks cellulose chains randomly. In this section, the DAE-QMOM was applied to solve the PBE in Model I. The results of these simulations from DAE-QMOM were compared to the asymptotic solution for Model I. The DAE-QMOM steps can be summarized as follows:

- (a) Simplify the PBE using a moment transformation which leads to a closure problem.
- (b) Transform the PBE into a QMOM formulation to eliminate the closure problem.
- (c) Solve the DAE system.

For the case $N=3$, the evolutions of the moments for $p(x, t)$ using DAE-QMOM method are shown in Figure 1. The numerical results were compared to the asymptotic solutions that are represented by circle markers on the line in the figure.

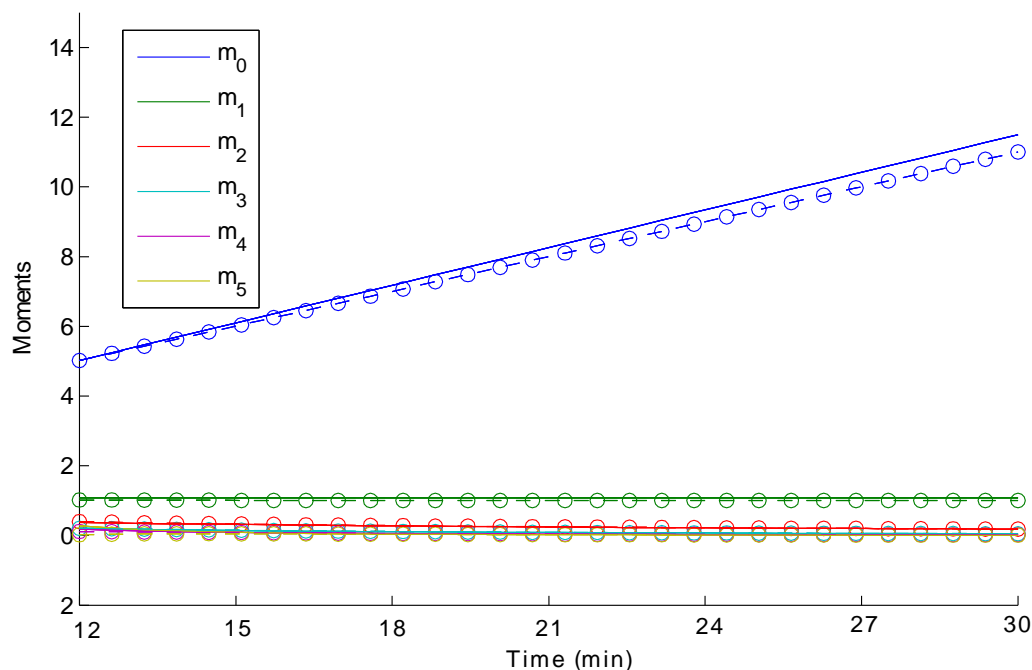


Figure 1. Comparison between DAE-QMOM method (continuous lines) with $N=3$ and asymptotic solution (circles) for Model I.

The results clearly showed that the zeroth moment of the particle size distribution increased, since during the breakage, the total number of particles increased. This result indicates the generation of shorter chains from longer cellulose chains during hydrolysis which is consistent with the findings reported in [3]. The behaviour of the first moment indicates that the total number of glucan units was conserved until the end of the hydrolysis process.

Excellent agreements were found between DAE-QMOM approach and asymptotic solution for Model I on moment evolution. To conclude, the DAE-QMOM has been validated against the asymptotic solution of Model I. Moreover, these results indicate that the DAE-QMOM is capable of predicting the moment evolutions tested in this study accurately. Next, DAE-QMOM was applied to solve the full kinetic model for cellulose hydrolysis.

2.2. Solving the full model using DAE-QMOM

Next, this study considered both CBH_1 and EG_1 acting simultaneously to depolymerize cellulose, which is also known as the full model. Since the DAE-QMOM was able to predict the moment evolution qualitatively for Model I, the usage of DAE-QMOM was extended to study the behaviour of the full system. The only difference when dealing with the full model compared to Model I was that the behaviour of two different types of population needed to be studied simultaneously, which were free cellulose chains, p , and CBH-threaded cellulose chains, p_B .

The moment operator was applied to p and p_B separately. Then, the dimensionless variables which involved characteristic time, initial total number of enzyme accessible cellulose particles, and thickness of single cellulose chains were introduced. Several parameters were grouped together to form dimensionless parameters. The parameters were chosen to be: $K_d = 1 \text{ mol} / \text{m}^3$, $p^{(0)}(0) = 100 \text{ ml} / \text{m}^3$, $R_0 = 1 \text{ nm}$, $k_h^{CBH} = 1 \text{ hr}^{-1}$, $k_h^{EG} = 1 \text{ m}^3 \text{ mol}^{-1} \text{ hr}^{-1}$, $k_f^{CBH} = 2 \text{ m}^3 \text{ mol}^{-1} \text{ hr}^{-1}$,

$\rho = 0.8 \text{ mol} / \text{m}^6$, $n = 1000$, and $L = 1000 \text{ m}$. For the moment equations, by applying QMOM, it was claimed that:

$$p^{(k)}(t) = \sum_{i=1}^N \omega_i(t) \xi_i(t)^k \text{ and } p_B^{(k)}(t) = \sum_{i=1}^N e_i(t) L_i(t)^k .$$

For $N = 2$, the DAE-QMOM system $M\dot{y} = F$ was developed with:

$$y = \left[p^{(0)}, p^{(1)}, p^{(2)}, p^{(3)}, p_B^{(0)}, p_B^{(1)}, p_B^{(2)}, p_B^{(3)}, \omega_1, \omega_2, \xi_1, \xi_2, e_1, e_2, L_1, L_2, R \right].$$

3. Results and Discussion

To study the effect of different enzyme loadings on the moment evolution, we tested various ratios of CBH₁ to EG₁ loading. Here, the total enzyme loading was fixed at $65 \text{ mol} / \text{m}^3$ and the ratio of each enzyme was varied. Figure 2 shows the zeroth and first moment evolution for p and p_B when the enzyme loading for CBH₁ and EG₁ was similar (CBH₁:EG₁ ratio is 1:1). From the graph, we can see that, $p^{(0)}$ (the total number of cellulose chains) increased due to the breakage event of cellulose chains by EG₁ and CBH₁ in the hydrolysis process. This result indicates the generation of shorter chains from longer cellulose chains during hydrolysis, which is consistent with the findings reported in [3]. Accordingly, the total number of monomeric glucans, $p^{(1)}$ also increased. On the other hand, $p_B^{(0)}$ (the total number of CBH₁-threaded cellulose chains) decreased due to the chain fragments generated by CBH₁, which were eventually solubilized by EG₁. This phenomenon implies that the free cellulose chains were generated from the CBH₁-threaded cellulose chains. Subsequently, the total number of CBH₁-threaded monomeric glucans, $p_B^{(1)}$ also decreased.

Furthermore, all curves in Figure 2 eventually stopped increasing or decreasing at a certain time and became a straight line. This behaviour indicates that at a certain time, all cellulose chains reached its minimum length and all cellulose cylindrical particles reached its minimum radius owing to the depletion of insoluble substrate during the hydrolysis process. In this situation, both enzymes (CBH₁ and EG₁) stopped their activity of cutting the cellulose chains.

Now, if the rate coefficients of CBH₁ are considered to be very small in the full model, the same result as in Model I will be obtained. In other words, if the effect of CBH₁ from the full model is simply neglected, the solution for Model I can be recovered. Therefore, the solution of the full model using DAE-QMOM is reliable and it can predict the enzymatic hydrolysis process accurately.

For CBH₁ case in Figure 2, the moment evolution was slower than the combined (EG₁+CBH₁) enzyme hydrolysis. However, it can be seen that for this distribution, CBH₁ was capable of solubilizing the substrate efficiently without the aid of EG₁ which agrees with the result of [3]. With a constant total enzyme loading, increasing the fraction of EG₁ also increase the moment. The addition of EG₁ resulted in cooperative hydrolysis of the substrate.

In addition, this study also tested higher than two-order truncation in Taylor series in solving the full model by DAE-QMOM, and it agrees with the second truncation error qualitatively. Therefore, it is sufficient to use the second truncation Taylor series in this study.

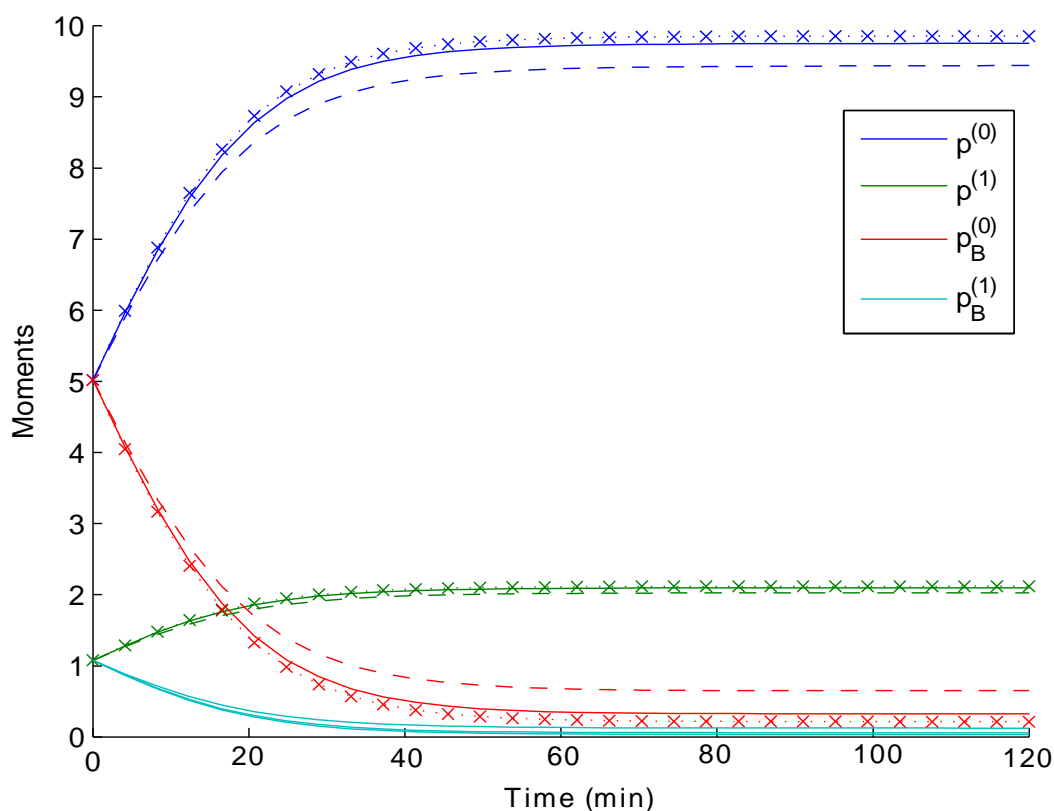


Figure 2. The zeroth and the first moment evolutions during the course of hydrolysis for combined CBH_1 and EG_1 actions with $CBH_1:EG_1$ ratio of 1:0 (continuous line) compared to ratio 1:1 (dashed lines) and 1:2 (cross line).

4. Conclusion

The DAE-QMOM method was applied to solve Model I which consists of differential equations for the moments and system of nonlinear equations resulted from quadrature approximation as a differential-algebraic equation system. The moments of PBE transformed the integrodifferential equation into a set of simultaneous, ordinary differential equations. The solution from the DAE-QMOM method for Model I was compared to the approximate analytical solution. The results indicate that the method is capable of predicting the moment evolution accurately. Furthermore, the solution for simultaneous action of CBH_1 and EG_1 in the full model was obtained using DAE-QMOM approach. By examining the evolution of moments during the enzymatic hydrolysis, an improved understanding of cellulose depolymerization can be achieved.

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